CRYSTAL FIELD ASPECTS OF VIBRATIONAL SPECTRA

by

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ABBREVIATIONS

asym. = asymmetric
at. no. = atomic number
CFSE = crystal field stabilization energy
CFT = crystal field theory
def. = infrared deformation vibration
Et = ethyl
IOS = inner orbital splitting
IR = infrared
L = ligand
L^- = anionic ligand
(L)H = free acid of anionic ligand
LFT = ligand field theory
Me = methyl
M = Central cation in inorganic complex
MOT = molecular orbital theory
m. pt. = melting point
NMR = nuclear magnetic resonance
non-TM = non - transition metal
Ph = phenyl
py = pyridine
R = alkyl or aryl group
str. = infrared stretching vibration
sym. = symmetric
TM = transition metal
UV = ultraviolet

(for abbreviations of beta-diketone ligands, see p. 5.)

INTRODUCTION

Crystal Field Theory (C.F.T.), and its congeners, Ligand Field Theory (L.F.T.) and Molecular Orbital Theory (M.O.T.), have been most successful in explaining many of the properties of transition metal complexes. This is particularly true of their electronic spectra, magnetochemistry, and chemical thermodynamic properties. However, these theories have been ignored in relation to the explanation of changes observed in the infrared spectra of series of transition metal complexes on change of central cation. The purpose of this work is to examine such changes in the light of these theories.

The basis of the above theories is the splitting of the inner orbitals of the metal ions, due to the field of the ligands surrounding them. The field may be considered to arise from electrostatic repulsion by the ligand electrons (C.F.T.), or as a result of the chemical bonding between the central cation and the ligands (L.F.T. and M.O.T.). The result of this inner orbital splitting is a stabilisation of the electrons of the orbital, as compared with their energy in the absence of the field.

The problem of estimating the contribution of inner orbital splitting (I.O.S.) effects to the stabilisation of series of transition metal complexes is approached in thermodynamic studies by plotting the thermodynamic parameters in question against the atomic number of the metal ion across the series. Effects other than I.O.S. effects, such as ionic contraction, are considered to vary linearly with increase in atomic number. These are estimated for ions in the series for which I.O.S. stabilisation is expected by interpolation between values of the parameter observed in ions for which no I.O.S. stabilisation is expected. In octahedral configuration for example, I.O.S. stabilisation is expected to be zero for the d^0, d^5, and d^{10} configurations. Stabilisation in excess of the interpolated values for other electronic configurations in such a series is then considered to arise from I.O.S. effects.

This approach has been adopted in examining I.O.S. effects in the IR spectra of transition metal complexes. The frequencies of the metal to ligand stretching vibrations resemble thermodynamic stabilisations of the metal to ligand bond, in that both are a measure of the strength of the bond. However, unlike thermodynamic properties, metal to ligand stretching frequencies depend also on the mass of the central cation in a transition metal complex. Since the increase in mass across a transition metal series is fairly regular, the mass effect on the IR spectrum will be accounted for by interpolation in the same way as ionic contraction in thermodynamic studies.

Electronic orbital degeneracy, and consequent splitting of the degenerate orbitals in the field of the surrounding ligands, may occur in partially filled p, d, and f shells. p-Shells are of no further interest, because of the much greater importance of their mixing with the orbitals of the other atom in the bond, than their actual splitting. In d-shells, the mixing is much less extensive, so that the IOS approach remains valid. In f-shells, both splitting and orbital mixing effects are extremely small, and affect the thermochemical properties of the f-block elements only very slightly. Thus, while IOS stabilisations of d-block element complexes may be as much as 100 kcal./mole, in f-block elements they are generally of the order of only 1 kcal/mole (10). Because IOS effects will therefore be easier to detect in d-block metal complexes, the discussion will, in the main, centre on these, although complexes of the Lanthanides will be dealt with briefly.

To obtain as complete a picture as possible of the part played by inner orbital splitting, an extensive study of non-transition metal complexes, and their IR spectra, was also undertaken. Since these are free from IOS effects, they are useful in ascertaining the role of effects other than inner orbital splitting. Factors other than the latter which have previously been found to be important, are change of ionic radius, and of ionisation potential of the central cation.

Cationic, neutral, and anionic types of complex have been included for the sake of completeness. However, the main body of work has centred around the beta-keto-enolates, or, as they are sometimes known, the beta diketonates. Several differently substituted forms of these complexes were studied (**Fig.**1), but the ligand most studied was acetylacetone (AcAc), which is the best known of all of the beta-diketonates. These complexes were found to be the most suitable for this study for several reasons. They are readily prepared, and beta-

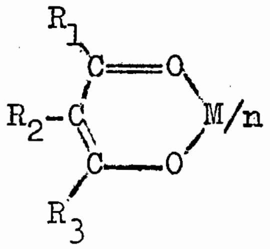


Fig. 1. Structures of different beta-diketonate ligands used in this study, and abbreviations used for them.

R_1	R_2	R_3	Ligand	Abbreviation[a]
$-CH_3$	$-H$	$-CH_3$	acetylacetone	Acac
$-CH_3$	$-H$	$-Ph$	benzoylacetone	Bzac
$-Ph$	$-H$	$-Ph$	dibenzoylmethane	DBM
$-CH_3$	$-H$	$-CF_3$	trifluoroacetylacetone	TFA
$-CF_3$	$-H$	$-CF_3$	hexafluoroacetylacetone	HFA
$-CH_3$	$-H$	$-C(CH_3)_3$	pivaloylacetone	Pvac
$-C(CH_3)_3$	$-H$	$-C(CH_3)_3$	dipivaloylmethane	DPM
$-CH_3$	$-H$	$-OCH_2CH_3$	ethylacetoacetate	EAA
$-CH_3$	$-CH_3$	$-CH_3$	3-methylacetylacetone	3-MeA
$-CH_3$	$-CH_2CH_3$	$-CH_3$	3-ethylacetylacetone	3-EtA
$-CH_3$	$-Br$	$-CH_3$	3-bromoacetylacetone	3-BrA
$-CH_3$	$-NO_2$	$-CH_3$	3-Nitroacetylacetone	3-NO_2A

[a] Free ligand = AcacH, BzacH, *etc.*, anion = $Acac^-$, $Bzac^-$, *etc.*

diketonate derivatives are known for most metals in the periodic system. The beta-diketonates of at least sixty five metals are reported in the literature, while complexes of forty-seven of these, in more than one valency state in many cases, were prepared for this study. The table below, arranged according to the periodic system, indicates all the elements with known beta-diketone derivatives. Those in brackets were not prepared by ourselves. The indices represent the different oxidation states of the elements for which beta-diketone derivatives are known.

Li Be (B)
Na Mg Al Si^{4}
K Ca Sc Ti^{3,4} V^{3,4} Cr$^{\underline{2},3}$ Mn^{2,3} Fe^{2,3} Co^{2,3} Ni^{2} Cu^{2} Zn^{2} Ga^{3} (Ge)^{4}
Rb Sr Y Zr^{4} (Nb)^{5} Mo^{3,6} – Ru^{3} Rh^{3} (Pd)^{2} Ag^{1} Cd^{2} In^{3} (Sn)^{4} (Sb)^{5}
Cs Ba La Hf^{4} (Ta)^{5} (W)^{6} (Re)^{3} (Os)^{3} (Ir)^{3} (Pt)^{2} (Au) Hg^{2} Tl$^{1,\underline{3}}$ Pb^{2}

Ce^{3} Pr^{3} Nd^{3} – Sm^{3} Eu^{3} Gd^{3} (Tb^{3}) Dy^{3} Ho^{3} Er^{3} (Tm)^{3} (Yb)^{3} (Lu)^{3}
Th^{4} – U$^{\underline{4},6}$

Underlined indices indicate that that particular oxidation state of the element was not prepared as a beta-diketonate derivatives in this study.

It is possible that (as will be discussed further on) changes of coordination number and stereochemistry across a series of complexes will change their IR spectra. In order to eliminate, as far as possible, effects other than IOS effects, series of complexes are required in which structure is constant throughout. Beta-diketonates are monobasic acids, but are bidentate ligands. In complexes of these ligands with trivalent ions of coordination number six, both the coordination number and oxidation state requirements are satisfied by the formation of complexes of the type $[M(Acac)_3]$. These have been shown by structural determination to be very similar structurally. In divalent beta-diketonates, the resulting complex $[M(Acac)_2]$ can satisfy the ions with coordination number of four only. In ions with coordination numbers of six, the covalency may be satisfied by coordination of a further acetylacetonate group, giving complexes of the type $[M(Acac)_3]^-$ (84). The two vacant positions may otherwise be occupied by neutral ligands such as H_2O, NH_3, Py, dipy and phen, giving complexes of the type $[M(Acac)_2(H_2O)_2]$. In the divalent series, the coordination number is often lower than six, whereas in the trivalent series it is invariably six, so that in the latter series structural constancy throughout is more frequently observed, making them more suitable for IOS studies than the divalent series.

A further reason for our choice of the beta-diketonates is the extensive literature already existing on these complexes. Most important of all in this respect, was the work done on determining spectroscopic (11) and thermodynamic (38),(39) IOS parameters (Dq), which are essential to an investigation of the effects of IOS. In addition, a large body of work already existed on the infrared spectra of these complexes, although no attempts to interpret them in terms of IOS effects have been made. The information gained from them did, however, form a very useful basis for our own work.

Investigations in the field of beta-diketonate IR spectra have been concentrated on two problems. The first of these is the question of band assignment. On complexation with a metal, resonance is possible in the chelate ring, with approaching equivalence of the ring C=C and C=O bond orders. The IR stretching vibrations are therefore expected very close together in the spectrum. Two bands are in fact observed in the range 1625 - 1500 cm^{-1}, which is where these two vibrations are expected to absorb. The question of the correct assignment of these two bands has been the subject of much discussion in the literature. The earliest attempts to distinguish between the two bands were those of Lecompte (49).

By considering the vibrations of acetylacetone to arise from the in- and out- of - phase coupling of the vibrations of acetone, he empirically assigned the higher of the two bands in the 1650 - 1500 cm^{-1} region of the acetylacetonate spectrum as the carbonyl stretching vibration (C=O str.). The lower was assigned to the carbon - to - carbon stretching vibration. (C=C str.) Bellamy and Branch (50), however, because the C=O str. in organic molecules was usually of greater intensity than the C=C str., suggested that, irrespective of position, the more intense of these two bands in any particular case should be regarded as being the C=O str.

Further attempts to resolve the problem were made in the form of normal coordinate treatments (NCT's). The earliest of these was that of Nakamoto _et_ _al_. (51). These authors used Cu(II) acetylacetonate for their study. The problem was simplified by considering a single ring only, and neglecting interactions between the two rings of the complex. A further simplification was that the methyl group was regarded for the purposes of calculation as a single atom of mass 15, and methyl vibrations assigned empirically. This same approach to the vibrations of ring substituents was adopted by these authors in their paper on the effect of change of the 1,3 substituents of beta-diketonates on the IR spectra of their copper chelates (55). This, and further work on the tris(acetylacetonates)of Cr(III), Fe(III), Co(III), and Al(III), (57), indicated that the assignments of Lecompte should be reversed. The higher band was thus assigned as the C=C str., and the lower as the C=O str.

Shimanouchi *et al.*(52) undertook a more refined treatment of the problem, in which the complete 29 - body problem for Cu(II) acetylacetonate, and 43-body problem for Fe(III) acetylacetonate, were considered. The results of this treatment substantially supported the work of Nakamoto, and indicated that the higher of these two bands was the C=C str. However, this assignment was almost simultaneously reversed by Nakamoto in his NCT of the complex $[PtAcacCl_2]^-$.(53)

The latter change of assignment is seen to be verified by Pinchas <u>et al</u>. (54), in their studies on ^{18}O - substituted acetylacetonates of Cr(III) and Mn(III). In comparing the IR spectra of the normal acetylacetonates with those of the ^{18}O - substituted complexes, it was found that a reduction of 13 cm^{-1} occured in the higher frequency band on insertion of the heavier isotope. No change occured in the second band. These authors were thus able to assign the higher band to the C=O str., and the lower to the C=C str.

The bands of greatest importance in relation to the effect of change of metal are the metal - oxygen stretching vibrations (M-O str.). The NCT of Nakamoto on Cu(II) acetylacetonate suggested that the band at 455 cm^{-1} in this complex, and the corresponding band in other beta-diketonates, was the M-O str. The work of Pinchas <u>et al</u>. on ^{18}O - substituted acetylacetonates has suggested that the bands in the 520 - 650 cm^{-1} region are in fact the purest M-O vibrations. This problem is not yet fully resolved, and the discussion of these assignments is deferred to the discussion on the beta-diketone spectrum in the 200 - 800 cm^{-1} region. (page 210)

The second problem in which work on the IR spectra of beta-diketonates has been concentrated has been the correlation of shifts of band frequencies with metal ion parameters, e.g. ionic radius and ionisation potential. Other parameters, such as stability constants, have also been used to obtain correlations (59). Due to earlier limitation of instrumentation with respect to range in the far IR, the C=O and C=C vibrations have received more attention than the longer wavelength M-L vibrations.

The previous literature on the IR of beta diketonates is of no direct interest to an IOS interpretation of shifts of bands in the spectra of transition metal (TM) complexes on change of metal. However, it will be briefly reviewed inasmuch as this will be useful in our discussion on the IR spectra of non-transition metal complexes.

Holtzclaw and Collman (59) found a correlation of the C=O str. with the stability constants of a series of seven acetylacetonates. Substituent effects at the 3-position of acetylacetone were also examined, and an apparent relationship of the C=O str. with the mass of the substituent found.

West and Riley (60) plotted the C=O str. against overall ionisation potential, I_z, of the metal, for eighteen metal derivatives of acetylacetone, and obtained good linear relationships. The C=O str. was found to decrease with increasing ionisation potential. This work was supported by Lawson(1), who now also observed a similar relationship for the C=C str. The latter vibration moved to higher wavenumber with increasing ionisation potential of the central cation, which was the inverse of the relationship exhibited by the C=O vibration.

Djordjević(63) examined the IR spectra of Al, Ga and In trisacetylacetonates. The spectra were reported from 4000 to 400 cm^{-1}, and comparisons of bond strengths made, assuming the M-O frequencies to arise from the oscillations of isolated M-O dipoles. It was concluded that force constants did not decrease markedly with increasing atomic number, and that the bonding type was the same in all cases. The decrease in M-O str. was therefore attributed entirely to a mass effect.

The papers of Kawasaki <u>et al</u>. (104) and Kline (105) <u>et al</u>. were found to be useful as sources of spectral frequencies of complexes which were not prepared by us.

Not many useful interpretations of the shifts observed in the IR spectra on change of ion in TM complex series, as distinct from non-TM complexes, have previously been reported. Forman and Orgel (3) have attributed the increasing complexity of bands in the 800 - 400 cm^{-1} region of the spectrum of Mn(III) acetylacetonate, as compared with those of Fe(III) and Cr(III) acetylacetonates, to Jahn-Teller distortion of the Mn complex.

The increase in frequency of the M-C str. in hexacyano complexes through the series Cr(III)<Mn(III)< Fe(III) < Co(III), has been interpreted as strengthening of the M-C bond due to increasing metal-ligand (M-π^*) π-bonding, with increase in the number of d-orbital electrons in the central cation (4). This was a most reasonable interpretation, since the study of the variation on the M-C str. was accompanied by observations of the integrated intensities of the $C\equiv N$ vibration. Insofar as ease of electron delocalisation leads to greater change of dipole moment during the vibration (and hence greater bond intensity), the latter may be interpreted in terms of the extent of π-bonding. This, as is supported by interpretations of the shifts in the M-C str. in the series, indicated that the extent of π-bonding increased in the same order as the M-C str.

For series of divalent transition metal ions, it has been observed that the strength of the metal to ligand bond (M-L), as indicated by the magnitudes of the M-L str., follows the trends predicted by the Irving - Williams stability order, which is derived from stability constant studies (5). The trends in it are interpreted in terms of the ionisation potentials and ionic radii of the metal ions. In addition, it has been noted that the stability order, as indicated by M-O stretching frequencies, follows the same trends for both tris(oxalato)-metallates and tris(acetylacetonates) (8).

The Irving - Williams stability order makes a significant advance over previous stability orders. It suggests a stabilty order of Mn<Fe<Co<Ni<Cu>Zn, which recognizes the necessity for treating the data for d-block elements separately from those of non-TM elements. This is not so in orders such as that of Mellor and Maley (5), viz. Mg<Mn<Fe<Cd<Zn<Co<Ni<Cu<Pd, which have a limited usefulness, in that they apply to only a limited number of ligand systems.

There appears also to have been some lack of systematic approach to the IR spectra of beta-diketonates. For example, the metals which were selected for comparison in correlations of the C=O str. with stability constants are Na^{I}, Ni^{II}, Mg^{II}, Cd^{II}, Mn^{II}, Co^{II}, Cu^{II}, and Pd^{II}(59). A further difficulty encountered in work of this nature is that in many cases verification of the precise composition of the complex subject to spectral examination has not been reported. For instance, the two complexes $[Ni(Acac)_2(H_2O)_2]$ and $[Ni(Acac)_2]_3$ have both been described as "nickel acetylacetonate" (1), ((55). We have attempted to obviate these difficulties by elemental microanalysis of the majority of complexes described, especially in those cases, as in the one mentioned above, where some doubt as to the precise identity of the complexes might conceivably arise. A complete elemental analysis was also performed for complexes such as $[Ti(Acac)_3]$, which are highly susceptible to oxidation. These were prepared under rigorously oxygen-free conditions in a nitrogen box.

In addition to the beta-diketonates, series of complexes with ligands such as the oxalate and the cyanide ion were also studied. The oxalates are particularly useful, since spectroscopic Dq values are reported for these in the literature (11). Much detailed information on the IR spectra of nitrogen-donor ligands already exists in the literature, so that this too was extensively used in supporting our conclusions.

To support the conclusions drawn from the IR studies, the UV spectra, and (to a lesser extent) the NMR spectra, were recorded for many of the complexes. It was hoped that the information on aspects such as the extent of π-bonding, which is yielded by these methods, would prove useful in explaining deviations from the simple CF approach to stabilisation of these complexes. A large volume of work is already available in the literature on this aspect of the work, most noteworthy of which is the work of Barnum (42), and Cotton (40), on the UV aspects, and Eaton (48), on the NMR aspects of the problem.

Finally, extensive precautions were taken by us in order to ensure the reproducibility and reliability of the frequencies reported here. In the course of our investigations, several of the spectra were recorded on as many as five different IR spectrophotometers. In many cases, alternative sampling techniques were employed. The latter included solution spectra in $CHCl_3$ and CCl_4, and also nujol mulls, and CsI and KBr pellets. No significant variations were observed, and in general reasonable agreement was found with reported literature values.

EXPERIMENTAL

A. PHYSICAL TECHNIQUES

1. IR Spectra

Due to difficulties in obtaining adequate instrumentation in the earlier stages of this work, spectra were determined on one or more of the following instruments: Beckman IR-8, Beckman IR-10, Beckman IR-12 and Perkin-Elmer 521 spectrophotometers, each calibrated against CO_2 and polystyrene. Later, the full-time use of a Beckman IR-12 spectrophotometer was available, and all spectra were repeated on this instrument. All frequencies reported in this work represent those recorded on this instrument, so as to ensure conditions of maximum reproducibility. The replicate spectra on the other instruments yielded good frequency agreement.

Nujol mulls were primarily used as sampling techniques for all of the complexes. Many spectra were, however, repeated using KBr and CsI pellets, and also as solution spectra in $CHCl_3$ and CCl_4. This was done in order to eliminate any possibility of effects due to the physical state of the sample (*e.g.* splitting of bands due to occupation of sites of lower symmetry in the crystal lattice by the molecule, which are obviated by recording the spectra in solution.) Also, in many cases the more refractory types of compounds do not give satisfactory spectra as mulls, so that these were recorded as CsI pellets.

The reasonably close agreement observed between the three different sampling techniques (Nujol Mulls, CsI pellets and $CHCl_3$ solution spectra) is illustrated by the frequencies observed for the series of complexes ML_3, (where M = Sc, V, Cr, Mn, Fe, Co, and L = Acac, Bzac and TFA.) The frequencies reported are the C=O str., C=C str. and (M–O + $C-CH_3$)str. (cm^{-1}).

Vibration	Sampling	L= Acac.					
	technique	M = Sc	V	Cr	Mn	Fe	Co
C–Cstr.	nujol mull	1580	1571	1574	1593	1575	1580
"	CsI pellet	1579	1569	1574	1590	1573	1581
"	$CHCl_3$ soln.	1582	1565	1579	1585	1576	1580
C–Cstr.	nujol mull	1529	1526	1522	1516	1530	1522
"	CsI pellet	1529	1531	1527	1516	1529	1521
"	$CHCl_3$ soln.	1529	1530	1528	1524	1531	1528

Vibration (cm^{-1})	Sampling technique	M = Sc	V	Cr	Mn	Fe	Co
		L = Acac					
(M–O + C–CH$_3$)str.	nujol mull	439	449	462	462	437	466
	CsI pellet	437	448	461	460	436	466
	CHCl$_3$ soln.	446	452	462	464	437	468
		L = Bzac					
C–Ostr.	nujol mull	1553	1547	1555	1560	1551	1561
	CsI pellet	1558	1551	1555	1557	1552	1562
	CHCl$_3$ soln.	1560	1552	1557	1560	1555	1561
C–Cstr.	nujol mull	1513	1513	1524	1515	1520	1525
	CsI pellet	1526	1523	1525	1517	1528	1524
	CHCl$_3$ soln.	1523	1525	1527	1520	1525	1525
(M–O + C–CH$_3$)str.	nujol mull	446	451	465	465	446	479
	CsI pellet	447	451	466	464	450	479
	CHCl$_3$ soln.	445	451	466	468	450	485
		L = TFA					
C–Ostr.	nujol mull	1624	1615	1615	1616	1616	1609
	CsI pellet	1621	1613	1614	1628	1615	1628
(M–O + C–CH$_3$)str.	nujol mull	426	429	437	432	424	445
	CsI pellet	424	428	437	432	427	447

The agreement between the frequencies of these vibrations in different media is fairly good. The differences observed, are however due to solvent effects rather than due to uncertainty in reading off the frequencies, since the resolution of the instrument is reported by the makers to be better than 0•5 cm^{-1} in the range in which the spectra were recorded. (Beckman IR 12.) Further, for the more important bands in relation to our study, scale expansion was used, so that the frequencies were read off a scale of 10 cm^{-1} = 1 inch, instead of the normal format of 100 cm^{-1} = 1 inch. CsBr plates were used for recording the spectra of the complexes recorded as nujol mulls.

2. UV Spectra.

The UV spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer. These were recorded in solution, mostly in $CHCl_3$ and/or MeOH. The more ionic types of complex, such as the oxalato- and cyano-complexes, were recorded in aqueous solution.

3. NMR spectra

The NMR spectra were recorded using a Varian A60 spectrometer. Tetramethylsilane was used as an internal calibrant, and deuterochloroform was used as the solvent in all cases.

4. Melting Points

Melting points were recorded using a Kofler hot-stage microscope. These agreed fairly with those in the literature, where reported. These literature melting points are reported along with our own, for the purposes of comparison.

5. Microanalyses

These were performed in the laboratory of Dr F. Pascher, Bonn, and also by Dr. Fuhr of the Chemistry Department, University of Cape Town.

B. Preparation of Compounds

In general, methods described in the literature were followed, although in many cases useful modifications were developed, so that these will be briefly described. The beta-diketonate ligands used are shown in Fig. 1.

1. Beta-diketonates of transition metal (III) ions

Scandium(III)

Sc_2O_3 (99%, 0.25 g) was dissolved in HCl (10M, 15 ml) and the solution evaporated to dryness. Water (10 ml) was added, and this then also evaporated to dryness. Further water (10 ml) was added, and to this solution was then added the stoichiometric quantity of the ligand in a little ethanol. An immediate precipitate occurred, which was collected by filtration. With the exception of the Bzac and DBM complexes, all of the chelates were purified by sublimation at 1 mm Hg and 100 - 150°C. The DBM complex was recrystallized from chloroform/ethanol, and the Bzac complex from benzene/heptane. Attempts to purify the DBM and Bzac complexes by sublimation lead to their pyrolysis

Unless otherwise stated, all complexes other than the DBM and Bzac complexes were purified by sublimation at 100 - 150°C and 1 mm Hg, and the Bzac and DBM complexes were purified by recrystallisation from the same solvents as above, for the metals Sc(III), V(III), Cr(III), Mn(III), Fe(III) and Co(III).

The crude Sc(III) beta-diketonates were pale orange to yellow, but on purification $Sc(Acac)_3$, $Sc(TFA)_3$, $Sc(3\text{-}MeA)_3$ and $Sc(3\text{-}EtA)_3$ were obtained as pure white crystalline substances. The colour remained yellow in the purified $Sc(DBM)_3$, $Sc(DPM)_3$ and $Sc(Bzac)_3$ complexes. Analyses and melting points for the complexes are as follows

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)
	(calculated)		(found)		
$Sc(Acac)_3$	52·5	6·2	52·5	6·3	188
$Sc(DPM)_3$	66·7	9·7	66·7	9·6	152-153
$Sc(3\text{-}MeA)_3$	56·2	7·1	56·0	7·1	125
$Sc(3\text{-}EtA)_3$	59·1	7·8	58·8	7·5	131-135
$Sc(TFA)_3$	35·8	2·4	35·9	2·5	105
$Sc(Bzac)_3$	68·2	5·2	67·9	5·4	222-224
$Sc(DBM)_3$	75·6	4·7	75·7	4·5	264

Titanium(III)

Only the tris(acetylacetonate) of Ti(III) was prepared. The method of Barnum (41) was used without modification. The complex is highly susceptible to oxidation, so that its preparation, as well as the preparation of a nujol mull for recording its IR spectrum, were performed under nitrogen in a dry-box. (The nitrogen used was extra-high purity, containing less than 1 p.p.m. of oxygen.) Weighing of a sample for analysis was carried by introducing a preweighed glass capsule plus platinum boat into the dry-box, placing a little of the sample in the boat, and then placing the boat inside the air-tight capsule. The latter, containing the boat plus sample, was removed from the dry-box and weighed. This method was found to give satisfactory analyses, since it eliminated contact of the highly oxygen-sensitive complex with the air.

The IR spectrum was recorded as a nujol mull. The mull was prepared under N_2, and placed between KBr plates which had previously been placed in the dry-box. The plates containing the mull were transported from the dry-box in an air-tight container. The product of oxidation is titanyl acetylacetonate, in which a strong Ti=O band at 990 cm^{-1} is observed. The absence of this band was taken as evidence that the spectrum recorded is that of $Ti(Acac)_3$.

Analysed for $TiC_{15}H_{21}O_6$: calcd; C = 52.2%, H = 6.1%, Ti (as TiO_2) = 13.9%. Found; C = 53.0%, H = 6.1% and Ti = 14.3%.

Vanadium(III)

These were prepared by the method of Morgan and Moss (70) reported for the acetylacetonate. For the preparation of $V(DBM)_3$ and $V(Bzac)_3$, a solution of the respective ligands in one part of ethanol to two parts of ether was used. This was found to be satisfactory, even though conventional methods have been reported in the literature to yield impure products, which are difficult to purify. The DBM complex in particular was obtained in high yield, and in a high state of purity. This method was found to be superior to the literature method (71) of reducing vanadyl dibenzoylmethanate ($VO(DBM)_2$) with zinc dust in the presence of excess ligand. As prepared by our method this complex is obtained as black prisms, which give red solutions in $CHCl_3$, whereas the complex is described in the literature (71) as being brown, and has reported melting points some 35°C lower than ours. As with $Ti(Acac)_3$, the absence of vanadyl peaks was taken to indicate that oxidation to the vanadyl complexes had not taken place. Because of the sensitivity of V(III) compounds, the spectra were recorded immediately after synthesis. Commercial samples (Koch-Light) of $V(Acac)_3$ were found to be the oxidation product, $VO(Acac)_2$.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.	M.Pt.(°C)
	(calculated)		(found)		(found)	(literature) ref.
$V(Acac)_3$	51·8	6·0	52·3	5·6	184	184 (72)
$V(3\text{-}MeA)_3$	55·4	7·0	55·5	6·7	179	–
$V(3\text{-}EtA)_3$	58·3	7·7	57·7	8·1	182	–
$V(DBM)_3$	75·0	4·6	75·0	5·0	245	210 (71)
"			75·0	4·7		
$V(Bzac)_3$	67·8	5·1	67·1	5·3	201	–
$V(TFA)_3$	35·3	2·4	35·3	2·4	129	–
$V(HFA)_3.H_2O$	25 4	0·7	25·4	0·7	–[a]	–

[a] The extreme volatility of this complex rendered the recording of a melting point impossible.

Chromium (III)

Except for the complex $Cr(DBM)_3$, all of the Cr(III) beta-diketonates were prepared according to the method of Fernelius and Blanch (73) for preparing the acetylacetonate. The dibenzoylmethanate was prepared by the method of ligand exchange (74), since conventional methods were found to be unsatisfactory.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.	M.Pt(°C)
	(calculated)		(found)		(found)	(literature) (ref.)
Cr(Acac)$_3$	51·6	6·1	51·9	6·1	213	216 (73)
Cr(3-MeA)$_3$	55·2	7·0	55·0	7·0	160	-
Cr(3-EtA)$_3$	58·2	7·7	58·7	7·8	155	-
Cr(DPM)$_3$	65·9	9·6	66·0	9·6	227	229 (75)
Cr(TFA)$_3$	35·2	2·4	35·0	2·6	136	-
Cr(Bzac)$_3$	67·3	5·1	68·7	5·1	255	-
Cr(DBM)$_3$	74·9	4·5	75·0	4·7	312	-

Manganese (III)

The procedure followed in all cases was that of Charles and Bryant (76) for the acetylacetonate. For solid ligands, an ethanolic solution of the ligand was used in place of the pure liquid ligand.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)	
	(calculated)		(found)		(found)	(literature) (ref.)
Mn(Acac)$_3$	51·2	6·0	50·7	6·4	150	150 (76)
Mn(DPM)$_3$	65·6	9·5	65·3	9·3	162	165 (75)
Mn(Bzac)$_3$	66·9	5·1	67·0	5·3	192	-
Mn(DBM)$_3$	74·6	4·6	74·3	4·8	250-251	-
Mn(TFA)$_3$	35·1	2·4	35·1	2·2	118	-

Iron (III)

The synthesis of the Fe(III) beta-diketonates was similar for all the differently substituted beta-diketonate ligands. The ligand dissolved in a little ethanol was added to a solution of the stoichiometric quantity of $FeCl_3.6H_2O$ in water, and buffered with sodium acetate. The red solution was shaken for twenty four hours and the bright red crystals which deposited were filtered off.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)	
	(calculated)		(found)		(found)	(literature)
$Fe(Acac)_3$	51·0	6·0	51·3	5·9	190	179 (77)
$Fe(DPM)_3$	65·4	9·5	65·0	9·2	164	163 (75)
$Fe(3\text{-}MeA)_3$	54·7	6·9	53·3	6·9	108	–
$Fe(3\text{-}EtA)_3$	57·5	7·6	56·7	7·6	122	–
$Fe(TFA)_3$	35·0	2·4	35·0	2·3	112	–
$Fe(HFA)_3$	26·6	0·5	26·5	0·7	98[a]	–
$Fe(Bzac)_3$	66·9	5·0	67·0	5·3	218	222–224 (77)
$Fe(DBM)_3$	74·5	4·6	75·2	4·7	258	262 (78)

[a] This value may be unreliable due to the extreme volatility of the product.

Cobalt(III)

The method reported for the acetylacetonate (79) was found to be satisfactory for the other ligands.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)	
	(calculated)		(found)		(found)	(literature)
$Co(Acac)_3$	50·6	6·0	50·5	6·1	213	213 (79)
$Co(DPM)_3$	65·1	9·4	65·1	9·4	236	245 (75)
$Co(Bzac)_3$	66·4	5·0	66·5	5·4	208	–
$Co(DBM)_3$	74·2	4·6	73·8	4·7	260	–
$Co(TFA)_3$	34·8	2·4	34·9	2·2	158	–

Gallium (III)

Both $Ga(Acac)_3$ and $Ga(TFA)_3$ were prepared by the method of Morgan and Drew (80) for the acetylacetonate.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)	
	(calculated)		(found)		(Found)	(literature)
$Ga(Acac)_3$	49·0	5·8	49·1	5·8	194	194 (62)
$Ga(TFA)_3$	34·1	2·3	34·3	2·3	128	–

Molybdenum (III)

The tris(acetylacetonate) was prepared by the method of Dunne and Cotton (81). Since a reference IR spectrum was reported by these authors, the identity of the complex was checked by comparison of our own spectrum with that reported, and no analysis was undertaken. Because of the extreme sensitivity of the complex to oxidation, the same procedure for recording spectra was adopted as for the Ti(III) complex.

Ruthenium (III)

Only the acetylacetonate was prepared. For this the method of Barbieri (82) was used, but poor yields were obtained. The yields were improved by buffering the solution with sodium acetate instead of sodium bicarbonate as in the literature.

Calculated for $Ru(C_{15}H_{21}O_6)$: C = 45·2, H = 5·3; found: C = 44·6, H = 5·0%. M.Pt. = 242°C.

Rhodium (III)

The method of Dwyer and Sargeson (83) was used to prepare both Rh(Acac)$_3$ and Rh(TFA)$_3$. Rh(Acac)$_3$ was purified by recrystallisation from benzene/heptane, while Rh(TFA)$_3$ was purified by sublimation at 150°C and 1 mm Hg.

Calcd for Rh($C_{15}H_{21}O_6$) : C = 45·0%, H = 5·3%. Found: C = 45·2%, H = 5·3%. M.Pt. = 258°C

Calculated for Rh($C_{15}H_{12}F_9O_6$): C = 32·0%, H = 2·2%. Found: C = 34·5%, H = 2·6%. M.Pt. = 175°C

Indium and Yttrium (III)

These were prepared by the same method as for the Ga(III) complexes.

Calculated for Y($C_{15}H_{12}F_9O_6$): C = 32·9%, H = 2·2%. Found: C = 32·1%, H = 2·4%. M.Pt. = 220°C(d)

Calculated for In($C_{15}H_{12}F_9O_6$): C = 31·39%, H = 2·1%. Found: C = 31·4%, H = 2·1%

2. Beta-diketonates of transition metal(II) ions.

Manganese (II)

The dihydrated bis(acetylacetonate) was prepared as described in the literature (85). The polymeric form was prepared by sublimation of the bis(aquo)-complex (85) at 150°C and 1 mm Hg. The diammine and tris(acetylacetonate) were prepared as in ref. 84. The tris(acetylacetonate) complex $K[Mn(Acac)_3]$ could not be analysed because of the difficulty of analysing for carbon in the presence of potassium. However, these anionic complexes are distinguishable from their neutral counterparts by the fact that they are soluble in water, whereas the latter are not. Since the Mn(II) tris(acetylacetonate) complex is susceptible to oxidation, it was prepared under nitrogen, with the same precautions as were used in the preparation of $Ti(Acac)_3$.

Calculated for $Mn(C_{10}H_{14}O_4)$: C = 47·4%, H = 5·6%.
Found C = 45·8, H = 5·3% M.Pt. - decomposes 250°C without melting.

Calculated for $Mn(C_{10}H_{14}O_4).2H_2O$: C = 41·5%, H = 6·3%.
Found C = 41·8%, H = 6·3%.

Iron (II)

The anhydrous complex was prepared according to the method of Buckingham *et al.* (86). The tris(acetylacetonate) was prepared according to the method of Dwyer and Sargeson (84), and was not analysed because of the difficulty of analysing for carbon in the presence of potassium, but as with the Mn(II) analogue, was distinguishable by its solubility in water.

Cobalt(II)

Whereas the Mn(II) and Fe(II) tris(acetylacetonates) were not analysed because of the presence of potassium, and because they could not last sufficiently long enough to be analysed commercially without oxidation to the M(III) compounds, $K[Co(Acac)_3]$ is stable towards air oxidation, and so was analysed commercially. The tris(acetylacetonate) complex, and the diammine and bis(pyridine)-bis(acetylacetonates) were prepared as in ref. 84. The complexes $[Co(Acac)_2]_4$ and $[Co(Acac)_2(H_2O)_2]$ were prepared as in ref. 87.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)
	(calculated)		(found)		
$Co(C_{10}H_{14}O_4)$	46•7	5•5	44•9	5•8	180
$Co(C_{10}H_{18}O_6)$	41•0	6•2	41•2	6•2	–[a]
$Co(C_{10}H_{20}N_2O_4)$	41•2	6•9	41•6	6•9	–
$Co(C_{20}H_{24}N_2O_4)$	57•8	5•8	55•2	5•6	–
$K[Co(C_{15}H_{23}O_7)]$	43•5	5•6	43•7	5•7	–

[a] The adducts of $Co(Acac)_2$ decompose on heating.

Nickel(II).

Essentially the same methods as used for preparing the analogous Co(II) complexes were used to prepare $[Ni(Acac)_2]_3$, $[Ni(Acac)_2(H_2O)_2]$, $[Ni(Acac)_2(NH_3)_2]$ $[Ni(Acac)_2(py)_2]$ and $K[Ni(Acac)_3]$.

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)
	(calculated)		(found)		
$Ni(C_{10}H_{14}O_4)$	46•7	5•5	45•0	5•7	232-235(d)
$Ni(C_{10}H_{18}O_6)$	41•0	6•2	40•0	5•8	–
$Ni(C_{10}H_{20}N_2O_4)$	41•3	6•9	41•6	6•9	–
$Ni(C_{20}H_{24}N_2O_4)$	57•8	5•8	54•1	6•0	–
$K[Ni(C_{15}H_{23}O_7)]$	43•5	5•6	43•9	5•4	–

Copper(II)

A large number of copper(II) beta-diketonates were prepared by the method reported (88) in the literature for Cu(Acac)$_2$. The complex [Cu(TFA)$_2$(H$_2$O)] was prepared by adding an ethanolic solution of methylamine to a stoichiometric mixture of Cu(II) acetate and (TFA)H in water. A deep blue crystalline precipitate is obtained, which on standing loses water to form the pale blue anhydrous complex. (The synthesis of this complex was as a result of attempts to prepare [Cu(TFA)$_2$.NH$_2$CH$_3$] The structure is supported by the occurrence of the O–H str. in the IR spectrum.)

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)
	(calculated)		(found)		
Cu(Acac)$_2$	45·9	5·4	46·0	5·4	270(d)
Cu(TFA)$_2$	32·5	2·2	33·3	2·5	190–195
Cu(TFA)$_2$(H$_2$O)	31·0	2·6	30·7	2·4	–(d)
Cu(Bzac)$_2$	62·3	4·7	62·0	4·7	–[a]
Cu(DBM)$_2$	70·6	4·3	70·6	4·4	–[a]
Cu(DPM)$_2$	61·4	5·4	61·3	5·4	–[a]
Cu(PvA)$_2$	55·6	7·6	55·7	7·8	290(d)
Cu(HFA)$_2$(H$_2$O)	24·2	0·8	24·4	1·3	161
Cu(EAA)$_2$	44·8	5·6	45·4	5·8	195

[a] decompose above 300°C without melting.

Zinc (II)

$[Zn(Acac)_2(H_2O)]$ was prepared by the method of Rudolph and Henry (89). The anhydrous complex , $[Zn(Acac)_2]_3$ was prepared by sublimation of the hydrated complex. $K[Zn(Acac)_3]$ was prepared by the method of Dwyer and Sargeson (84), as was also the complex $[Zn(Acac)_2py]$.

Complex	C(%)	H(%)	C(%)	H(%)
	(calculated)		(found)	
$K[Zn(Acac)_3] \cdot 2H_2O$	41·2	5·8	41·5	5·5
$[Zn(Acac)_2(H_2O)]$	42·7	5·8	43·1	5·7
$[Zn(Acac)_2py]$	52·6	5·6	51·7	5·5

3. Group I beta-diketonates

All of the group Ia beta-diketonates were prepared by adding the stoichiometric quantity of the ligand (or, if solid, a saturated methanolic solution of the ligand) to a saturated solution of the metal hydroxide in methanol. An immediate precipitate occurred, but care had to be taken in adding the ligand, since if addition was too rapid, the exothermic reaction caused a considerable evolution of heat, which led to hydrolysis of the ligand, and consequently poor yields. The complexes were purified by recrystallisation from ethanol and isopropyl alcohol. The analyses indicated that, with few exceptions, the complexes were the (aquo)-adducts. Analysis of the Cs and Rb complexes did not appear to give reliable results, so that analysis of these was abandoned.

Complex	C(%)	H(%)	C(%)	H(%)
	(calculated)		(found)	
$[Na(Acac)(H_2O)_2]$	37·9	7·0	37·6	7·0
$[Li(Acac)]$	56·6	6·6	55·5	6·6
$[K(Acac)(H_2O)]$	38·5	5·8	39·7	5·5
$[Li(DPM)(H_2O)_2]$	58·4	10·2	59·2	9·4
$[K(HFA)(H_2O)_2]$	21·3	1·8	22·3	0·9
$[K(Bzac)(H_2O)]$	55·0	5·1	53·5	5·1
$[Na(Bzac)(H_2O)]$	59·4	5·4	58·0	4·6
$[K(TFA)]$	31·2	2·1	29·0	2·6

4. Group II A beta-diketonates

$Be(Acac)_2$ was prepared as in ref. 90. $K[Ca(Acac)_3]$ was prepared as in ref. 84. The complexes $[Ca(Acac)_2(H_2O)_2]$

$[Sr(Acac)_2(H_2O)_2]$ and $[Ba(Acac)_2(H_2O)_2]$ were prepared by adding methanolic solutions of acetylacetone to solutions of the stoichiometric quantity of the nitrate in water, and precipitating the complex by adding sodium hydroxide. Prolonged drying in a drying pistol lead to dehydration of these complexes, and formation of the anhydrous complexes e.g. $Ca(Acac)_2$.

The Mg(II) complex isolated by this method appeared also to be the bis(aquo)- complex, as evidenced by analytical data, and the presence of strong O-H str. vibrations in the IR spectrum. Frequencies in the IR spectrum otherwise agreed with those reported for the anhydrous complex (1).

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt(°C)	
	(calculated)		(found)		(found)	(ref.)
$[Be(Acac)_2]$	57·9	6·8	55·4	6·8	105	108 (90)
$[Mg(Acac)_2(H_2O)_2]$	46·4	7·0	47·2	7·5	-	
$[Ca(Acac)_2]$	50·4	5·9	49·7	5·5	-	
$[Ca(Acac)_2(H_2O)_2]$	43·8	6·6	44·6	5·9	-	
$[Sr(Acac)_2(H_2O)_2]$	37·3	5·6	37·3	5·3	-	
$K\ Ca(Acac)_3\ (H_2O)$	45.6	5.9	45.7	6.0	-	

5. Beta-diketonates of Al(III)

$Al(HFA)_3$ was prepared by the method of Morris, Moshier and Sievers (94). The other Al(III) beta-diketonates were prepared by the method described for the acetylacetonate (91).

Complex	C(%)	H(%)	C(%)	H(%)	M.Pt.(°C)	
	(calculated)		(found)		(found)	(ref.)
$Al(Acac)_3$	55·6	6·5	55·7	6·6	194	194 (91)
$Al(DPM)_3$	68·7	10·0	68·4	9·9	262	264 (75)
$Al(Bzac)_3$	70·6	5·3	70·2	5·4	222	-
$Al(DBM)_3$	77·6	4·8	76·9	4·3	294	-
$Al(TFA)_3$	37·1	2·5	37·1	2·5	121	-
$Al(HFA)_3$	27·8	0·6	27·2	0·7	72	73 (94)

6. Group IV beta-diketonates

$[Si(Acac)_3]Cl.HCl$ and $[Si(Acac)_3].ZnCl_3$ were prepared by the methods reported in Inorganic Syntheses, 7, 33. $Zr(Acac)_4$, $Hf(Acac)_4$ and $Th(Acac)_4$ were prepared by methods reported in the literature.(92, 93.) The identity of the complexes was checked by their melting points. $Hf(Acac)_4$ M.Pt. = 169°C (reported 171·5 in ref. 93) and $Zr(Acac)_4$ M.Pt = 194°C (194°C in ref.92)

7. The Rare-earth trivalent acetylacetonates.

The tris(acetylacetonates) of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Ho(III) and Er(III) were prepared as described in the literature (95). A pH meter was used for monitoring the pH so as to prevent the precipitation of the metal hydroxides.

8. Dipivaloylmethanates of divalent metals.

The complexes [Ni(DPM)$_2$], [Ni(DPM)$_2$(H$_2$O)$_2$], [Zn(DPM)$_2$] and [Co(DPM)$_2$] were prepared as described in ref. 75.

Complex	C(%)	H(%)	C(%)	H(%)
	(calculated)		(found)	
[Zn(DPM)$_2$]	61·2	8·9	60·2	8·8
[Ni(DPM)$_2$(H$_2$O)$_2$]	57·3	9·2	58·7	8·6
[Co(DPM)$_2$(H$_2$O)$_2$]	57·3	9·2	57·6	9·1

9. Beta-iminoketone complexes of Cu(II), Ni(II) and Co(II)

The complexes Cu(AAI)$_2$ and Cu(EDDAA) (Fig. 18) were prepared by the methods described in the literature (96, 97). Cu(EDBSA), Ni(AAI)$_2$, Ni(EDDAA), Ni(EDBSA), Co(EDBSA), Cu(PDBSA) and Ni(PDBSA) werer prepared by analogous methods.

Complex	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
	(calculated)			(found)		
Cu(AII)$_2$	46·3	6·2	10·8	46·3	6·2	11·1
Ni(AII)$_2$	47·1	6·3	11·0	47·3	6·9	10·6
Cu(EDDAA)	50·4	6·4	9·8	49·5	6·3	9·4
Ni(EDDAA)	51·3	6·6	10·0	49·8	6·5	9·9
Cu(PDBSA)	59·4	4·7	8·2	59·8	4·9	8·2
Co(EDBSA)	59·1	4·3	8·6	59·2	4·1	8·1

10. 8-hydroxyquinoline complexes.

The 8-hydroxyquinoline complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared as described in the literature (98). Since 8-hydroxyquinoline is itself a reagent for gravimetric determination, it was not felt that analysis of these complexes was necessary. The IR spectra in the region 200–2000 cm^{-1} agreed well with those reported in the literature for these complexes (36).

11. Hexacyano- complexes of first transition period ions

Preparations described in Inorganic Syntheses were used to prepare the complexes $K_3[Mn(CN)_6]$ (99), $K_3[Cr(CN)_6]$ (100) and $K_3[Co(CN)_6]$ (101). $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were obtained commercially. The IR frequencies agreed well with those reported in the literature (4).

12. Tris(oxalato)-metallate(III) ions of the first transition period

The complexes $K_3[Cr(C_2O_4)_3].3H_2O$, $K_3[Fe(C_2O_4)_3].3H_2O$ and $K_3[Co(C_2O_4)_3].3H_2O$ were prepared as described in the literature (102). $K_3[Sc(C_2O_4)_3].3H_2O$ was prepared by a method analogous to that reported for the Al(III) compound.(102). $K_3[V(C_2O_4)_3].3H_2O$ was prepared by adding an aqueous solution of $K_2C_2O_4$ to the stoichiometric quantity of VCl_3 dissolved in the minimum of water. Bright green crystalline tris(oxalato)-vanadium(III) is susceptible to oxidation to the vanadyl compound, so that elemental analysis was considered necessary for this complex. The Mn(III) complex was prepared accordto the method of Cartledge and Erichs (103). This complex is highly sensitive to heat, and is also photosensitive. Synthesis was therefore carried out in a darkened fume-cupboard, and the complex stored at 0°C in the dark. Unfortunately, because of the presence of potassium in the complex we were unable to analyse it ourselves, and it was too unstable to survive long enough to be sent away for commercial analysis. Reference IR spectra were available (8) for checking the identity of the Cr(III), V(III) and Co(III) complexes.

Calculated for $K_3[V(C_2O_4)_3].3H_2O$: C = 15·1%, H = 1·3%, K = 49·3%, O = 24·1%.
Found: C = 15·4%, H = 1·2%, K = 48·3%, O = 23·9%

13. Acetylacetonates of oxo-cations

$VO(Acac)_2$ was obtained as the product of oxidation of $V(Acac)_3$, and was purified by sublimation. $UO_2(Acac)_2$ was prepared by adding a methanolic solution of (Acac)H to a methanolic solution of uranyl nitrate. The molybdenyl complex was prepared as in ref. 104.

Analysed for $VO(Acac)_2$: calculated: C = 45·3, H = 5·3%. Found: C = 45·8% , H = 5·6%

Analysed for $UO_2(Acac)_2.H_2O$: Calculated: C = 24·7%, H = 3·3%. Found: C = 24·7%, H = 3.3%

14. Beta-diketonate ligands

These were all obtained commercially except for dipivaloylmethane and pivaloylacetone. These were both prepared as reported in the literature for dipivaloylmethane (106), by the condensation of t-butylmethyl ketone with ethyl t-butyrate and ethyl acetate respectively.

C. RESULTS

1. IR frequency data

The IR frequencies observed for the complexes synthesised are recorded in the following tables. The reasons for the band assignments made will be discussed later. All frequencies are in cm^{-1}.

Table I. Trivalent transition metal tris(acetylacetonates of the first transition period. Nujol. 200–2000cm^{-1}.

Sc	Ti	V	Cr	Mn	Fe	Co	Ga	Assignment
1580	1565	1571	1574	1593	1575	1580	1586	C=O str.
1529	1530	1526	1522	1516	1530	1522	1535	C=C str.
1276	1276	1276	1279	1256	1276	1280	1281	C=C + C–CH_3 str.
1191	1185	1190	1193	1190	1190	1193	1194	C–H in-plane bend
1026	1021	1025	1025	1016	1024	1016	1025	CH_3 rock
929	930	932	933	925	929	936	935	C=O + C–CH_3 str.
802	801	803	791	802	802	782	800	C–H out-of-plane bend
776	775	772	773	775	772	773	770	
665	667	668	682	672	667	695	683	M–O str. + ring/def.
665	650	658	660	655	655	655	655	ring def.
550	568	587	611	598	560	665	584	M–O str.
542	556	572	595	570	550	637	584	M–O str.
				560				extra band in Mn(III)
439	429	449	462	462	437	466	445	M–O + C–CH_3 str.
408	–	413	415	428 404	406	437	425	O–M–O bend.
331	–	316	355	333	299	383	411	
317	–	–	–	–	202	–	272	

Table II

Trivalent transition metal acetylacetonates of the second transition period, plus the tris(acetylacetonates) of Al(III) and La(III). Units are cm^{-1}.

Y	Mo	Ru	Rh	In	Al	La	Assignment
1611	1571	1555	1575	1584	1597	1594	C=O str.
1532	1524	1525	1522	1529	1535	1527	C=C str.
1265	1278	1273	1272	1269	1290	1257	C=C + C-CH$_3$ str.
1203	1197	1203	1202	1202	1192	1195	C-H in-plane bend
1021	1028	1028	1020	1025	1030	1015	CH$_3$ rock.
920 937	942	940	935	933	937	915	C=O + C-CH$_3$
790	785	782	792	805	799	-	C-H out-of-plane bend
766	785	782	775	781	770	777	
658	676	690	700	675	687	-	M-O str. + ring def.
563	599	645	675	675	596	534	M-O str.
658	657	660	663	651	661	655	ring def.
536	599	621	650	572	580	527	M-O str.
425	449	463	467	436	493	412	M-Ostr. + C-CH$_3$str.
404	-	325	437	415	424	-	O-M-O bend.
337	-	212	348	404	-	-	

Table III

Divalent tris(acetylacetonates) of first transition period metal(II) ions. (Recorded as the potassium salts.) Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Ca	Mn	Fe	Co	Ni	Zn	Assignment
1597	1601	1583	1593	1596	1590	C=O str.
1527	1525	1530	1522	1525	1520	C=C str.
1254	1259	1262	1259	1260	1256	C=C + $C-CH_3$
1206	1199	1195	1202	1202	1200	C-H in-plane bend
1041	1033	1042	1026	1021	1019	CH_3 rock.
1015	1018	1018				
919	920	928	926	925	923	C=O + $C-CH_3$ str.
793	778	-	787	785	784	C-H out-of-plane bend
764	769	770	766	768	771	
655	656	659	659	658	655	ring def.
-	-	-	-	-	-	M-C str. + ring def.
-	-	-	-	-	-	M-Ostr.
537	543	558	561	568	547	M-Ostr.
415	416	419	422	426	415	M-O + $C-CH_3$ str.
400	401	-	407	408	407	O-M-O bend
-	-	-	-	-	-	

Table IV

Anhydrous bis(acetylacetonates) of first transition period divalent ions. Nujol. 200 - 2000 cm^{-1}. Units = cm^{-1}.

Mn	Fe	Co	Ni	Cu	Zn	Assignments
1611	1581	1591	1620	1580	1586	C=O str.
1520	1522	1530	1527	1555 1536	1530	C=C str.
1260	1261	1262	1265	1277	1270	C=C + C-CH_3 str.
1196	1200	1200	1200	1190	1203	C-H in-plane bend
1017	1018	1020	1023	1022	1020	CH_3 rock
939 924	918	922	932	939	932	C=O + C-CH_3 str.
802	800	789	785	-	800	C-H out-of-plane bend
770	772	771	770	784	777	
-	664	670	674	686	684	M-O str. + ring def.
655	655	650	656	655	655	ring def.
-	-	-	-	-	585	M-Ostr.
545	558	581	593	615	565	M-Ostr.
448	434	425	440	455	466	M-O + C-CH_3 str.
-	-	-	-	431	422	C-M-C bend
-	-	-	-	-	-	

Table V

Dihydrated bis(acetylacetonates) of first transition period divalent ions $M(Acac)_2(H_2O)_2$, plus $Cd(Acac)_2$. Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Mn	Co	Ni	Zn[a]	Cd	Assignment.
1616	1612	1598	1604	1609	C=O str.
1527	1528	1522	1525	1522	C=C str.
1257	1265	1265	1265	1250	C=C + $C-CH_3$ str.
1203	1203	1201	1197	1170	C-H in-plane bend
1020	1023	1019	1022	1021	CH_3 rock
929	935	925	933	923	C=O + $C-CH_3$ str.
768	771	775	772	782	C-H out-of-plane bend
-	-	-	-	740	"
-	676	-	-	684	M-O str. + ring def.
660	660	660	655	655	ring def.
-	-	-	-	625	M-O str.
551	568	571	559	556	M-O str.
-	426	437	412	423	M-O + $C-CH_3$
-	-	-	-	318	O-M-O bend

[a] Is the monohydrate $Zn(Acac)_2(H_2O)$

Table VI

Ammonia and pyridine adducts of bis(acetylacetonato)-metal(II) complexes. Nujol. 4000 - 200 cm^{-1}. Units are cm^{-1}.

$M(Acac)_2(NH_3)_2$				$M(Acac)_2(py)_2$				
Mn	Co	Ni	Zn[a]	Mn	Co	Ni	Zn[a]	Assignments
3360	3360	3355	3363	-	-	-	-	N-H str.
3280	3280	3276	3282	-	-	-	-	N-H str.
-	-	-	3234	-	-	-	-	N-H str.
1626	1620	1626	1628	-	-	-	-	N-H def.
-	-	-	-	1611	1609	1600	1611	C-C py
-	-	-	-	1601	1588	1593	1588	C=O str.
1527	1528	1522	1525	1522	1528	1525	1531	C=C str.
1257	1254	1256	1265	1255	1261	1259	1265	C=C + $C-CH_3$ str.
1220	1235	1246	1230	-	-	-	-	NH_3
1204	1203	1216	1203	-	-	-	-	
-	-	-	-	1219	1216	1216	1222	pyridine
1184	1203	1203	1196	1195	1203	1202	1197	C-H in-plane def.
-	-	-	-	1160	1159	1151	1163	pyridine
-	-	-	-	1075	1071	1078	1079	
-	-	-	-	1035	1040	1039	1046	
1018	1017	1018	1018	1013	1017	1014	1017	CH_3 rock
926	927	927	925	921	924	922	928	C=O + $C-CH_3$ str.
767	765	764	765	758	778	768	787	C-H out-of-plane bend
-	-	-	-	750	759	760	761	
-	-	-	-	702	705	701	705	
-	-	-	-	-	675	680	668	M-O + $C-CH_3$ str.
660	661	660	659	652	651	655	656	ring def.
-	-	-	-	622	628	632	640	py
547	560	572	549	542	563	576	554	M-O str.
408	414	420	412	416	417	437	424	M-O + $C-CH_3$ str.

[a] These are the mono-adducts $Zn(Acac)_2(NH_3)$ and $Zn(Acac)_2Py$.

Table VII

Monovalent acetylacetonates of Group I, and Tl(I) acetylacetonate. Nujol. 2000 – 200 cm^{-1}. Units are cm^{-1}.

Li	Na	K	Rb	Cs[a]	Tl	Assignment
1609	1617	1619	1620	-	1608	C=O str.
1523	1515	1511	1510	1506	1503	C=C str.
1266	1245	1237	1232	1230	1235	C=C + $C-CH_3$ str.
1199	1200	1201	1200	1199	1199	C–H in-plane bend
1173	1171	1171	1172	-	-	C–H in-plane bend
1019	1015	1010	1007	1008	1010	CH_3 rock
940						
919	915	911	906	909	915	C=O + $C-CH_3$ rock
802	-	-	-	-	-	C–H out-of-plane bend
766	767	762	760	763	770	
-	-	-	-	-	-	M–O + ring def.
659	661	655	655	655	655	ring def.
-	-	-	-		-	M–O str.
557	534	522	520		526	M–O str.
508	520	-	-		-	$M-OH_2$?(very broad)
439	408	410	409		406	M–O $\mp$ $C-CH_3$ str.
427	-	-	-		-	
404	-	-	-		-	
357	-	-	-		-	
342	-	-	-		-	

[a] recorded on Beckman IR-8 in KBr. C=O str. not reliable.

Table VIII

Divalent acetylacetonates of Group IIa elements.
Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Be[a]	Mg[b]	Ca[b]	Sr[b]	Ba[b]	Ca[a]	Assignment
1588	1615	1609	1611	1610	1616	C=O str.
1535	1528	1522	1522	1514	1525	C=C str.
1300	1265	1256	1251	1247	1245	C=C + C-CH_3 str.
-	1202	1200	1200	1200	1200	C-H in-plane bend
1190	1175	1170	1171	1170	1170	"
1040	1022	1018	1015	1015	1018	CH_3 rock
963	932	918	917	914	922	C=O + C-CH_3 str.
782	-	-	-	-	785	C-H out-of-plane bend
768	766	768	762	771	765	
936	690 725	-	-	-	-	M-O str. + ring def.
663	663	657	655	655	657	ring def.
827	624	570	572	-	-	M-O str.
748	563	535	528	524	535	M-O str.
498	477	427	422	411	445	M-O + C-CH_3 str.
425	-	-	-	-	421	O-M-O bend

[a] $M(Acac)_2$. [b] $M(Acac)_2(H_2O)_2$.

Table IX

Acetylacetonates of Group IV elements, and of oxo-metal cations (VO^{++}, MoO_2^{++}, UO_2^{++}). Units are cm^{-1}.

Si^{IV}_a	Zr^{IV}	Hf^{IV}	Th^{IV}	UO_2^{++}	MoO_2^{++}	VO^{++}	Assignment
1575	1591	1593	1590	1590	1592	1565	C=O str.
1555	1540	1539	1538	1520	1511	1530	C=C str.
1315	1281	1279	1270	1275	1285	1290	C=C + $C-CH_3$ str.
1193	1190	1190	1192	1170	1170	1190	C-H in-plane bend
1173	-	-	-	-	-	-	
1045	1028	1027	1022	1035	1025	1025	CH_3 rock
970	957	954	947	-	936	942	C=O + $C-CH_3$ str.
950	935	937	927	-	-	-	
-	-	-	-	924	909	999	M=O asym. str.
838	779	775	781	798	801	800	} C-H out-of-plane bend
752	759	760	770	783	-	790	
-	-	-	-	670	678	688	M-O ring def.
663	662	660	655	655	654	658	ring def.
730	570	-	565	569	578	-	M-O str.
628	545	542	524	531	551	609	M-O str.
544	428	427	406	408	455	484	M-O + $C-CH_3$ str.
470	300	-	-	-	413	434	O-M-O bend
-	-	-	-	-	287	367	

[a] Si(IV) was recorded as $[Si(Acac)_3]^+(ZnCl_3)^-$.

Table X

Tris(acetylacetonates) of rare-earth trivalent ions[a]

Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Assignment
1608	1606	1605	1605	1595	1596	1608	1610	1606	C=O str.
1523	1521	1523	1527	1534	1539	1534	1525	1527	C=C str.
1258	1257	1260	1262	1268	1271	1264	1265	1266	C=C + C-CH_3str.
1191	1195	1197	1195	-	1202	1192	1195	1190	C-H in-plane bend
1172	1189	-	1170	1171	1170	-	-	-	
-	-	-	-	1158	-	-	-	-	
1019	1016	1020	1020	1021	1023	1021	1023	1019	CH_3 rock
920	917	919	920	926	929	922	922	921	C=O + C-CH_3str.
-	-	850	-	895	870	-	-	-	
766	767	768	768	757	760	768	788	789	C-H out-of-plane bend
756	760	761	-	-	-	759	768	767	
-	-	-	-	-	-	-	-	757	
674	-	-	-	694	697	-	-	-	M-O +ring def.
655	655	657	654	655	657	657	660	655	ring def.
538	552	568	566	620	-	567	-	566	M-O str.
529	531	533	534	534	538	536	535	536	M-O str.
410	412	412	414	415	423	420	422	424	M-O + C-CH_3str.

[a] All have the octa-coordinate structure $M(Acac)_3.2H_2O$ (62). For the frequencies for $La(Acac)_3.2H_2O$ see Table II.

Table XI

Spectra of the tris(trifluoroacetylacetonates) of the first transition period M(III) ions. Nujol. Units are cm^{-1}.

Sc	V	Cr	Mn	Fe	Co	Ga	Assignment
1624	1615	1615	1616	1616	1609	1624	C=O str.
1542	1533	1532	1534	1531	1531	1540	C=C str.
1300	1299	1300	1290	1294	1302	1302	C=C + C–R str.
1235	1231	1230	1226	1230	1230	1235	} CF_3
1204	1196	1197	1195	1196	1199	1199	
1154	1150	–	1149	1150	1150	1153	C–H in-plane bend
1144	1134	1132	1135	1139	1130	1146	C–H in-plane bend
1028	1024	1020	1024	1025	1024	1026	} CH_3 rock
1009	1006	1011	1005	1006	1011	1009	
980	977	976	972	–	975	973	C–F bend
954	947	950	948	949	954	950	C=O + C–R str.
–	–	896	897	–	890	–	
861	863	866	861	863	872	867	C–CF_3 str.
805	803	799	802	802	793	802	} C–H out-of-plane bend
794	796	787	787	789	780	789	
758	750	755	–	752	753	756	C–CF_3 str.
730	732	735	732	731	740	736	C–CF_3 str.
610	620	626	620	609	657 681	621	M–O str. + ring def.
581	592	599	582	585	605	592	M–Ostr.
520	522	520	519	516	522	518	CF_3
500	522	533	538	505	550	518	M–O str.
426	429	437	432	424	445	429	M–O + C–CH_3 str.
–	–	379	409	–	418	–	O–M–O bend
323	320	339	320	310	382	345	

Table XII

Trifluoroacetylacetonates of second period M(III) ions, and Al(III), K(I), Cu(II) (both Cu(TFA)$_2$ and Cu(TFA)$_2$(H$_2$O)) Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Y	Rh	In	Al	Cu^a	Cu^b	K	Assignment
1640	1606	1624	1632	1616	1623	1661	C=O str.
1542	1530	1539	1548	1599 1536	1543	1555	C=C str.
1297	1303	1296	1310	1311	1312	1277	C=C + C-CH$_3$ str.
1231	1235	1236	1236	1229	1232	1219	CF$_3$
1195	1199	1204 1198	1200	1196	1196	1189	
1142	1146	1151	1152	1155	1142	1132	C-H in-plane bend
-	-	-	-	1140	-	1115 1090	C-H in-plane bend
1025	1019	1025	1026	1029	1020	1017	CH$_3$ rock
1003	-	1007	1012	1015	-	992	
948	947	943	958	951	954	928	C=O + C-CH$_3$ str.
-	977	-	-	974	-	-	C-F bend
892	-	-	-	-	-	-	
856	877	866	869	870	868	843	C-CF$_3$ str.
-	-	807	800	799	799	806	C-H out-of-plane bend
783	795	795	787	-	788	765	
759	746	755	760	762	762	740	C-CF$_3$ str.
728	726 677	735	736	739	737	722	C-CF$_3$ str.
610	665	612	625	637	632	600	M-Ostr. + ring def.
565	610	590	601	602	601	550	M-O str.
520	523	520	521	520	520	518	CF$_3$
-	547	507	545	534	525	-	M-O str.
406	445	425	464	445	440	387	M-O + C-CH$_3$ str.
-	435	425	445	-	422	-	O-M-O bend
-	387	307	420	-	-	-	
-	-	293	-	-	-	-	

a = Cu(TFA)$_2$, b = Cu(TFA)$_2$(H$_2$O)

Table XIII

Tris(benzoylacetonates) of the first transition period M(III) ions. Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Sc	V	Cr	Mn	Fe	Co	Assignment
1591	1590	1590	1592	1591	1590	C=C phenyl
1553	1546	1555	1557	1551	1561	C=O str.
1513	1513	1524	1515	1520	1525	C=C str.
1489	1490	1490	1488	1489	1491	C=C phenyl
1308	1308	1309	1305	1309	1308	C=C + C-R str.
1294	1297	1299	1283	1294	1297	
1208	1210	1210	1210	1209	1213	C-H in-plane bend
1180	1182	1182	1182	1181	1183	
1159	1158	1158	1159	1158	1159	C-H phenyl
1110	1114	1111	1108	1109	1113	
1071	1072	1073	1072	1072	1074	
1030	1029	1029	1030	1029	1030	CH_3 rock
1009	1010	1011	1009	1009	1012	C-H phenyl
1000	1000	1000	1001	1001	1002	
961	959	961	956	960	965	C=O + C-CH_3
931	930	930	928	931	931	C-H phenyl
847	850	854	850	850	861	
811	817	803	816	818	799	C-H out-of-plane bend
806	804		804	806		
791	788	792	790	793	790	C-H out-of-plane bend
776	773	770	774	775	768	
724	722	-	723	723	718	C-H phenyl
718	716	715	715	715	707	
690	685	695	692	685	693	C-H phenyl
683	685	691	686	685	693	M-O + ring def.
620	619	621	620	619	619	C-H phenyl
603	608	600	602	603	601	C-H phenyl
570	-	-		579	-	C-H phenyl
544	586	612	585	549	650	M-O str.
544	551	558	560	541	566	M-O str.
			540			extra band in Mn(III)
446	451	465	465	446	479	M-O + C-CH_3
426	427	436	427	427	442	
332	312	375	332	328	418	
-	-	326	-	292	-	

Table XIV

Benzoylacetonates of Li(I), Na(I), K(I), Cu(II), Al(III).
Nujol. 2000 - 200 cm^{-1}. Units are cm^{-1}.

Li	Na	K	Cu	Al	Assignment
1606	1606	1606	1591	1597	C=C phenyl
1580	1585	1597	1562	1569	C=O str.
1520	1516	1512	1524	1523	C=C str.
1300	1300	1300	1300	1314	C=C + C-R str.
1280	1265	1259	1292	1314	
1184	1186	1173	1182	1173	
1112	1112	1104	1108	1112	C-H phenyl
-	-	-	1096	-	
1077	1073	1072	1071	1071	
1030	1030	1027	1029	1030	CH_3 rock
-	-	-	1010	1004	C-H phenyl
1000	995	996	1003	998	
962	945	933	960	966	C=O + C-CH_3 str.
848	843	838	856	855	C-H phenyl
807	804	805	-	816	C-H out-of-plane bend
-	-	-	-	804	
-	793	-	-	797	C-H out-of-plane bend
776	769	762	774	773	
724	722	723	723	723	C-H phenyl
699	696	698	694	692	
-	676	676	684	688	M-O + ring def.
577	560	550	629	593	M-O str.
530	521	-	555	552	M-O str.
500	508	504	-	-	
427	427	427	427	437	phenyl vibration
412	400	404	459	472	M-O + C-CH_3 str.

Table XV

Spectral data for dibenzoylmethanate complexes. Units = cm^{-1}.

Sc^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Al^{3+}	Cu^{2+}	K^{+}	Assignment
1592	1591	1591	1593	1592	1591	1597	1595	1607	C=C phenyl
1540	1530	1540	1554	1533	1547	1556	1549	1569	C=O str.
1529		1526	1520	1528	1526	1534	1538 1532	1516	C=C str.
1484	1485	1483	1484	1484	1489	1480	1487	1506	C=C phenyl
1318	1317	1319	1304	1309	1320	1328	1316	1301	C=C + C–Ph str.
1299	1292	1308	1285	1300	1308	1306	1293	1272	C=C + C–Ph str.
1227	1229	1228	1224	1225	1229	1230	1234	1221	C–H in-plane
1184	1181	1182	1180	1180	1181	1181	1185	1176	
1156	1166	–	–	1157	1158	1162	1168	1159	
1128	1124	1130	1123	1128	1133	1133	1131	–	
1097	1098	1098	1098	1096	1098	1100	1098	1071	C–H phenyl
1064	1066	1070	1070	1067	1073	1078	1070	1051	
1026	1026	1025	1023	1025	1026	1025	1024	1021	
1001	1001	1001	1001	1001	1001	1001	1001	1001	
973	973	973	974	973	973	974	975	975	
941	941	945	939	940	939	950	945	940	C–Ph str.
928	926	921	–	925	927	930	935	925	C–Ph str.
894	895	892	897	895	890	890	890	886	C–H phenyl
835	835	835	851	850	844	849	841	842	
817	814	811	813	813	808	814	810	812	C–H out-of-plane bend
786	790	787	787	789	786	789	782	793	
769	772	–	769	770	–	–	–	–	
758	757	756	757	759	754	757	745	759	
723	730	723	727	727	732	727	709	725	
715	715	–	715	713	717	–	–	–	C–H phenyl
697	705	–	705	705	703	702	697	–	
687	693	695	694	692	–	–	690	698	
681	686	687	686	685	688	687	685	677	
620	620	620	620	619	619	620	620	618	
612	630	643	649 631	623	665	634	658	610	M–O str. Mn(III) extra/band
549	559	569	576	551	575	589	574	564	M–Ostr.
536	543	544	560 523	537	551	560 532	549	521	
450	456	465	462	455	486	453	465	355	M–O + C–CH$_3$ str.
439	444	450	458	440	461	427	440	–	O–M–O bend
374	–	–	–	387	443	–	–	–	
317	315	333	327	291	329	–	–	–	

Table XVI

Spectral data for dipivaloylmethanates of first transition period trivalent ions. 2000 – 200 cm^{-1}. Nujol. Units are cm^{-1}.

Sc	V	Cr	Mn	Fe	Co	Ga	Assignment
1571	–	1588	1595	1592	–	1595	C=O str.
1561	1563	1566^{s}	1573^{s}	1563	1576^{s}	1577^{s}	
1556^{s}	1549^{s}	1549	1551	1550^{s}	1565	1556	
1513	1508	1504	1501	1510	1496	1506	C=C str.
1297	1297	1297	1288	1294	1310	1301	C=C + C–$C(CH_3)_3$ str.
1251	1250	1249	1250	1248	1246	1253	$C(CH_3)_3$ skeletal
1229	1227	1229	1225	1229	1230	1228	
1199	1201	1199	1200	1199	1200	1200	C–H in-plane bend
1179	1176	1180	1178	1178	1180	1183	$C(CH_3)_3$ skeletal
1146	1145	1148	1136	1146	1150	1146	
1026	1025	1026	1025	1028	1027	1026	CH_3 rock
965	965	965	960	962	969	964	C=O + C–$C(CH_3)_3$ str.
939	933	937	933	939	938	940	
			938				C–H in $C(CH_3)_3$
873	875	874	873	874	877	877	
–	–	–	823	821	826	826	
804	804	–	–	803	–	–	
799	796	792	793	795	785	794	C–H out-of-plane
765	762	761	761	760	754	765	C–H in $C(CH_3)_3$
740	740	741	741	740	–	745	
620	630	644	645	624	664	641	M–O str.
508	510	517	509	504	520	511	M–O str.
467	483	485	482	479	505	486	M–O + ring def.
429	435	446	443	430	460	438	O–M–O bend
337	–	355	–	–	–	–	

s = the most intense band in the carbonyl region of the spectrum of each individual complex.

Table XVII

Spectral data for Group I dipivaloylmethanates and $Al(DPM)_3$. 2000 - 200 cm^{-1}. (cm^{-1}). Nujol.

Li	Na	K	Rb	Cs	Al	Assignment
1596	1593	1592	1591^s	1605^s	-	C=O str.
1577^s	1581^s	1581^s	1576	1578	1582	
1556	-	1556	1551	-	1560	
1540	1543	1540	1540	1540	-	
1517^s	1505^s	1496^s	1497^s	1497^s	1515^s	C=C str.
1507	-	1515	1516	-	-	
1285	1277	1271	1271	1269	1305	C=C + $C-C(CH_3)_3$ str.
1247	1244	1249	1244	1242	1253	$C(CH_3)_3$ skeletal
1217	1224	1226	1221	1223	1233	
1195	1185	1187	1192	1185	1199	C-H in-plane-bend
1172	-	-	-	-	-	$C(CH_3)_3$ skeletal
1133	1128	1125	1128	1121	1155	
1025	1021	1028	1025	1020	1028	CH_3 rock
960	956	954	955	951	973	C=O + $C-C(CH_3)_3$ str.
937	938	933	935	935	940	
868	865	865	865	865	878	
795	793	792	792	791	795	C-H out-of-plane bend
769	754	762	761	767	764	C-H in $C(CH_3)_3$
740	736	733	736	735	741	
665						
603	595	585	-	585	661	M-O str.
-	-	533	-	-	-	$M-OH_2$?(very broad)
507	-	-	-	-	531	M-O str.
483	478	474	482	476	486	M-O + ring def.
451	-	-	-	-	450	O-M-O bend
-	-	-	-	-	396	

s = the most intense band in the carbonyl region of the spectrum of each individual complex.

Table XVIII

Spectral data for dipivaloylmethanate complexes of first transition period M(II) ions. (cm^{-1}). Nujol. 2000 - 200cm^{-1}.

Ca	Co	Ni^a	Ni^b	Cu	Zn	Assignment
1598^s	-	1590	1600	1596	-	
1590	-	1567	1587^s	1571	-	
-	1558^s	1549^s	-	1555^s	1555^s	C=O str.
-	-	1534	-	1540	-	
1507	1518	1501	1505	1504	1510	C=C str.
1284	1296	1310	1290	1297	1293	C=C + C–C(CH$_3$)$_3$
1249	1252	1257	-	1250	1248	C(CH$_3$)$_3$ skeletal
1226	1223	1230	1226	1230	1221	
1191	1202	1202	1187	1202	1202	C–H in-plane bend
-	1186	1178	-	1180	1186	
1138	1144	1158	1138	1152	1140	C(CH$_3$)$_3$ skeletal
1025	1030	1028	1020	1026	1024	CH$_3$ rock
960	959	972	960	964	954	C=O + C–C(CH$_3$)$_3$ str.
939	940	938	932	937	940	C–H in C(CH$_3$)$_3$
870	877	879	873	876	875	
796	800	794	791	796	798	C–H out-of plane
762	771	769	760	771	771	C–H in C(CH$_3$)$_3$
739	746	759 744	743	745	744	
605	636	664	636	646	646	M–O str.
-	522	521	-	518	516	M–O str.
485	483	518	487	496	480	M–O + ring def.
-	427	444	-	441	422	O–M–O bend

^{a}Ni(DPM)$_2$. ^{b} Ni(DPM)$_2$(H$_2$O)$_2$. ^{s} Strongest band in the carbonyl region for each individual complex.

Table XIX

Spectral data for hexafluoroacetylacetonates. (cm^{-1}).

Al^{3+}	Cu^{2+}	K^{+}	V^{3+}	Fe^{3+}	Assignment
1655	1655	1677	1649	1647	C=O str.
1630	1618	1555	1612	1623	C=C str.
1578	1568	1534	1570	1575	C=O str. + C-H bend
1555	1542	1510	1551	1553	C=O str. + C-H bend
1262	1278	1259	1271	1271	CF_3
1211	1205	1212	1211	1215	
1168	1148	1151	1156	1160	
1146	1148	1132	1139	1145	C-H in-plane bend
1119	-	1070	1103	1110	
977	976	977	971	-	C-F bend
966	-	945	-	953	
920	922	-	-	920	
-	893	894	-	-	$C-CF_3$ str.
-	844	839	835	-	
815	807	805	824 816	820	C-H out-of-plane bend
770	771	775	771	770	C-H out-of-plane bend
750	744	754	747	746	$C-CF_3$ str.
740	739	737	735	738	$C-CF_3$ str.
672	675	663	671	666	M-O + ring def.
610	-	-	-	-	M-C + ring def.
598	596	580	597	595	M-O str.
548	530	528	531	530	CF_3
532	517	-	523	517	
424	414	364	-	408	M-O + $C-CF_3$ str.
374	-	-	355	323 285	

Table XX

Spectral data (cm^{-1}) for 3-methyl and 3-ethyl acetylacetonate complexes. 2000 - 200 cm^{-1}. Nujol.

3-MeA

Sc	V	Cr	Fe	Sc	V	Cr	Fe	Al	Assignment
1588	1573	1577	1580	1578	1575	1581	1575	1598	C=O str.
1530	1527	1521	1538	1528	1542	1540	1538	-	C=C str.
1298	1297	1295	1296	1293	1289	1295	1290	1307	C=C + C-CH_3str.
-	-	1247	-	1263	1263	1265	1261	1266	
1174	1176	1176	1175	1178	1176	1174	1173	1180	C-H in-plane/ bend
1073	1077	1079	1077	1065	1066	1064	1065	1066	
1026	1027	1031	-	-	-	-	-	-	} CH_3 rock
1001	1007	1008	1010	995	1005	1006	998	1005	
976	980	981	980	954	954	953	954	956	
891	893	895	893	908	910	913	909	918	C=O + C-CH_3str.
836	-	836	-	836	-	836	836	-	
806	806	807	807	-	-	-	-	-	} C-H out-of-plane bend
770	770	778	775	780	783	784	782	782	
722	723	730	722	711	715	722	710	727	M-O + ring def.
658	660	659	658	680	683	684	679	683	ring def.
561	600	623	580	-	600	622	-	-	M-O + ring def.
541	580	608	560	555	585	609	575	597	M-O str.
450	460	468	446	452	465	476	446	503	M-O + C-CH_3str.
438	-	-	-	-	430	433	-	466	O-M-O bend
338	330	359	290	339	333	361	320	-	

Table XXI

Spectral data (cm^{-1}) for acetylacetoneimime complexes of Cu(II) and Ni(II), and for bis(acetylacetone)ethylenediamine complexes of Ni(II) and Cu(II). Nujol. 4000 - 200 cm^{-1}.

$M(AAI)_2$		M(EDDAA)		
Cu	Ni	Cu	Ni	Assignment
3298	3292	-	-	N-H str.
1597	1592	1600	1593	C=O + C=N str.
1540	1555	1528	1515	C=C str.
	1315	1287	1287	
1230	1250	1228	1224	
1182	1185	1162	1160	C-H in-plane bend
-	-	1117	1129	
-	-	1074	1076	$-CH_2-$ group
-	-	1045	1051	
1021	1028	1017	1019	CH_3 rock
938	938	949	956	C=O + C=N + $C-CH_3$ str.
820	814	807	817	C-H out-of-plane bend
760	758	755	770	C-H out-of-plane bend
692	710	687	696	M-O + ring def.
650	685	650		M-O + ring def.
620	661	611	617	M-O str.
580	630	572	591	M-N str.
466	486	462	484	M-O + $C-CH_3$
437	458	421	-	
-	448	-	-	
-	425	-	-	

Table XXIII

Spectral data for bis(salicylaldehyde)ethylenediamine complexes of Co(II), Ni(II), Cu(II) and Zn(II), and bis(salicylaldehyde)propylenediammine complexes of Cu(II) and Ni(II). Nujol. Units are cm^{-1}.

M(EDBSA)				M(PDBSA)			
Co	Ni	Cu	Zn	Ni	Cu	Assignment	
1640	1630	1637	1650	1630	1637	C=O str.	
1611	1607	1609	1607	1615	1608	C=C str.	
1532	1545	1550	1545	1542	1542	C=C str.	
1352	1358	1344	1344	1354	1351		
1333	1324	-	-	-	1324		
1292	1245	1290	1250	1225	-		
1203	1207	1210	1190	1208	1202		
1151	1158	1167	1155	1149	1154		
1145	-	-	-	-	-		
1133	1134	1135	1132	1136	1136		
1098	1096	1070	-	-	-		
1055	-	1050	1050	1058	1055		
1047	1037	-	1046	1034	1036		
1026	-	1019	1027	-	1015		
986	974	-	986	-	990		
957	954	-	950	950	972		
907	908	907	905	908	906		
859	856	850	864	841	860		
753	754	765	753	748	752		
746	744	746	745	-	-		
737	-	-	-	733	732		
658	690	-	-	-	-		
650	662	662	654	677	663	M-O str.	all coupled to ligand vibrations.
625	637	628	615	627	627	M-O str.	
599	615	607	570	614	609	M-O str.	
560	555	576	550	558	555	M-N str.	
510	523	530	505	535	535		
460	470	462	455	466	-	M-O str.	

Table XXIV

Spectral data (cm^{-1}) for 8-hydroxyquinoline complexes of first transition period divalent ions. Nujol. 2000 - 200 cm^{-1}.

Co	Ni	Cu	Zn	Assignment
1608	1605	1603	1610	C=C aromatic
1585	1585	1577	1581	
1504	1505	1505	1507	
1321	1328	1328	1327	
1280	1287	1284	1281	
1238	1230	1236	1243	
1210	-	1223	1213	
1178	-	1181	1181	
1112	1116	1120	1113	
1035	-	1035	1037	
915	-	-	910	
891	-	-	892	
826	828	821	830	
805	-	805	806	
791	793	787	794	
752	749	745	753	
734	740	725	736	
681	680	-	678	
652	658	646	648	
618	-	-	617	
605	612	633	606	M-O + ring def.
573	-	587	570	M-O + ring def.
511	505	524	508	M-O str.
495	505	475	492	
411	404	408	410	
-	-	330	-	

Table XXV

Frequency data (cm^{-1}) for tris(oxalato)metallate(III) complexes. Nujol and CsI pellets. 2000 - 200 cm^{-1}.

CsI pellets

Sc	V	Cr	Mn	Fe	Co	Assignment
1720	1721	1720	1718	1720	1710	C=O str. (asym.)
-	1691	1687	1683	1688	1683	C=O str. (asym.)
1647	1645	1646	1645	1648	1635	C-O + C-C str.
1364	1396	1392	1400	1392	1402	C-O + C-C str.
1325	1267	1264	1280	1275	1256	C-O str. + O-C=O def.
932	900	900	896	894	907	C-O str. + O-C=O def.
812	812	817	811	806	811	O-C=O def. + M-O str.
580	584	600	592	583	-	
531	534	544	524	534	569	M-O + C-C str.
480	500	487	492	505	477	ring def. + O-C=O def.
320	367	416	372	354	446	M-O str. + ring def.
340	341	358	330	345	358	O-C=O bend

Nujol

1720			1718	1730	
-			1683	1690	
1647			1645	1650	
1367			-	-	
1317			-	1278	
932			-	890	
812			811	808	
531			592	584	
			524	535	
480			492	504	
320			368	350	
-			-	-	

Table XXVI

Spectral data for hexacyano- complexes. (cm^{-1}). Nujol. 4000 - 200 cm^{-1}.

Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Fe^{2+}	Assignment
2131	2112	2119	2131	2044	C≡N str.
465	485	512	566	583	M-C≡N bend
342	361	389	413	416	M-C str.

2. UV spectral data

Table XXVII

Absorption bands in potassium salts of beta-diketonate ligands. Values are in mμ. 200 - 800 mμ.

Complex	Solvent	$\pi_3 - \pi_5^*$	$\pi_3 -- \pi_4^*$
K(Acac)	Methanol	(204)[a]	276
K(Bzac)	"	246	307
K(DBM)	"	250	340
K(TFA)	"	(207)[a]	292
K(HFA)	"	212	303
K(DPM)	"	(203)[a]	276

[a] These are doubtful values since they border on the region of strong absorption of the solvent.

Table XXVIII

UV absorption bands 200 – 800 mµ of Al(III) beta-diketonates. (mµ).

Complex	Solvent	$\pi_3 - \pi_5^*$	$\pi_3 - \pi_4^*$
$Al(Acac)_3$	chloroform	(205)	284
$Al(Bzac)_3$	"	248	319
$Al(DBM)_3$	"	255	349
$Al(TFA)_3$	"	(204)	291
$Al(HFA)_3$	"	(209)	303
$Al(3\text{-}EtA)_3$	"	–	298

Table XXIX

UV absorption bands 200 – 800 mµ of Sc(III) beta-diketonates. (mµ).

Complex	Solvent	$\pi_3 - \pi_5^*$	$\pi_3 - \pi_4^*$
$Sc(3\text{-}MeA)_3$	chloroform	–	301
$Sc(3\text{-}EtA)_3$	"	–	300
$Sc(Acac)_3$	"		296
$Sc(Bzac)_3$	"	253	327
$Sc(DBM)_3$	"	260	354
$Sc(TFA)_3$	"	–	299
$Sc(DPM)_3$	"	–	294

Table XXX

UV absorbtion maxima 200 - 1500 mμ for V(111) beta-diketonates. (mμ).

Complex	Solvent	$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$	${}^3T_{1g} - {}^3T_{2g}$
$V(Acac)_3$	chloroform	281	366	535
$V(DBM)_3$	"	266	344	523

Table XXXI

UV absorbtion maxima 200 - 1500 mμ for Cr(111) beta-diketonates. (mμ).

Complex	Solvent	$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$	${}^4A_{2g} - {}^4T_{1g}$	${}^4A_{2g} - {}^4T_{2g}$
$Cr(Acac)_3$	chloroform	274 (4·06)[a]	335 (4·01)	381 (2·63)	554 (1.80)
$Cr(Bzac)_3$	"	292 (4.60)	357 (4.49)	-	555 (2.99)
$Cr(DBM)_3$	"	320 (4.76)	380 (4.63)	-	560 (2.20)
$Cr(TFA)_3$	"	279 (3.12)	343 (3.20)		560 (1.90)

[a] Values in parentheses are $\log \varepsilon_{max}$ for each respective absorption maximum.

Table XXXII

UV absorption maxima 200 – 1500 mμ for Mn(III) beta-diketonates. Values in parentheses are logε_{max} for each complex. Wavelength is in mμ.

Complex	Solvent	$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$	$^5E_g - ^5T_{2g}$	$^5E_g - ^3T_{1g}$
$Mn(Acac)_3$	chloroform	272 (4·36)	315 (3·92)	400 (2·90)	1125 (1·8)
$Mn(Bzac)_3$	"	309 (3·72)	–	–	1120 (2·08)
$Mn(DBM)_3$	"	343 (4·92)	–	–	1125 (1·17)
$Mn(TFA)_3$	"	292 (4·27)	340 (3·83)	–	1125 (2·07)
$Mn(DPM)_3$	"	274 (3·63)	–	–	1100 (2·14)

Table XXXIII

UV absorption maxima 200 – 1500 mμ for Fe(III) beta-diketonates. Values in parentheses are logε_{max} for each absorption maximum. Wavelength is in mμ. The solvent is chloroform in all cases.

Complex		$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$		$^6A_{1g} - ^4T_{2g}$	$^6A_{1g} - ^4T_{1g}$
$Fe(Acac)_3$	240 (4·30)	272 (4·52)	348 (3·63)	435 (3·57)	725 (0·23)	1013 (–0·02)
$Fe(Bzac)_3$	247 (4·97)	301 (5·14)	377 (4·16)	446 (3·92)	725 (0·18)	1020 (0·05)
$Fe(DBM)_3$	253 (4·66)	333 (4·80)	400 (4·13)	474 (3·54)	725 (0·82)	1020 (0·59)

Table XXXIII(contd.)

Complex		$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$		$^6A_{1g} - {}^4T_{2g}$	$^6A_{1g} - {}^4T_{1g}$
$Fe(TFA)_3$	243 (4·20)	274 (4·49)	366 (3·56)	431 (3·60)	715 (0·47)	970 (0·27)
$Fe(HFA)_3$	243 (4·08)	277 (4·23)	372 (3·79)	-	-	-
$Fe(DPM)_3$	-	276 (5·57)	347 (3·54)	415 (3·35)	-	-

Table XXXIV

Absorption maxima 200 - 1500 mμ in Co(III) and Rh(III) beta-diketonates. Values in parentheses are log ε_{max} for each absorption maximum. Wavelength is in mμ. The solvent is chloroform in all cases.

Complex	$\pi_3 - \pi_4^*$	$\delta_\varepsilon - \pi_4^*$			$^1A_{1g} - {}^3T_{2g}$	$^1A_{1g} - {}^3T_{1g}$
$Co(Acac)_3$	259 (4·60)	324 (4·10)	400 (2·70)	585 (2·06)	800 (0·63)	1100 (0·32)
$Co(DBM)_3$	298 (5·15)	379 (4·59)	-	598 (2·61)	800 (1·00)	1100 (0·8)
$Co(TFA)_3$	261 (4·69)	329 (3·81)	-	590 (2·56)	-	-
$Rh(Acac)_3$	258 (4·23)	320 (4·29)	-	-	-	-

Table XXXV

UV absorption maxima 200 - 1500 mμ for Ga(111) beta-diketonates. (mμ).

Complex	Solvent	$\pi_3 - \pi_4^*$
Ga(Acac)$_3$	chloroform	282
Ga(TFA)$_3$	"	292

DISCUSSION

1. The Crystal Field Theory

CFT represents the simplest approach to stabilisation resulting from IOS. It will therefore be used initially in interpretations of the shifts in M-L frequency trends in the IR spectra of the series of TM complexes examined. The cations in the majority of these occurred in the six-coordinate octahedral environment. We therefore first consider the CFT approach to M-L bonding in complexes in which coordination to the central cation is octahedral.

The heterolytic bonding energy ($-\Delta H$) of complex formation in the gas phase from the free ions corresponds to (10) the equation

$$M^{n+}_{(g)} + nL^{-}_{(g)} = ML_{n(s)} - \Delta H$$

for an ion M of valency n with a bidentate monobasic ligand L. (e.g. the acetylacetonate anion). The heterolytic bonding energy may be divided into a CFSE contribution ($-\delta H$) and an ionic contraction contribution (E_r), which may be expressed as

$$-\Delta H = -\delta H - E_r \qquad (1)$$

Therefore, in order to derive $-\delta H$ from thermochemically determined $-\Delta H$ for any particular TM complex $-E_r$ for that complex must be known. The ionic radius of ions of the same valency decreases fairly regularly with increasing at. no. across TM periods. It is therefore assumed that the increase of $-E_r$ across these series of ions is also linear with respect to increase of at. no.

$-\delta H$ for the complexes of ions having certain electronic configurations of their d-orbitals (the d^0, d^5 and d^{10} configuration for ions in octahedral environments) is zero, so that for these $-\Delta H = -E_r$. $-E_r$ is thus determined for the complexes for which CF stabilisation is expected by plotting the variation of $-\Delta H$ of the complexes against the at. no. of their central cations, and interpolating between $-\Delta H$ for the complexes of the ions of d^0, d^5 and d^{10} configuration, for which $-\Delta H = -E_r$. In this way, $-\delta H$ may be derived thermodynamically from eq.(1).

Thermodynamically determined $-\delta H$ is related (10) to 10Dq (the energy difference between the e_g and t_{2g}

levels of the d-orbital) by the expression

$$-\delta H = -10Dq\ (0{\cdot}4n_t - 0{\cdot}6n_e) \qquad (2)$$

where n_t and n_e are the numbers of electrons in the t_{2g} and e_g levels respectively. In addition, the interelectronic repulsions on spin-pairing must be accounted for in the complexes of low-spin ions, by making allowance for the spin pairing energy (P). Eq. (2) then becomes

$$-\delta H = -10Dq\ (0{\cdot}4n_t - 0{\cdot}6n_e) + P \qquad (3)$$

10Dq may be derived empirically from thermo - dynamic $-\delta H$ values, or directly from the electronic spectra of the complexes themselves. As was mentioned earlier , the IR stretching frequencies of M-L bonds resemble thermodynamic stabilisations of the latter, in that both are a measure of the strength of the M-L bond. The same approach as used in the CF interpretation of the thermochemical stability of TM complexes may thus be adopted for interpreting the variations of M-L frequencies in the spectra of complexes of TM ions of increasing at. no. across a period of the periodic classification. Mass effects should increase linearly with at. no., so will be accounted for in the process of interpolation between values of the M-L str. for which no CFSE is observed.

The IR spectra of the series $[M(Acac)_3]$ (M = Sc, Ti, V, Cr, Mn, Fe, Co and Ga.) will be examined first in relation to CFT expectations, since both spectroscopic and thermodynamic 10Dq values are reported in the literature for this series. The spectra of these complexes are seen in Figs. 2a-d.

A. Effect of CFSE on IR spectra of first period trivalent tris(acetylacetonates)

The spectroscopic 10Dq values of Piper and Carlin (11) were used for the purposes of calculating $-\delta H$ for each of these complexes. The $-\delta H$ values are given in Table 1, and are also plotted against the at. no. of the central cation in each of the complexes. (Fig. 3b) Co(III) is the only spin-paired ion in the series. P for d^6 ions is given (10) by

$$P = 5B + 8c$$

where B and C are the Racah electrostatic interaction parameters. Racah parameters are reported (12) for the Co(III) ion (B = 1065, C = 5120 cm^{-1}) in the gaseous state, which give a value of P = 118 kcal/mole. (It should be noted that P as used here is the **total** pairing energy, not the energy of pairing per pair of electrons paired.) Pairing energies of ions in the solid state are lowered (10) by 20 - 30% from their gas-phase values, so that a value of about 90 kcal/mole would serve as a reasonable estimate of P for the Co(III) ion in the solid state.

Fig. 3a illustrates the relationship between the M-O str. of the complexes and the at. no. of their central cations. The strength of the M-O bonds as indicated by M-O str. frequency trends across the series exhibits a good qualitative relationship with that predicted by spectroscopically determined $-\delta H$ values. The rise in the M-O str. with at. no. of the complexes of ions for which $-\delta H = 0$ (Sc<Fe<Ga) is attributed to the stabilizing effects of ionic contraction.

E_r contributions to the stabilisation of the M-O str. of each of the CF stabilized complexes may be estimated by interpolation between the M-O str. frequencies of the complexes of the non-CF stabilized ions,

Figs 2a - 2d

Spectra in the region 2000 - 200 cm^{-1} of the first transition period trivalent tris(acetylacetonates).

($M(Acac)_3$, M = Sc, Ti, V, Cr, Mn, Fe, Co and Ga.)

Key to band assignments

a = C=O str.
b = C=C str.
c = C=C + $C-CH_3$ str.
d = ring def.

1 = M-O str. + ring def.
2 = M-O str.
3 = M-O str.[a]
4 = M-O + $C-CH_3$ str.
5 = O-M-O bend[b]
6 = M-O + ring def.[b]

[a] This is the band assigned to M-O str. by Pinchas et. al. (54), and is the band referred to as M-O str. in this discussion. [b] These assignments are at the best only very tentative, and will be discussed further in the section on band assignment in beta-diketonate complexes.

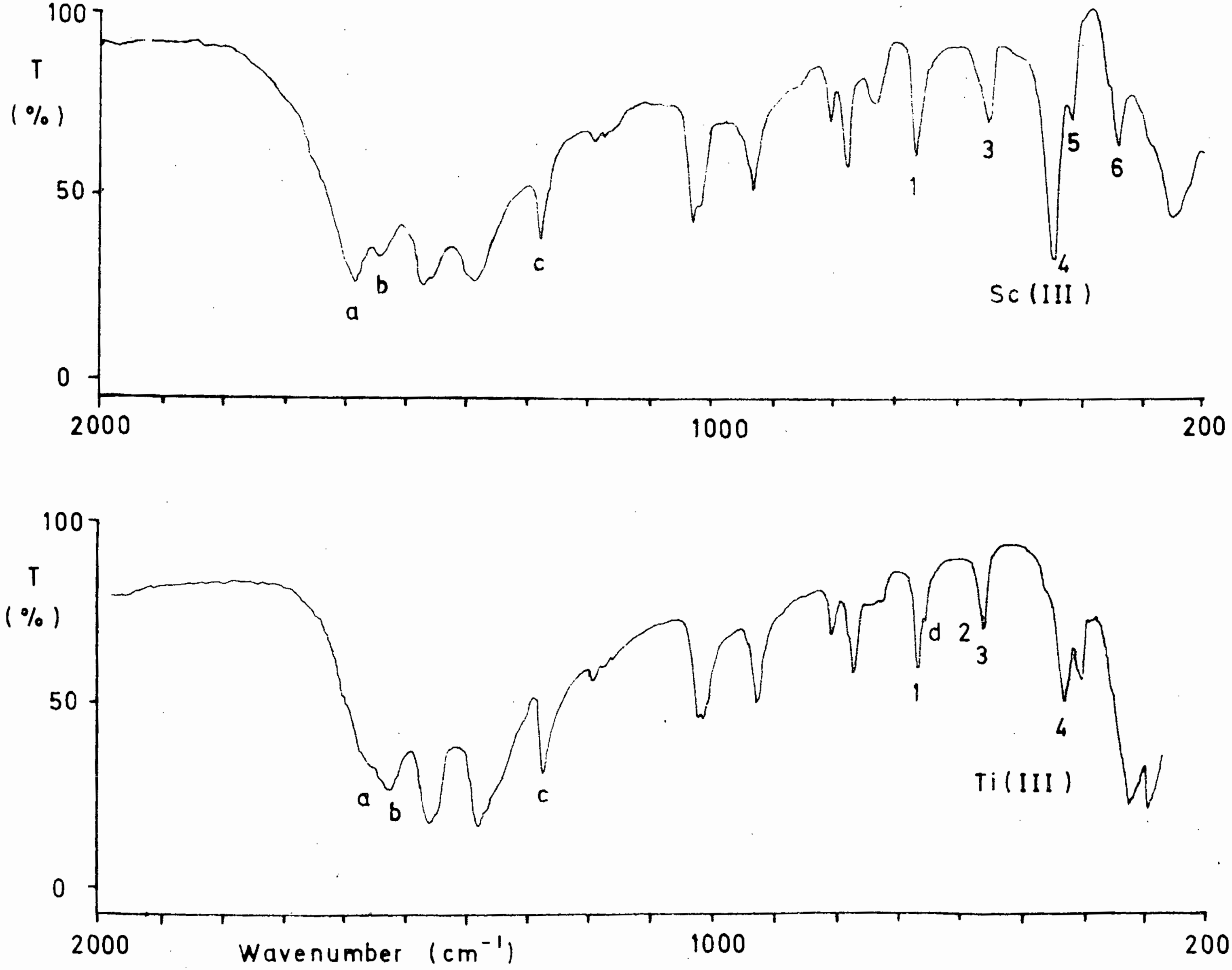


Fig. 2a. Spectra of $Sc(Acac)_3$ and $Ti(Acac)_3$ in the region 200-2000 cm⁻¹.

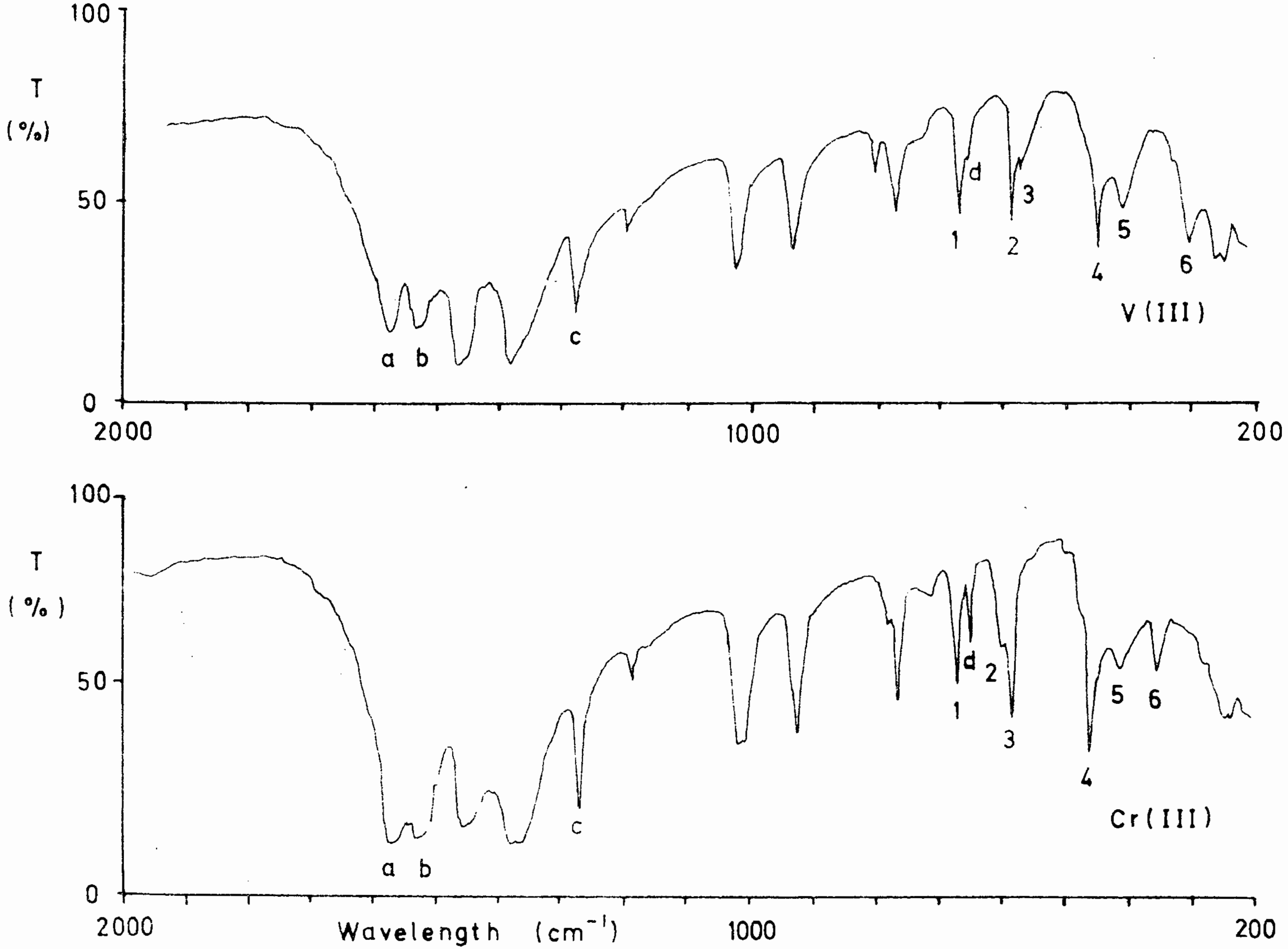


Fig. 2b. Spectra of V(Acac)$_3$ and Cr(Acac)$_3$ in the region 200-2000 cm^{-1}.

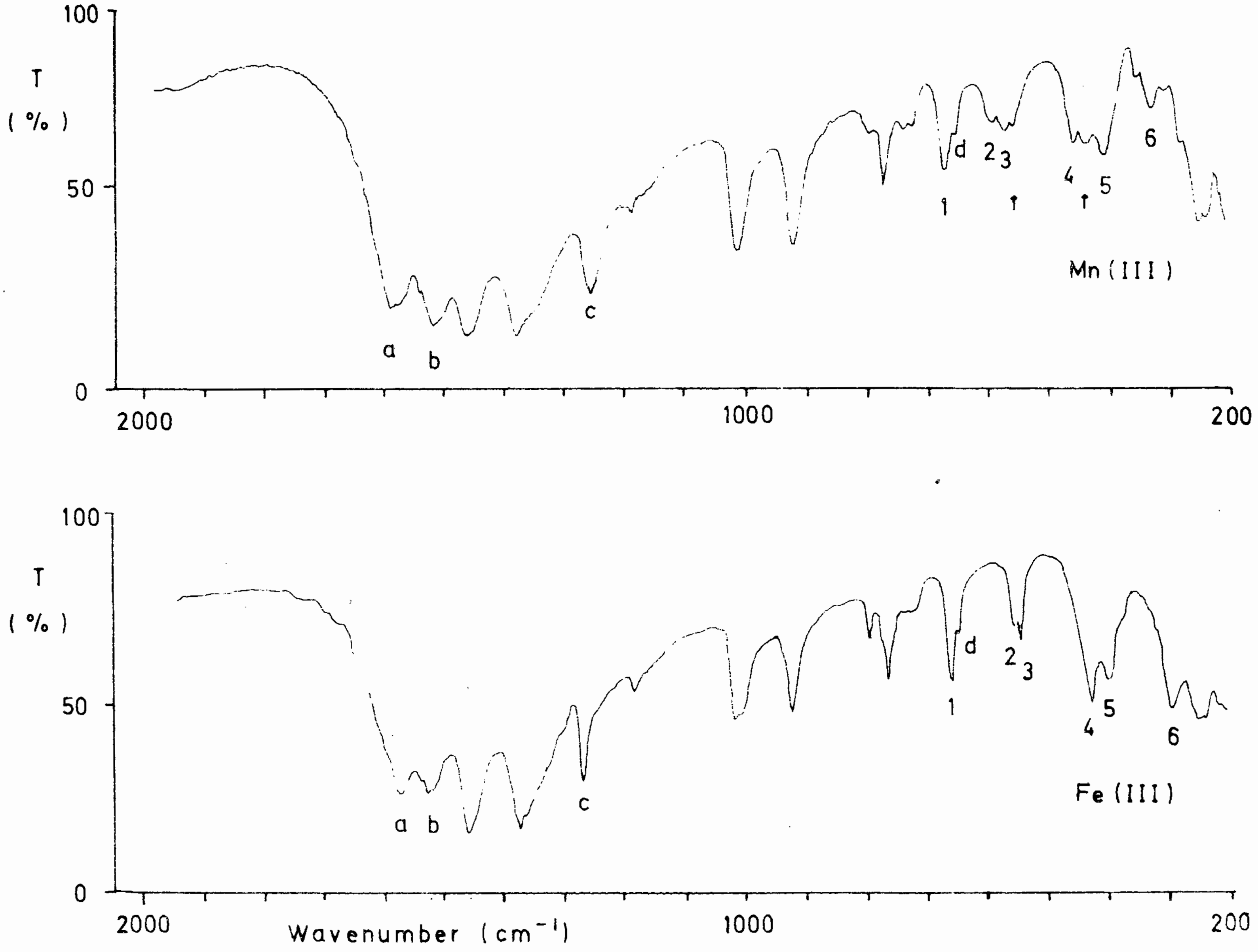


Fig. 2c. Spectra of $Mn(Acac)_3$ and $Fe(Acac)_3$ in the region 200-2000 cm^{-1}.

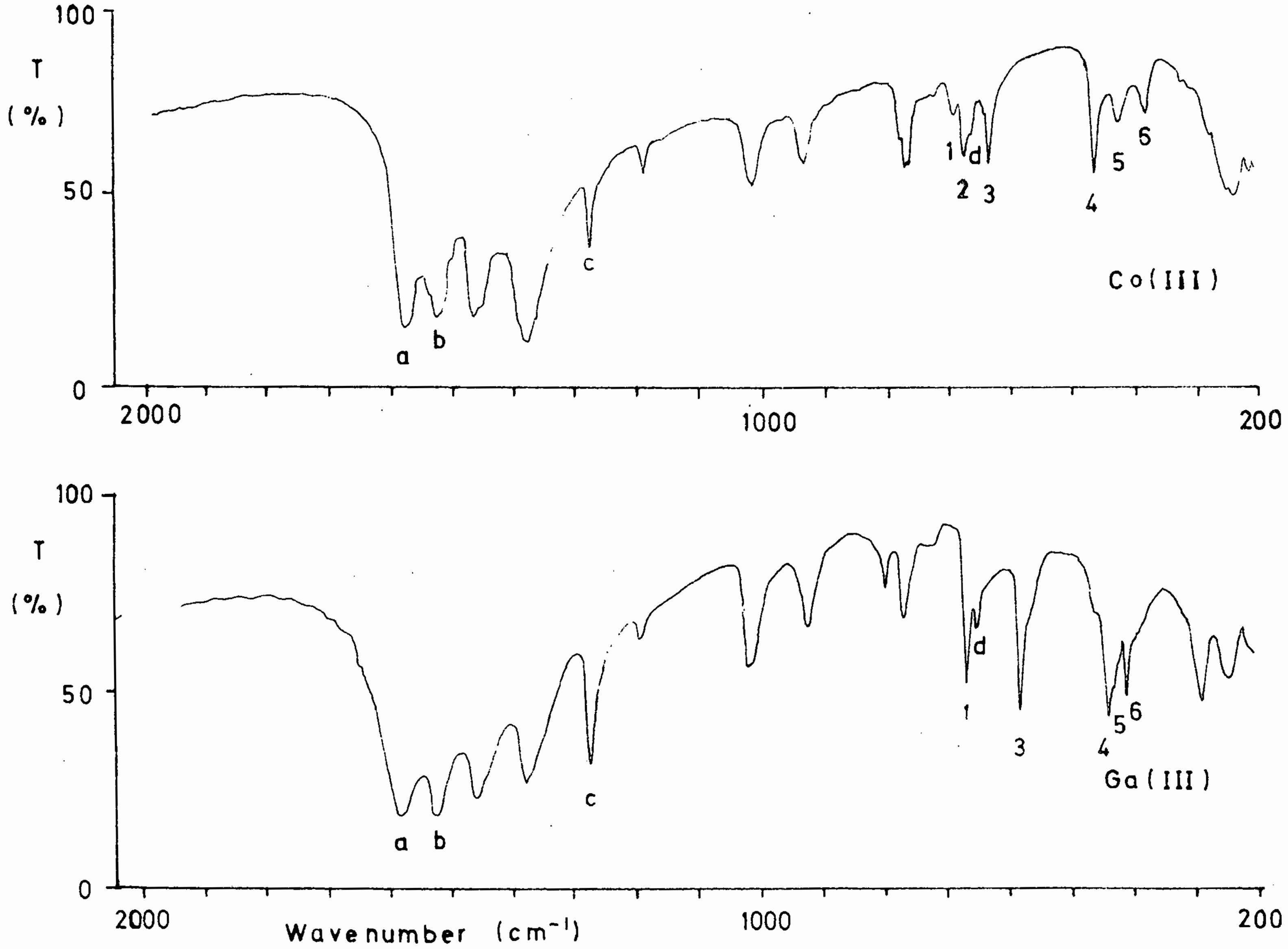


Fig. 2d. Spectra of Co(Acac)$_3$ and Ga(Acac)$_3$ in the region 200-2000 cm^{-1}.

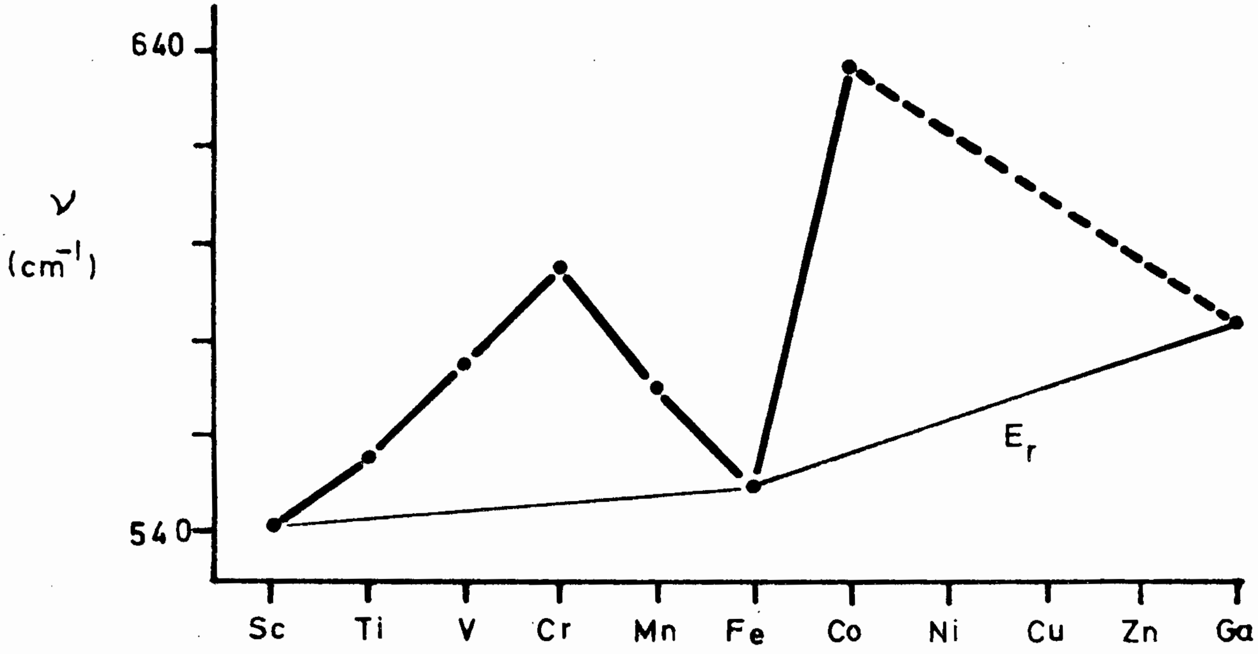


Fig. 3a. Variation of ν(M-O) with at.no. in the first transition period trivalent tris(acetylacetonates).

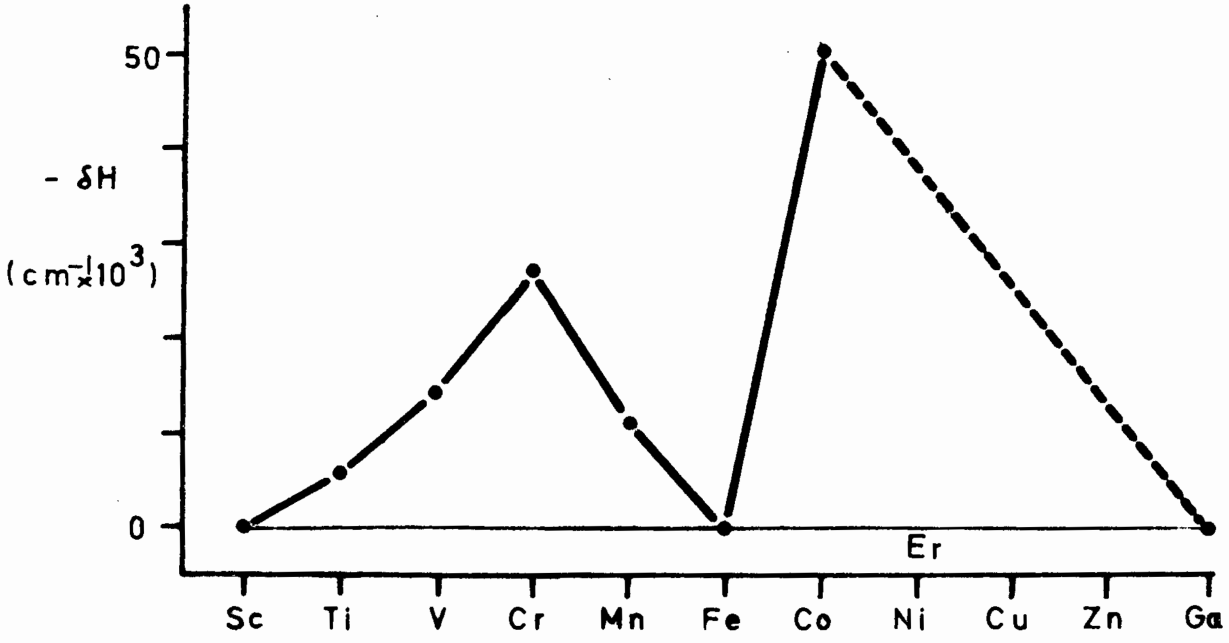


Fig. 3b. Variation of -δH with at.no. in the same series as above.

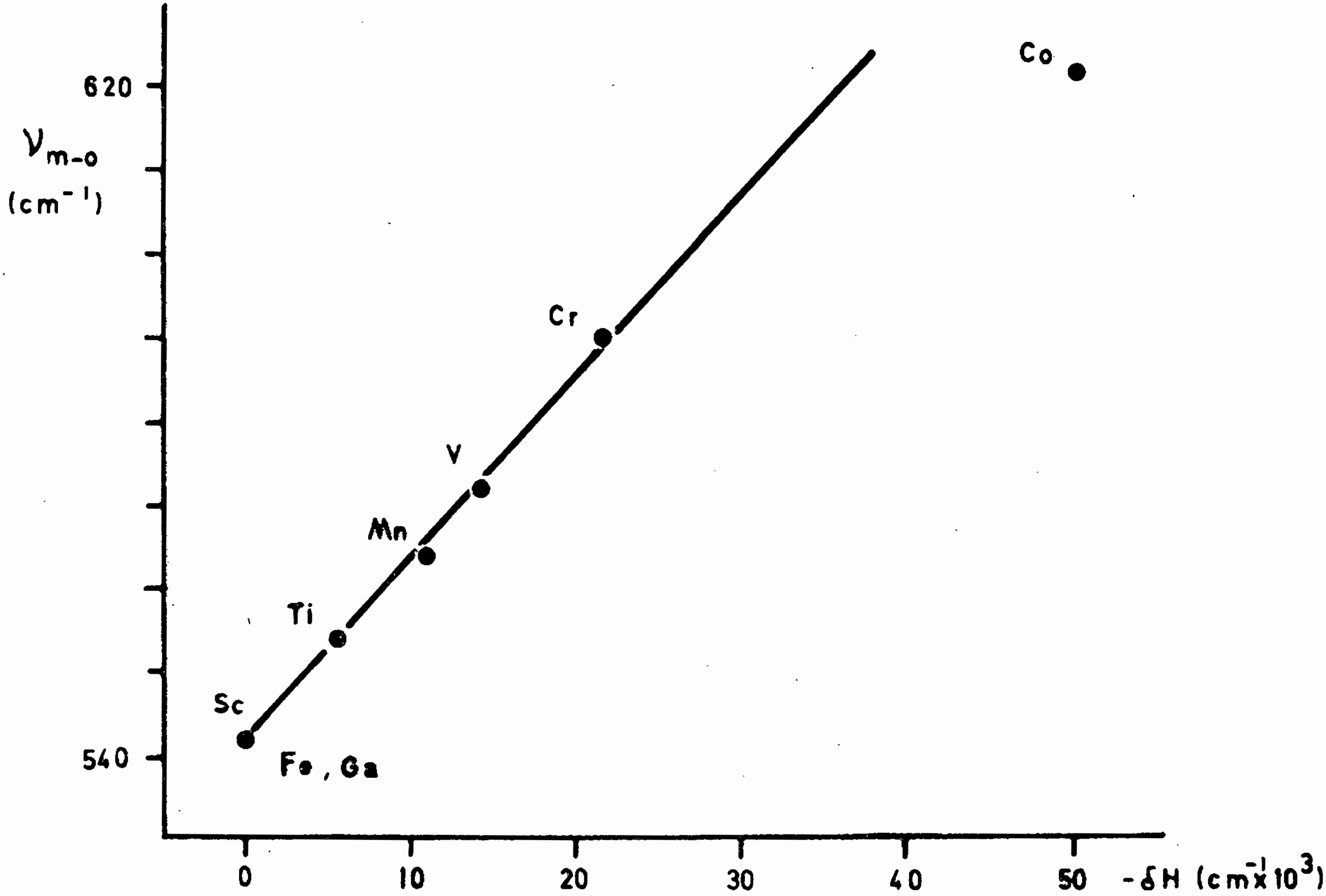


Fig. 4. Variation of ν(M–O) with $-\delta H$ for first transition period M(Acac)$_3$ complexes

Sc(III), Fe(III) and Ga(III). As in thermodynamic CF studies, it is assumed that the stabilisation of the M–O bond (as indicated by the frequency of the M–O str.) in excess of the interpolated E_r stabilisations is due to CF effects. Subtraction of the stabilisation due to E_r in the M–O str. from the values of M–O str. observed will therefore yield a set of M–O str. frequencies which have been corrected for ionic contraction effects. Because these contain no ionic contraction contribution, they may therefore be compared directly with spectroscopically determined $-\delta H$ values.

(The rise of the M–O str. with at. no. through the complexes of the ions Sc(III), Fe(III) and Ga(III) is non-linear (Fig. 3), in that the Fe–O str. lies below the interpolation line between Sc–O and Ga–O str. The two segments of the interpolation line are therefore interpolated separately as Sc–O – Fe–Ostr., and Fe–O – Ga–O str. This practice is also followed in the thermodynamic approach, where the increase of $-\Delta H$ ($= E_r$) is non-linear for the complexes of the ions Sc(III), Fe(III) and Ga(III),(10) relative to their at. no.'s.)

The M–O str.'s corrected for E_r are seen to give a good linear relationship with $-\delta H$ (Fig 4). P for the Co(III) complex has been neglected in calculating $-\delta H$, since there is a large degree of uncertainty in the value of P for the ion in the solid state. This accounts for the fact that the point for Co(III) is lower than would be expected from extrapolation of the best straight line through the points for the other ions . This difference amounts to 37 kcal/mole which is low by a factor of over one half compared to the pairing energy calculated for this ion (90 kcal/mole). This difference between P as indicated by the M-O str. frequencies, and as estimated from Racah parameters may possibly arise from lack of precision in estimating the magnitude of P, or the fact that the CF model does not take into account the additional stabilisation arising from pi-bonding effects.

In order to express the magnitude of the M-O str. of a TM complex in terms of its CFSE the following modification of eq.2 may be used

$$\nu(\text{M–O})_{\text{obs.}} = \nu(\text{M–O})^{\circ} + K\,\delta H + K'n \quad .. \ (4)$$

where K is a constant (= 0·0020 for the acetylacetonates. $-\delta H$ is expressed in cm^{-1}.); K′ is the slope of the interpolation line indicating E_r (= 1·6 cm^{-1} per at. no. unit for the (Sc–O) – (Fe–O)str., segment, and 6·8 cm^{-1} per at. no. unit for the (Fe–O) – (Ga–O)str. segment in the case of the tris(acetylacetonates); n is the number of electrons in the d-orbital of the ion for which $\nu(M\text{–}O)_{obs}$ was observed; $\nu(M\text{–}O)^{o}$ is the (M–O)str. of the complex of the ion of d^0 configuration. (In the case of ions with more than five d-orbital electrons, n is the number of electrons in the d-orbital in excess of five, and $\nu(M\text{–}O)^{o}$ is the (M–O)str. of the complex of the ion with the d^5 configuration.)

Table 1

CFSE and frequency data (cm^{-1}) for the first period tri-valent tris(acetylacetonates. $\nu(M\text{–}O)_{obs}$ is the observed frequency; $\nu(M\text{–}O)_{corr}$ is corrected for ionic contraction; $\nu(M\text{–}O)_{calc}$ is (M–O)str. calculated from eq.4.

Ion	CFSE (cm^{-1})	$\nu(M\text{–}O)_{obs}$	$\nu(M\text{–}O)_{calc}$	$\nu(M\text{–}O)_{corr}$
Sc(III)	–	542	–	(542)
Ti(III)	5,600	556	554	554
V(III)	14,400	572	575	569
Cr(III)	21,700	595	590	590
Mn(III)	10,200	570	571	564
Fe(III)	–	550	–	(542)
Co(III)	50,400	637	609	622
Ga(III)	–	584	–	(542)

Using eq.4, values of the (M-O)str. are predicted which agree well with those observed (Table 1). We see that for the first period tris(acetylacetonates) the CF interpretation provides a good rationalisation of the observed (M-O)str. frequencies. To test the CF interpretation further, series of complexes of these ions with alternative ligand systems were prepared and their spectra examined.

B. 1,3- and 2-substituted beta-diketonates other than the acetylacetonates

In addition to the acetylacetonates, the TM complexes of several other beta-diketone ligands were prepared and their spectra recorded. These included the complexes $[M(Bzac)_3]$, $[M(DBM)_3]$, $[M(TFA)_3]$, $[M(DPM)_3]$ (where M = Sc, V, Cr, Mn, Fe, Co, Ga.) and $[M(3\text{-}MeA)_3]$, $[M(3\text{-}EtA)_3]$ (where M = Sc, V, Cr, Fe), as well as the complexes $[V(HFA)_3]$ and $[Fe(HFA)_3]$.

No Dq values are available for these complexes, but the d-d transitions in their electronic spectra are little changed from those of the corresponding acetylacetonates. Therefore, the Dq values pertaining to the acetylacetonate series will be used for the calculation of $-\delta H$ for the substituted forms.

Fig. 5 illustrates the variation of the (M-O)str. across these series of complexes, with atomic number of their central cations. The qualitative agreement with CFT predictions of thermodynamic stability variations across the series (Fig. 3a) is seen to be good. Correcting the (M-O)str. frequencies for ionic contraction across the series in the same way as was done for the acetylacetonate series, corrected (M-O)str. values are obtained which may be related directly to the $-\delta H$ energies of the complexes.

Fig.6 illustrates the relationship between the (M-O)str. and $-\delta H$ for the complexes of the series of substituted beta-diketonates prepared. A good linear relationship between the (M-O)str. and $-\delta H$ is observed for each ligand. The point for the Co(III) complexes is lower than would be suggested by extrapolation of the best straight line drawn through the points for the complexes of the other ions in each series, as was also observed for the Co(III) complex in the acetylacetonate series. In each case P was neglected in calculating $-\delta H$ for the Co(III) complexes, so that, as with the acetylacetonates, we may assume this difference to re-

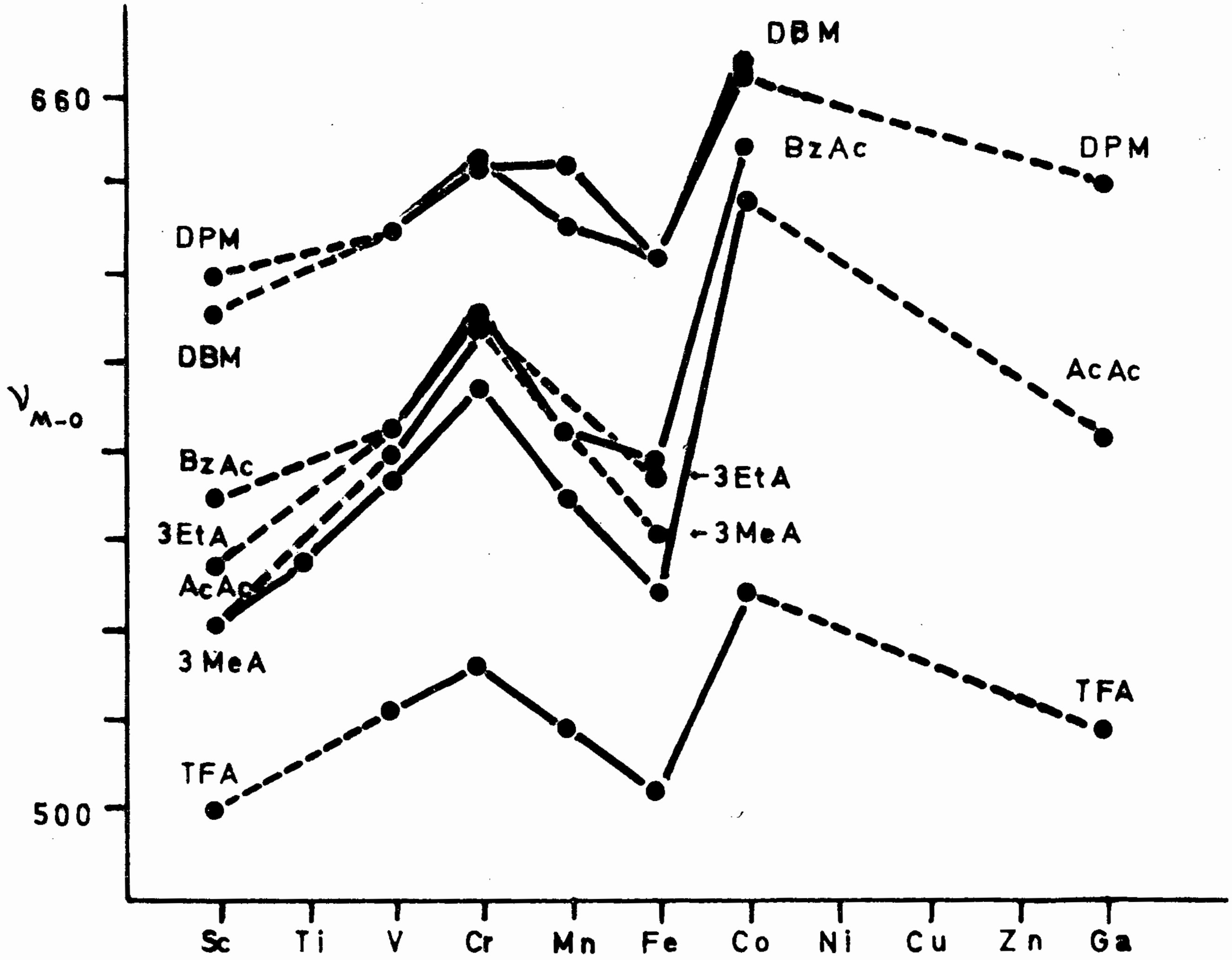


Fig. 5. Variation of ν(M-O) with at.no. in 1,3- and 2- substituted β-diketonates of metal(III) ions of the first transition period.

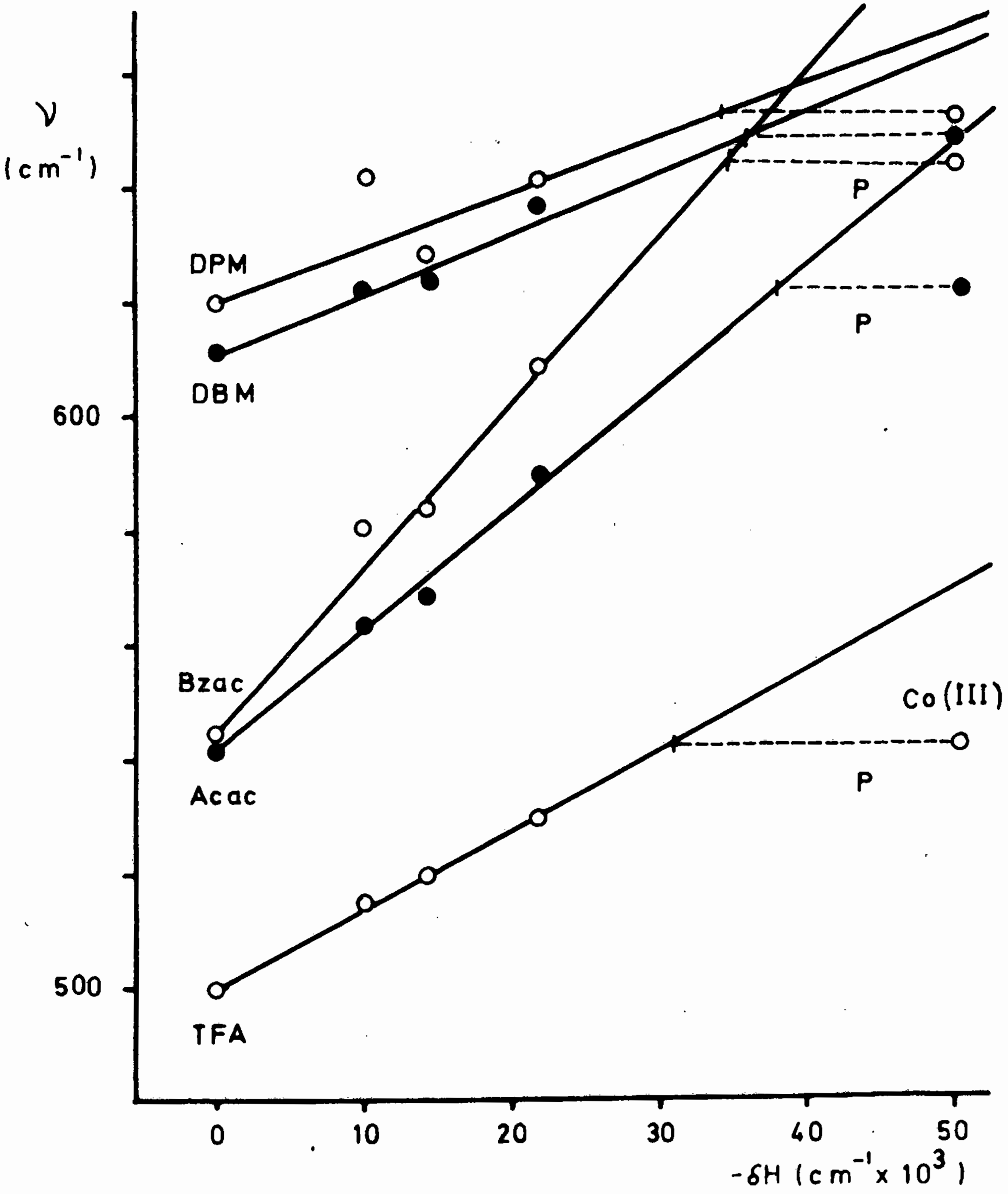


Fig. 6. Variation of ν(M-O) with -δH for 1,3- substituted β-diketonates of first transition period M(III) ions.

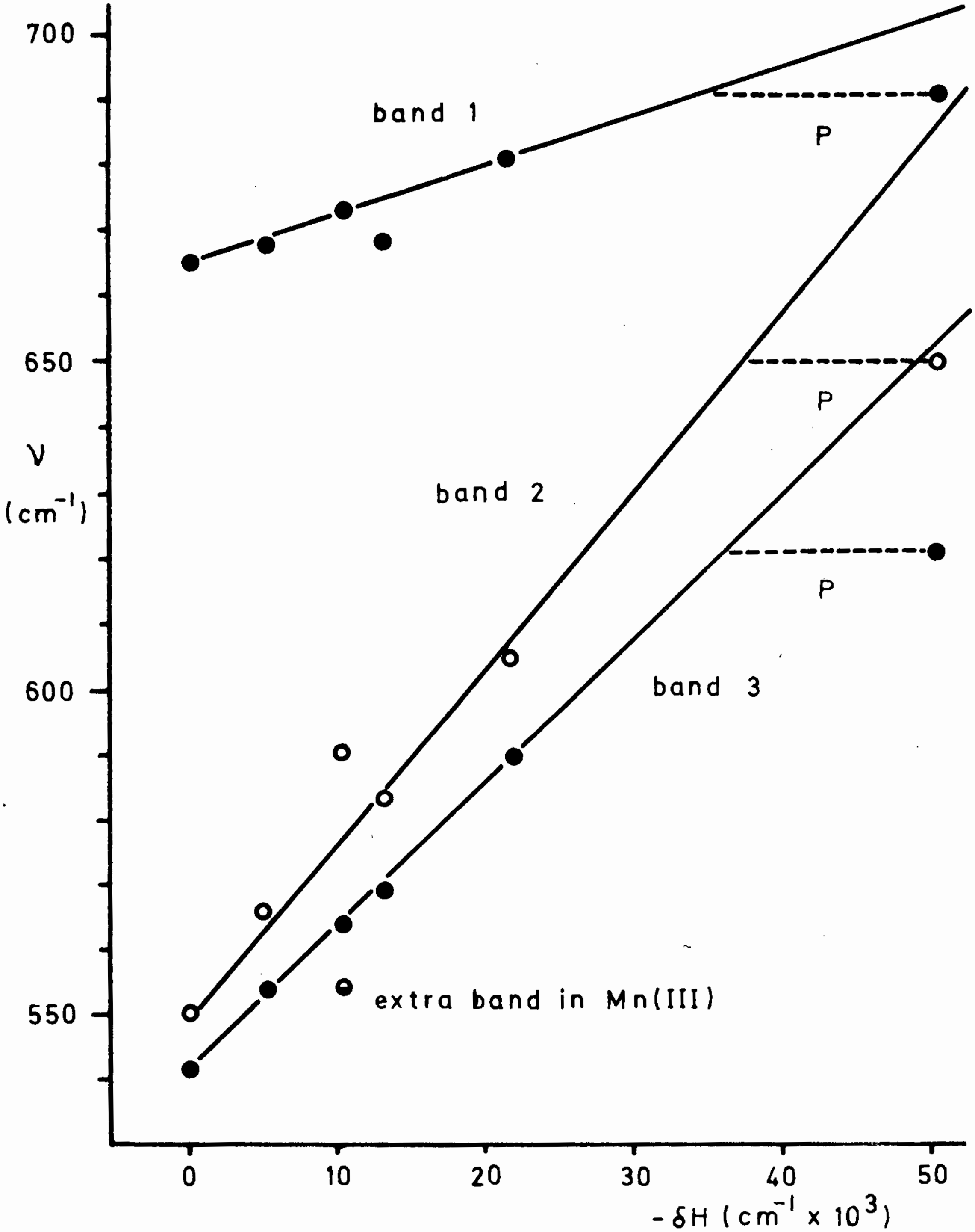


Fig. 7. Variation of metal-sensitive bands in the 500-700 cm^{-1} region of the spectra of first transion period trivalent acetylacetonates with at.no.

present the energy for spin-pairing in the Co(III) ion in the solid state. The values for P thus determined graphically from the plots of (M-O)str. against - δH are for [Co(TFA)$_3$], P = 60 kcal/mole., [Co(Bzac)$_3$] P = 47 kcal/mole., [Co(DBM)$_3$] P = 40 kcal/mole., [Co(DPM)$_3$] P = 38 kcal/mole, as compared with 37 kcal/mole for [Co(Acac)$_3$]. The value which would be expected for all of them from the Racah parameters is 90 kcal/mole.

As will be discussed later, three highly metal-sensitive vibrations occur in the IR spectra of all the beta diketonates of the first period trivalent transition metals, in the region 500 - 700 cm^{-1}. The frequency trends of all of these bands across the series of all the ligands examined follow the variations in stability predicted by the CFT. From the linear relationships with - δH for the complexes yielded by these bands, when corrected for ionic contraction, graphically determined values of P for the Co(III) complexes may be derived in the same way as was done using the relationship between the (M-O)str. and - δ H. This is illustrated in Fig. 7 for the three bands in the 500 - 700 cm^{-1} range of the acetylacetonate series. The values of P for Co(III) with each of the substituted beta-diketonates, as determined using each of the three bands are as in Table 2 below.

Table 2

Pairing energies (P) in kcal/mole for Co(III) calcd. from the variation of bands 1,2 and 3 in the beta-diketonate spectrum (500 - 700 cm^{-1}) with $-\delta H$ for the complexes.

Complex	P(band 1)	P(band 2)	P(band 3)
Co(Acac)$_3$	38	36	37
Co(Bzac)$_3$	-[a]	47	47
Co(DBM)$_3$	40	57	41
Co(DPM)$_3$	38	-	-
Co(TFA)$_3$	-24	-	60

[a] Values for the more metal insensitive bands (i.e. those varying over a range of less than 30 cm^{-1} across the series) are omitted as being unreliable.

The reasonably close agreement observed for all these different calculations of P from IR frequencies supports the value observed earlier for the Co(III) acetylacetonate. For each of these series relationships similar to eq.4 may be used with fair success in predicting IR frequencies for each of the three bands in the 500 - 700 cm^{-1} region . The value of K in eq. 4 must be adjusted to a best fit for each band in each series of complexes. We thus see that the rationalisation of the variation of the (M-O)str., and other bands highly sensitive to change of metal, in terms of CF effects holds good for a large number of variously substituted beta-diketonate complexes of the first transition period trivalent ions. To test the CF interpretation further, series of alternative oxygen-donor-ligand complexes with these ions were prepared, and their spectra recorded.

C. The tris(oxalato) metallates of the trivalent ions of the first transition period

In the trivalent tris(oxalato) metallates of the first transition period, the spin states of the ions(13) are reported to be the same as in their beta-diketonate complexes. Spectroscopic 10Dq values are reported (15) in the literature, so that $-\delta H$ values for each of the complexes may be calculated using eq. 3. The variation of $-\delta H$ for these complexes is seen in Fig. 8a.

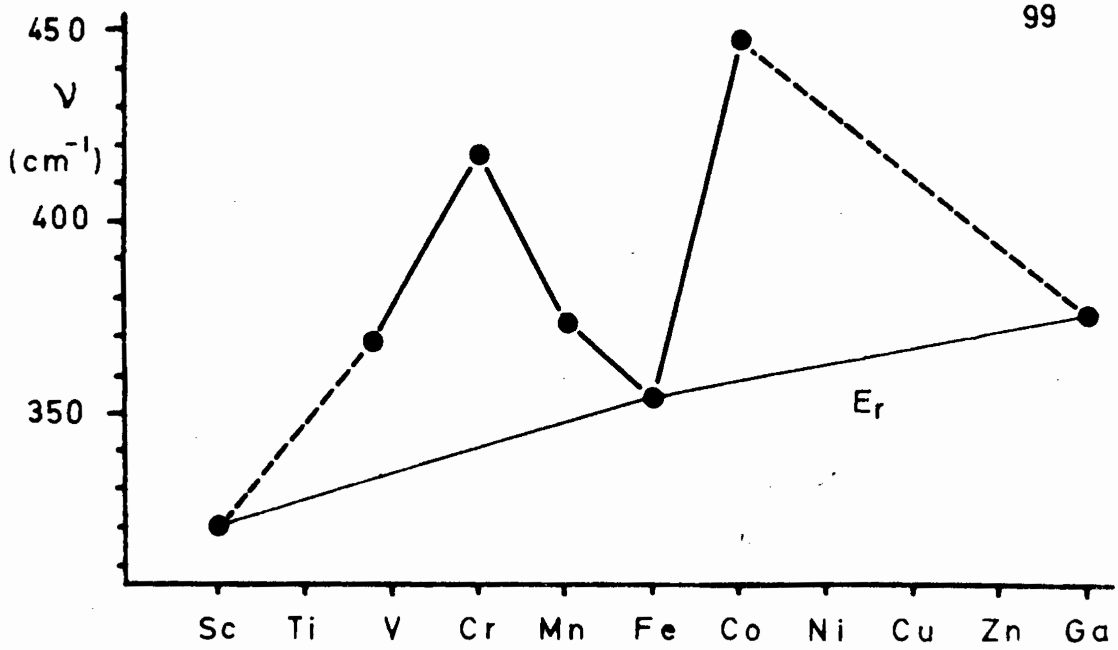


Fig.8a. Variation of (νM-O + ring def.) with at.no. in the tris(oxalato)-metallate(III) ions of the first period.

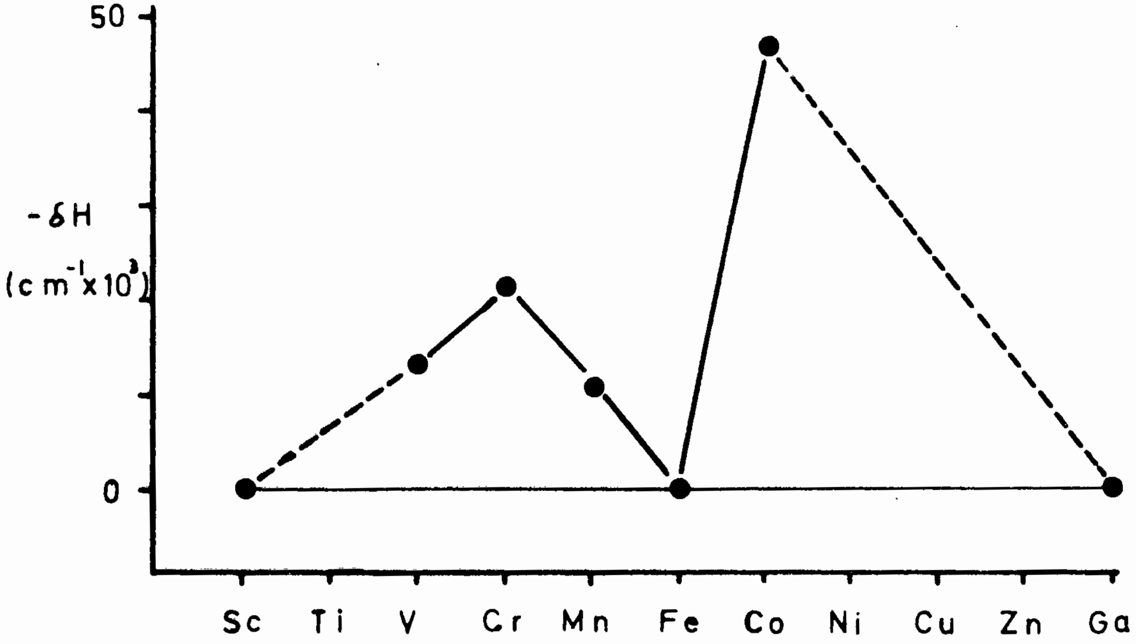


Fig.8b. Variation of -δH with at.no. in the same series as above.

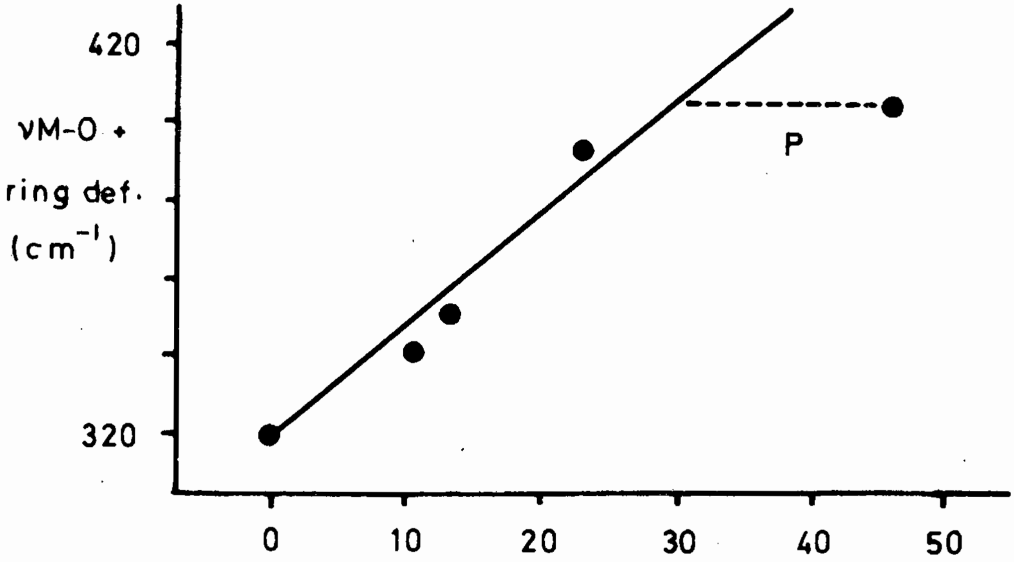


Fig.9a. Variation of νM-O with -δH for tris(oxalato) metallate(III) complexes.

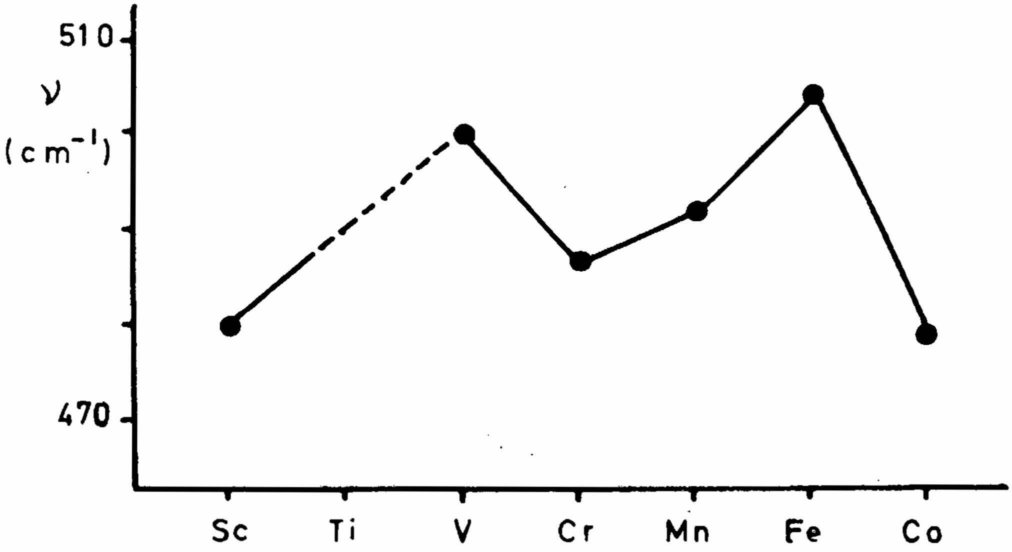


Fig. 9b Variation of ring def.+ O-C=O def. with at.no. in M(III) tris(oxalato)- complexes.

The complexes were all prepared as their potassium salts, $K_3[M(C_2O_4)_3].3H_2O$. The IR frequencies for the Ga(III) complex are from a reported spectrum (16) and are for the ammonium salt $(NH_4)_3[M(C_2O_4)_3].3H_2O$. A normal coordinate treatment of the tris(oxalato)metallates of D_3 symmetry, such as $[Al(C_2O_4)_3]^{3-}$, has already been performed (14)and band assignments made. Further, the assignment of M-O character to certain of the bands below 600 cm^{-1} is consistent with the CF interpretation of the variation of band frequencies across TM series. This is illustrated by the bands at 340 - 446 cm^{-1} and 531 - 569 cm^{-1}, which both exhibit frequency trends consistent with CF theory, and their assignment as (16) (M-Ostr. + ring def.) and (M-Ostr. + C-Cstr.) respectively. The variation of (M-O + ring def.) with at. no of the central cation of the complex is illustrated in Fig 8b for comparing with the variation of $-\delta H$ across the series.

From Fig 8 the qualitative agreement between the frequency trend and the CFSE across the series is seen to be reasonable. As with the beta-diketonates of these ions, ionic contraction effects may be estimated, and allowed for by interpolation between the frequencies for the complexes of the d^0, d^5 and d^{10} configuration ions. These frequencies may then be directly related to $-\delta H$ for the complexes. As with the beta-diketonates, frequencies containing a large percentage of M-O character yield linear relationships with $-\delta H$ (Fig 9) from which empirical values of P for the Co(III) complex may be estimated. The value for P thus graphically determined for $[Co(C_2O_4)_3]^{3-}$ is 38 kcal/mole using (M-Ostr. + ring def.). The non-linearity of the relationship of the (M-O + C-C)str. vibration with $-\delta H$ renders the determination of P too unreliable. (The non-linearity of the relationship of the latter frequency with $-\delta H$ possibly is related to there being a smaller percentage of M-O character in this vibration than in (M-Ostr. + ring def.) This idea on the relative degree of coupling to the M-O vibration in each of the two bands is suggested by their relative sensitivity to change of metal. The range over which (M-O + C-C)str. varies is 38 cm^{-1}, while the range of variation of (M-Ostr. + ring def) is 126 cm^{-1}.)

The value of P = 38 kcal/mole determined from the variation of (M-O str. + ring def), agrees well with the values determined for the beta-diketonates (e.g. 37 kcal/mole in the acetylacetonate series.). This similarity in frequency trends across the series is as would be expected from the similarity of the environment of the cations in each of the two types of complex, since in each the central cation is surrounded by six octahedrally coordinated oxygen atoms. A feature observed in the tris(oxalate) spectrum which is not seen in the beta-diketonate spectrum is the band at 477 - 505 cm^{-1}, which exhibits a relationship to $-\delta H$ across the series which is the inverse of that exhibited by bands containing a high percentage of M-O character.(Fig 9b) This observation is in agreement with the assignment (14) of this band to (ring def + O-C=Odef), in that the latter assignment suggests very little M-O str. character in the vibration.

D. The effect of change of spin-state - the second transition period trivalent tris(acetylacetonates)

Examination of eq.2 reveals that the high M-O str. for Co(III) complexes is mainly dependent on their possession of a spin-paired configuration. (Occupation of the t_{2g} levels is in CFT more favourable energetically than electronic occupation of the e_g level.) From eq.3

it is evident that the assumption of either the spin-free or the spin-paired state for any particular ion is dependent on the magnitude of P. Spin-paired states occur only in ions for which the increase in CFSE (relative to the spin-free state) on spin-pairing is greater than the pairing energy (P). The large pairing energies pertaining to d^4 and (in particular) d^5 ions account for the high-spin state of Mn(III) and Fe(III) in most of their complexes.

Thus, for example, we may consider the origin of the high-spin state of Fe(III) tris(acetylacetonate). P for d^5 ions is very large. It is given (10) by the expression

$$P = 15B + 10C$$

Racah paramaters are reported (11) in the literature for Fe(III) acetylacetonate. These (B = 530 , C = 3570 cm^{-1}) yield a value of P = 130 kcal/mole. CFSE for the high-spin state is zero. For the low-spin state, using a literature value (11) of 10Dq for Fe(III) acetylacetonate (10Dq = 16400 cm^{-1}), CFSE is calculated as being only 94 kcal/mole. Since this is less than the energy of spin-pairing, the spin-free state is the one observed . (The spin-free state in Fe(III) acetylacetonate is more stable than the spin-paired state by 36 kcal/mole.)

The CFT model predicts that in the complexes of d^5 ions change from high to low-spin state should be accompanied by an increase of $-\delta H$ relative to the value of E_r estimated for the complex by interpolation. (Assuming that the requirement of $-\delta H > P$ for the assumption of low-spin states in d^5 complexes is met.) This prediction should then also apply to the frequency trends of the M-L vibrations of series of complexes in which the d^5 ion has a low-spin configuration.

The tris(acetylacetonates) of the second transition period trivalent ions present an ideal series for comparison with their first transition period analogues, since Ru(III) in this series has a d^5 low-spin configuration (13) as opposed to the corresponding first transition period ion, Fe(III) which is high spin. The complexes $[M(Acac)_3]$, M = Y(III), Mo(III), Ru(III), Rh(III) and In(III) were prepared and their spectra recorded. The variation of the (M-O)str. of these complexes with at. no. of their central cations is seen in Fig. 10.

The variation of the (M-O)str. with at. no. in the complexes of the analogous first period ions is also included in Fig. 10 for comparison with the frequency trend observed in the second transition period.

The frequency trends across both the first and second periods (Fig. 10) are very similar, with the difference occurring at the (M-O)str's of the complexes of the d^5 configuration ions. The cusp in the frequency trend at the d^5 configuration in the second period ions is very shallow indeed as compared with the first period analogues. This is in agreement with the larger CF stabilisation associated with low-spin states. The fact that change to a low-spin state has been accompanied by the CF predicted increase in the (M-O)str. lends good qualitative support to the rationalisation of M-L frequency trends in series of TM complexes in terms of CFT.

Two factors account for the low-spin state of Ru(III) actylacetonate. Firstly, 10Dq in second transition period ions is (10) reported to be about 50% higher than in analogous first transition period ions. Jorgensen (20) reports the ratio

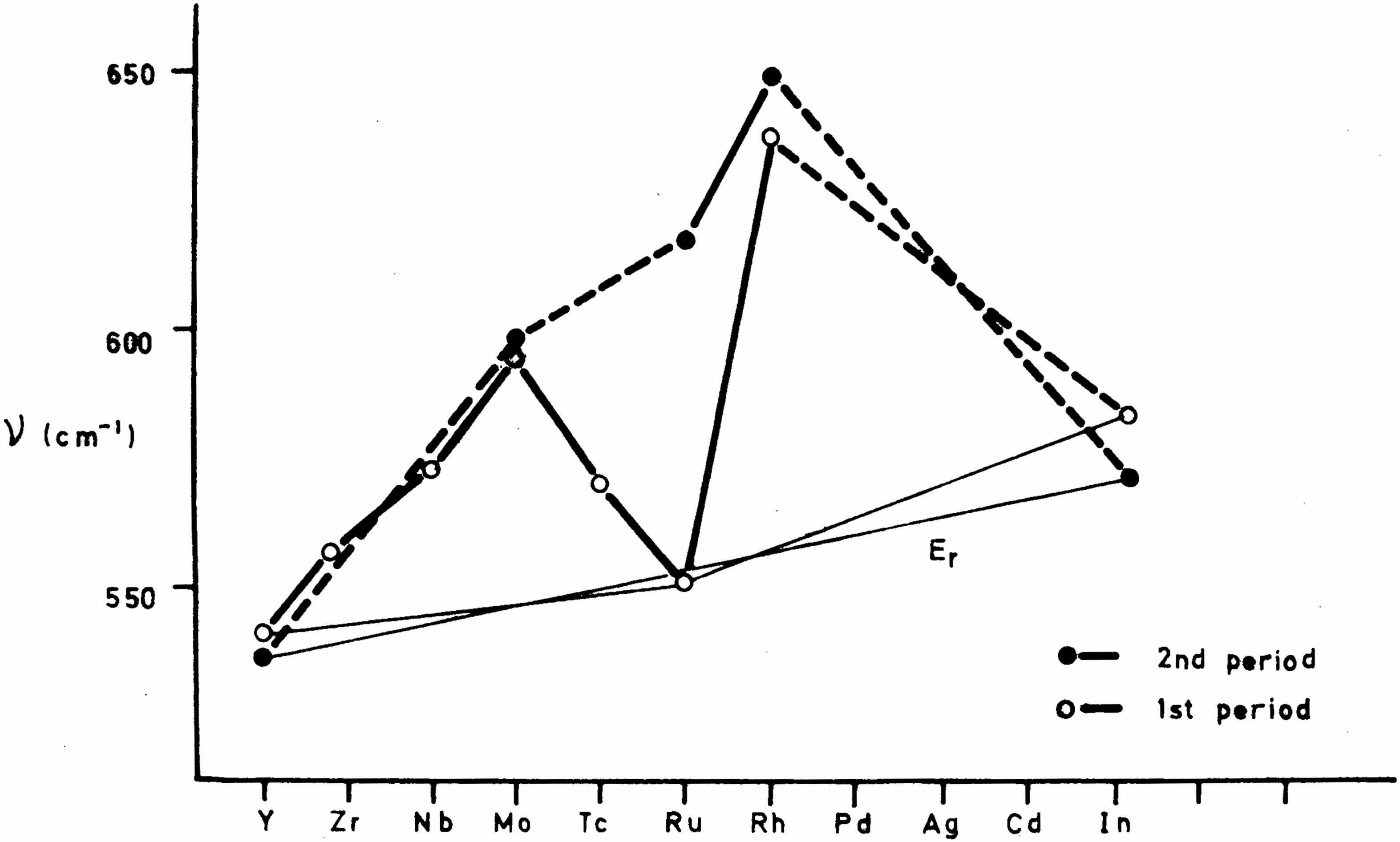


Fig.10. Variatian of ν(M-O) with at.no. in second transion period metal (III) tris(acetylacetonates). The frequencies for the first period analogues are also included.

$$\frac{10Dq(\text{ 2nd period})}{10Dq(\text{1st period})} = 1{\cdot}54 \quad \ldots\ldots \quad (5)$$

It is thus possible to estimate 10Dq for the complexes of Mo(III), Ru(III) and Rh(III) from 10Dq for the analogous first transition period ions. This would imply $-\delta H$ for the tris(acetylacetonates) of the second transition period of (kcal/mole)

Y(III)	–
Mo(III)	95·1
Ru(III)	93·7
Rh(III)	221·7
In(III)	–

The second factor accounting for the low-spin state of Ru(III) acetylacetonate is the lower spin-pairing energy in second transition period ions, as compared with their first period analogues.(10) Few values of P for second transition period ions are found in the literature. We may, however make an estimate of the order of magnitude of this lowering of P by comparing the lattice energies of MnO (first transition period high spin d^5 ion) and TcO (second transition period low-spin d^5 ion). $-\delta H$ (i.e. -CFSE + P) as determined from lattice energies is approximately 80 kcal/mole (10) for TcO, while $-\delta H$ for MnO is zero. (high-spin d^5.) Using a value of 10Dq = 29.0 kcal/mole. (derived from f = 1·3 for the oxide system, g = 22·3 for Mn(II) (12).) in eq.5, 10Dq may be estimated as 44·7 kcal/mole for TcO. From eq.2 a CF contribution of 89·5 kcal/mole. to the lattice energy of TcO is predicted. The value observed in practice is 80 kcal/mole, the difference between the two values being **P**, the energy of pairing. The pairing energy of Mn(II), on the other hand, is 104 kcal/mole as calculated from Racah parameters (10) and corrected for the solid state. The difference between P for Tc(II) (about 10 kcal/mole.) and Mn(II) (104 kcal/mole.) therefore indicates a severalfold decrease in the magnitude of P on passing from the first to the second period ions. (Assuming the reported thermodynamic data to be reliable and the assumptions made in the estimation of the respective values of P to be valid.)

The fact that Racah parameters are not available for the second period trivalent ions does not allow a reliable estimate of the pairing energies to be made.

Further, there is a considerable increase in mass on passing from the first to the second transition period, and the effect of this on M-O str. frequencies is unknown in magnitude. Thus, since both P and the magnitude of the mass effect are not known with any degree of reliability, it is not possible to estimate the size of K in eq. 4 (relating the (M-O)str. frequency to $-\delta H$) for the low-spin ions Rh(III) and Ru(III).

No pairing energy is associated with the Mo(III) complex, however, so that K may be estimated for this complex. A value of 0·0017 (where $-\delta H$ is expressed in cm^{-1}) is found for Mo(III) acetylacetonate, as compared with K = 0·0020 in the tris(acetylacetonates) of first transition period trivalent ions. This decrease in K in the second relative to the first transition period is probably associated with the increase in mass.

If this value of K = 0·0017 is now used in eq. 4 together with the appropriate values of $-\delta H$ and (M-O) str., a value of about 25% the value of P in Fe(III) acetylacetonate is found in the Ru(III) complex, and about 50% the Co(III) value is observed for P in the Rh complex. It is possible that these large dedreases in P are actually attributable to effects not taken into account by the CF model. This possibility will be discussed further in the section on the IR spectra of the trivalent hexacyano complexes, $[M(CN)_6]^{3-}$, in which series the Mn(III) and Fe(III) complexes are low-spin.

E. The first transition period divalent tris(acetylacetonates)

As was mentioned earlier, the divalent bis-(acetylacetonates) present difficulties in respect to a CF study of their IR spectra because of structural differences across the series. Anionic complexes $K[M(Acac)_3]$ are known for these ions, with three acetylacetonate groups coordinated octahedrally to the central cation. These are undoubtedly structurally similar throughout the series (84). These authors have also (84) determined the third dissoiation constant of these complexes, demonstrating the fact that the third acetylacetonate group is coordinated to the divalent ion, rather than that the complexes are only stoichiometric mixtures of the bis compounds and the group Ia (Na or K) acetylacetonate. This is supported by their IR

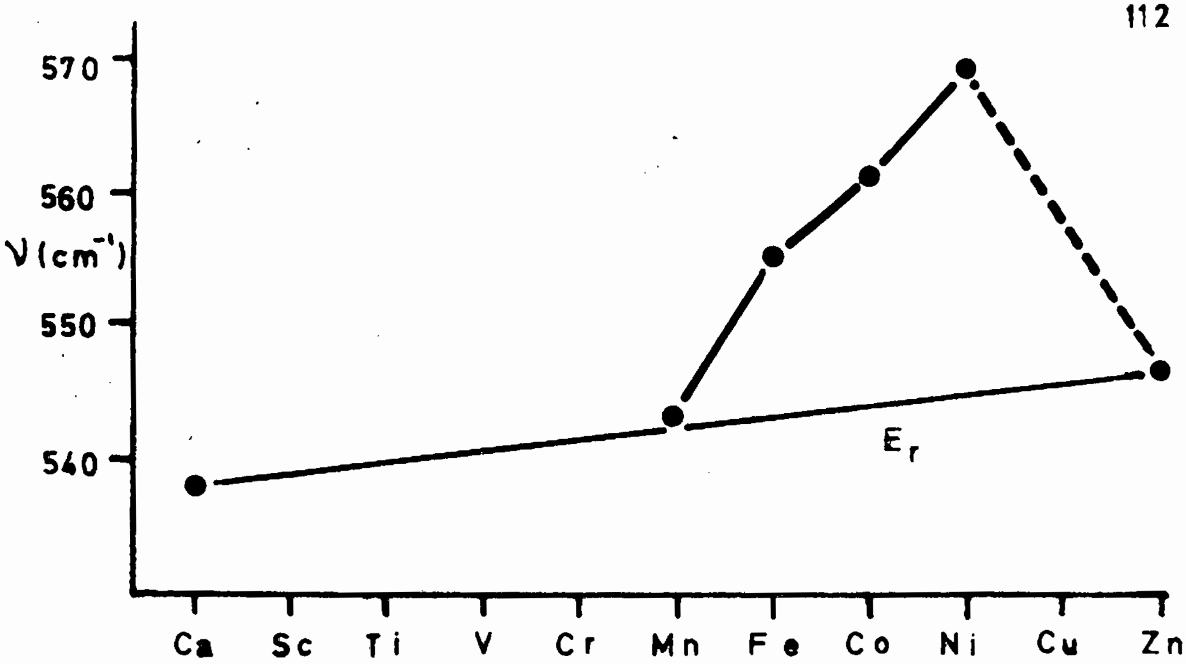


Fig. 11a. Variation of ν(M-O) with at.no. in tris(acetylacetonate) complexes of 1st transition period metal (II) ions.

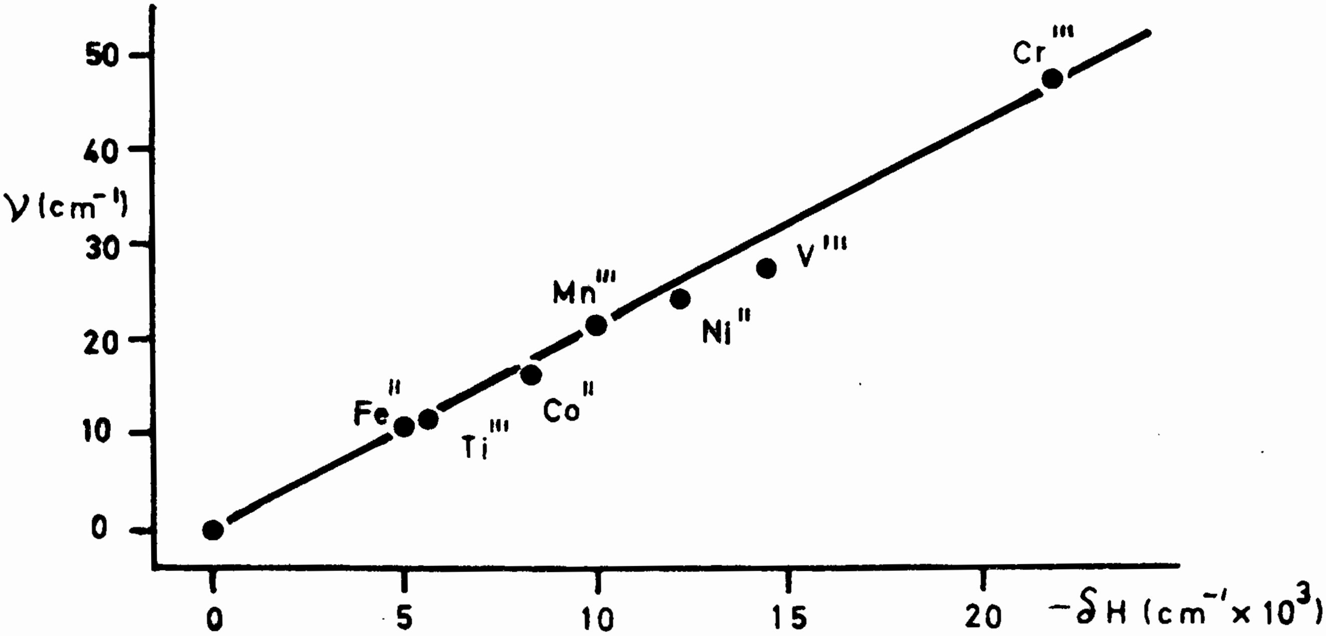


Fig. 11b. Variation of KδH with $-\delta$H for first period M(II) and M(III) tris(acetylacetonates). (KδH = empirical from eq. 4)

spectra (Fig 14), which differ from the spectra of both the divalent bisacetylacetonate (Fig 14) and the group 1a acetylacetonate (K acetylacetonate, Fig. 29). The proposed structure for the Ni(II) complex is seen in Fig. 15.

Because of this structural similarity throughout the series, these complexes represent an ideal series for a CF study. The series M' [M"(Acac)$_3$] (where M' = K, M" = Ca, Mn, Fe, Co, Ni, Zn.) was thus prepared, and the IR spectra of the complexes recorded.

No electronic spectral data are available for these complexes. Jørgensen's f and g values for the ligand and ion respectively (20) will thus be used for calculating Dq. An f value of 1·2 is reported for the acetylacetonate anion. The g values of the ions were obtained from ref. 20. $-\delta$ H calculated from these values for the ions Ca, Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) are given in Table 2.

Fig 11a illustrates the variation of the (M-O)str. with at. no. across the series. The masses of the central cations in the divalent series are of course the same as those of their trivalent counterparts. It is thus not surprising that the value of K in eq. 4 is the same for both the divalent and trivalent series. This supports the idea that the decrease in K on passing from the first to the second period series is a mass effect, since there is an increase in the mass of the second period ions relative to the first period analogues. In Fig 11b the stabilisation of the (M-O) str. due to CF effects for both first period divalent and trivalent tris(acetylacetonates) is plotted against $-\delta H$ for the complexes. A reasonably good linear relationship is observed, illustrating the fact that K is similar in magnitude for both series.

The d^6 high-spin configuration of the Fe(II) complex in the trisacetylacetonate series gives another example of the effect of change of spin-state. The low-spin d^6 configuration in the Co(III) complex in the trivalent series gives rise to a high (M-O)str. frequency at 637 cm^{-1}. If we use eq. 4 to calculate the (M-O)str. for the hypothetical high-spin Co(III) complex, a value of 574 cm^{-1} is obtained. (M-O)str. in $[Fe(Acac)_3]^-$ occurs at 555 cm^{-1}, the lower value (as compared with high-spin Co(III)) being due to larger ionic radius and smaller Dq in the divalent complex.

Table 3

$-\delta H$ (cm^{-1}) and the (M-O)str. observed and calculated from eq. 4 for the divalent tris(acetylacetonates). All figures are in cm^{-1}.

Complex	$-\delta H$	ν(M-O)$_{obs}$	ν(M-O)$_{calc}$
K[Ca(Acac)$_3$]	-	537	-
K[Cr(Acac)$_3$]	10,020	-	561
K[Mn(Acac)$_3$]	-	543	542
K[Fe(Acac)$_3$]	5,000	555	553
K[Co(Acac)$_3$]	8,960	561	562
K[Ni(Acac)$_3$]	12,240	568	569
K[Cu(Acac)$_3$]	9,060	-	564
K[Zn(Acac)$_3$]	-	547	-

The M-O frequencies in Fe(II) and Fe(III) tris-(acetylacetonates) are interesting in relation to the reverse spinel structure observed in Fe_3O_4, which is a mixed oxide of Fe(II) and Fe(III). In oxides of the composition M_3O_4, both octahedral and tetrahedral sites for coordination of metal ions to oxygen occur in the crystal lattice. The same ion in an octahedral site has greater CFSE than when it occupies a tetrahedral site (Dq(tetrahedral) = $\frac{4}{9}$ Dq(octahedral) for the same ion in each of the two different configurations.), so that the most stable structure for the oxide is that where ions in which CFSE is greatest occupy the octahedral sites in the lattice. Ions in their trivalent states normally have greater CFSE than in their divalent state ($Dq_{3+}/Dq_{2+} = 1.5$ for isoelectronic trivalent and divalent ions (10)), so that ions in the higher oxidation state occupy the octahedral sites, giving rise to the structure known as the spinel structure.

In a few cases, however, CFSE for the divalent ion is greater than that for the trivalent ion and reverse spinel structure results with the divalent ions occupying the octahedral sites. Thus we find that with Fe(II) (CFSE = 4 Dq) and Fe(III) (CFSE = 0) both in octahedral oxygen environments (tris(acetylacetonate)) (M-O)str. for the Fe(II) complex (555 cm^{-1}) is higher than that for the Fe(III) complex (550 cm^{-1}), which is in agreement with the reverse spinel structure observed in Fe_3O_4.

Figs 11, 12 and 13

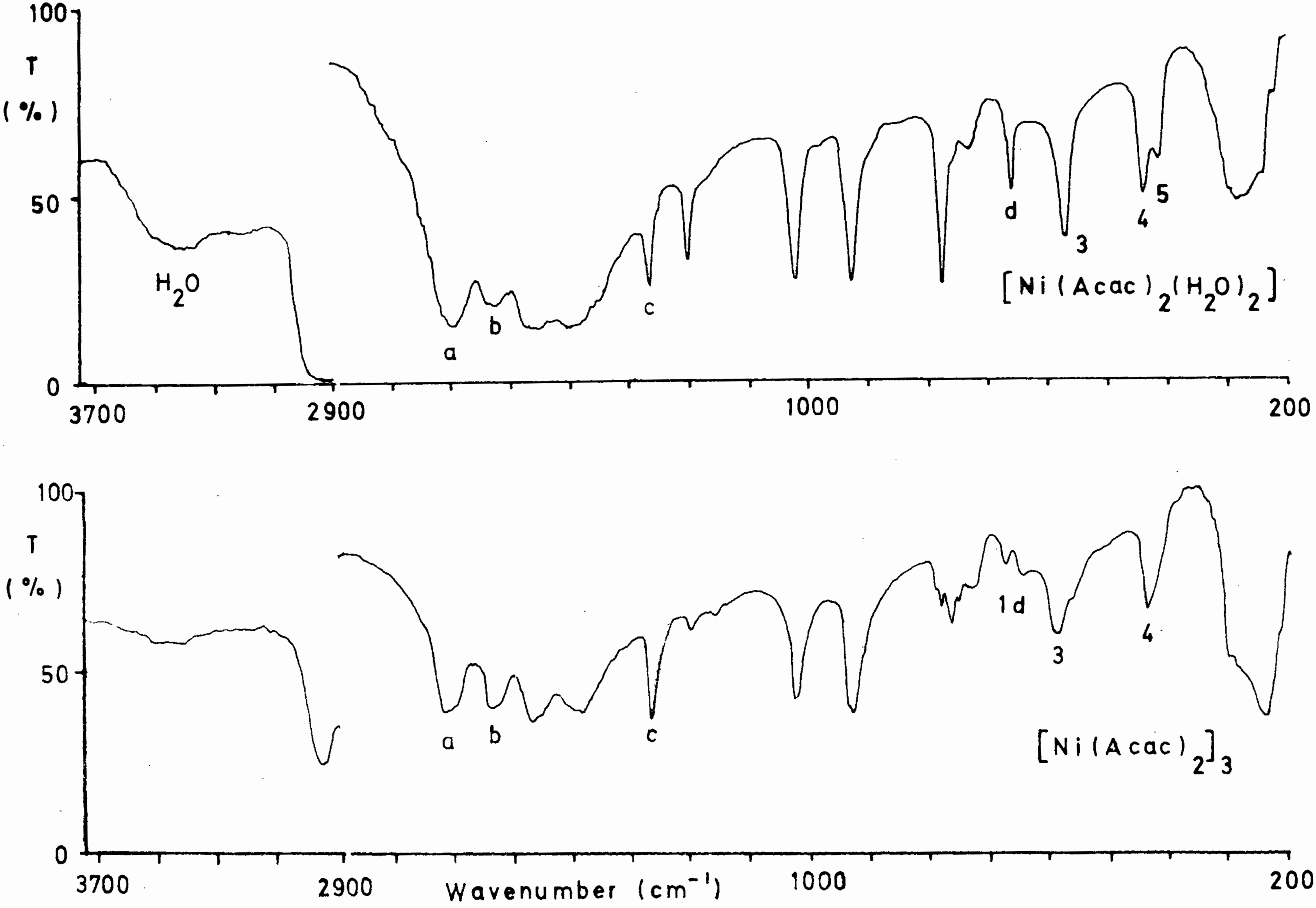
IR spectra of different Ni(II) beta-diketonate complexes in the region 4000 - 200 cm^{-1}.

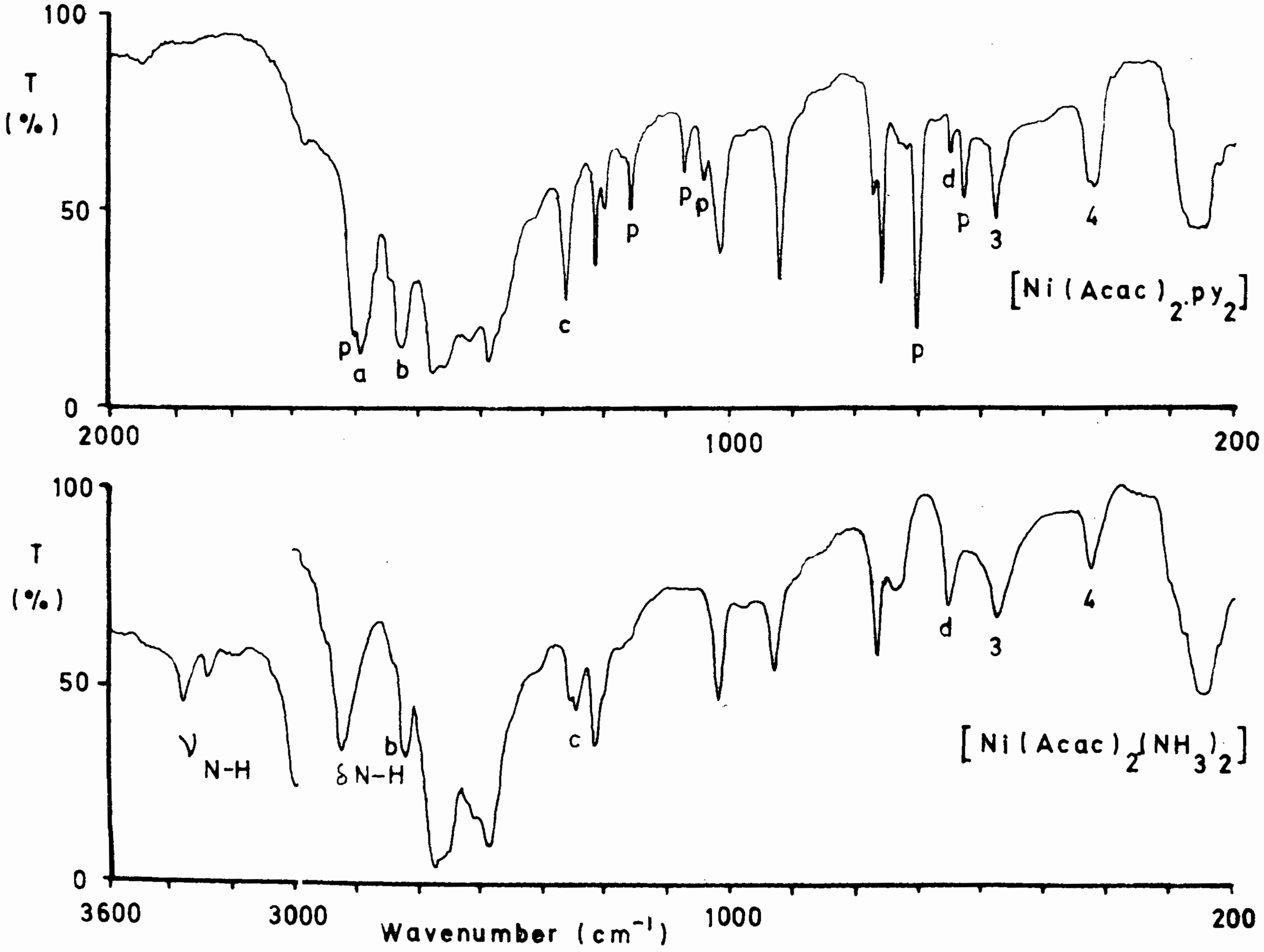
Key to band assignments

a = C=O str.
b = C=C str.
c = C=C + C-CH_3 str.
d = ring def.

1 = M-O str. + ring def.
2 = M-O str.
3 = M-O str.[a]
4 = M-O + C-CH_3 str.
5 = O-M-O bend[b]
6 = M-O + ring def.[b]

[a] This is the band assigned to M-O str. by Pinchas *et. al.* (54)., and is the band referred to as the M-O str. in this discussion. [b] As mentioned before (p 81), these assignments are only tentative.


100
T
(%)
50
0
3700
2900
1000
200
H_2O
a
b
c
d
3
4
5
$[Ni(Acac)_2(H_2O)_2]$
100
T
(%)
50
0
3700
2900
1000
200
a
b
c
1d
3
4
$[Ni(Acac)_2]_3$
Wavenumber (cm^{-1})


100
T
(%)
50
0
2000
1000
200
p
a
b
c
p
Pp
p
d
p
3
4
[Ni(Acac)$_2$.py$_2$]
100
T
(%)
50
0
3600
3000
1000
200
ν N-H
δ N-H
b
c
d
3
4
[Ni(Acac)$_2$(NH$_3$)$_2$]
Wavenumber (cm^{-1})

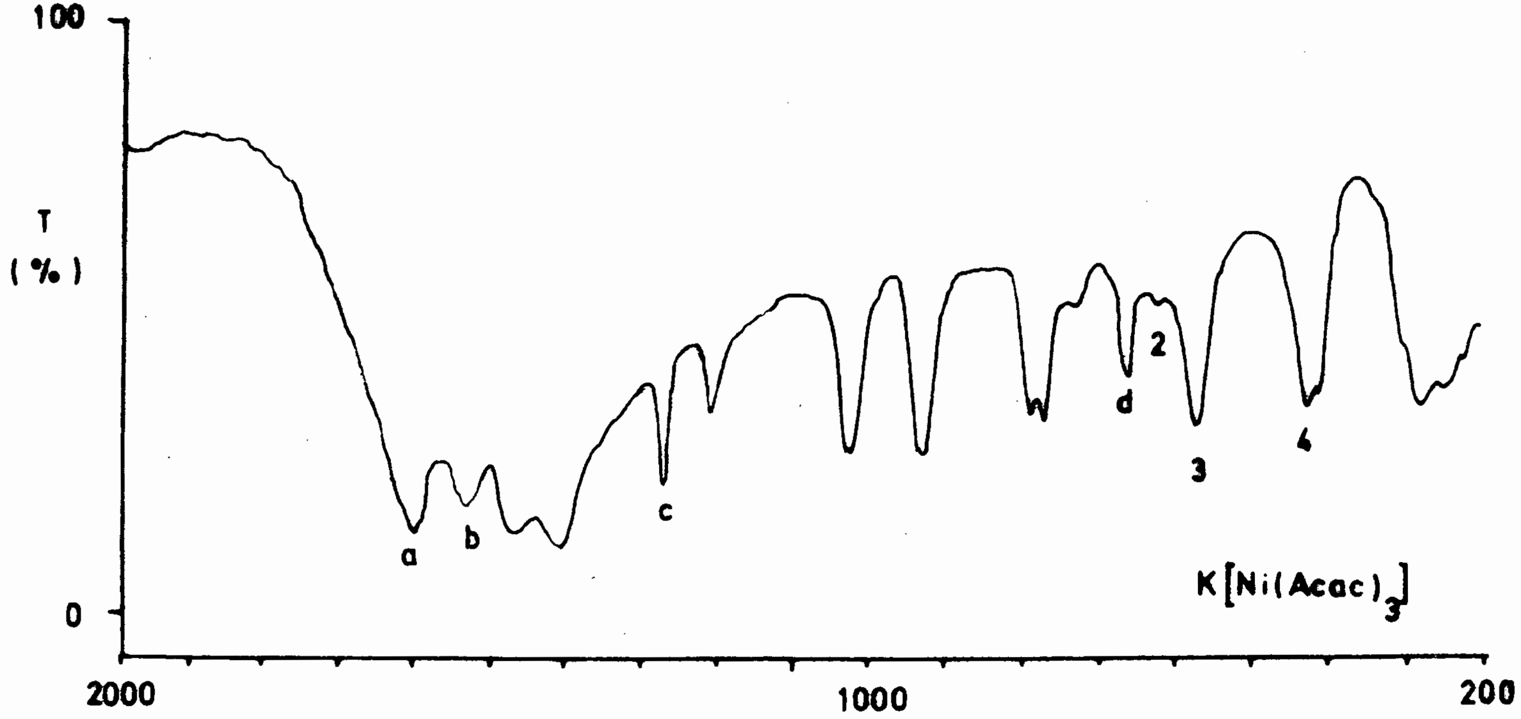
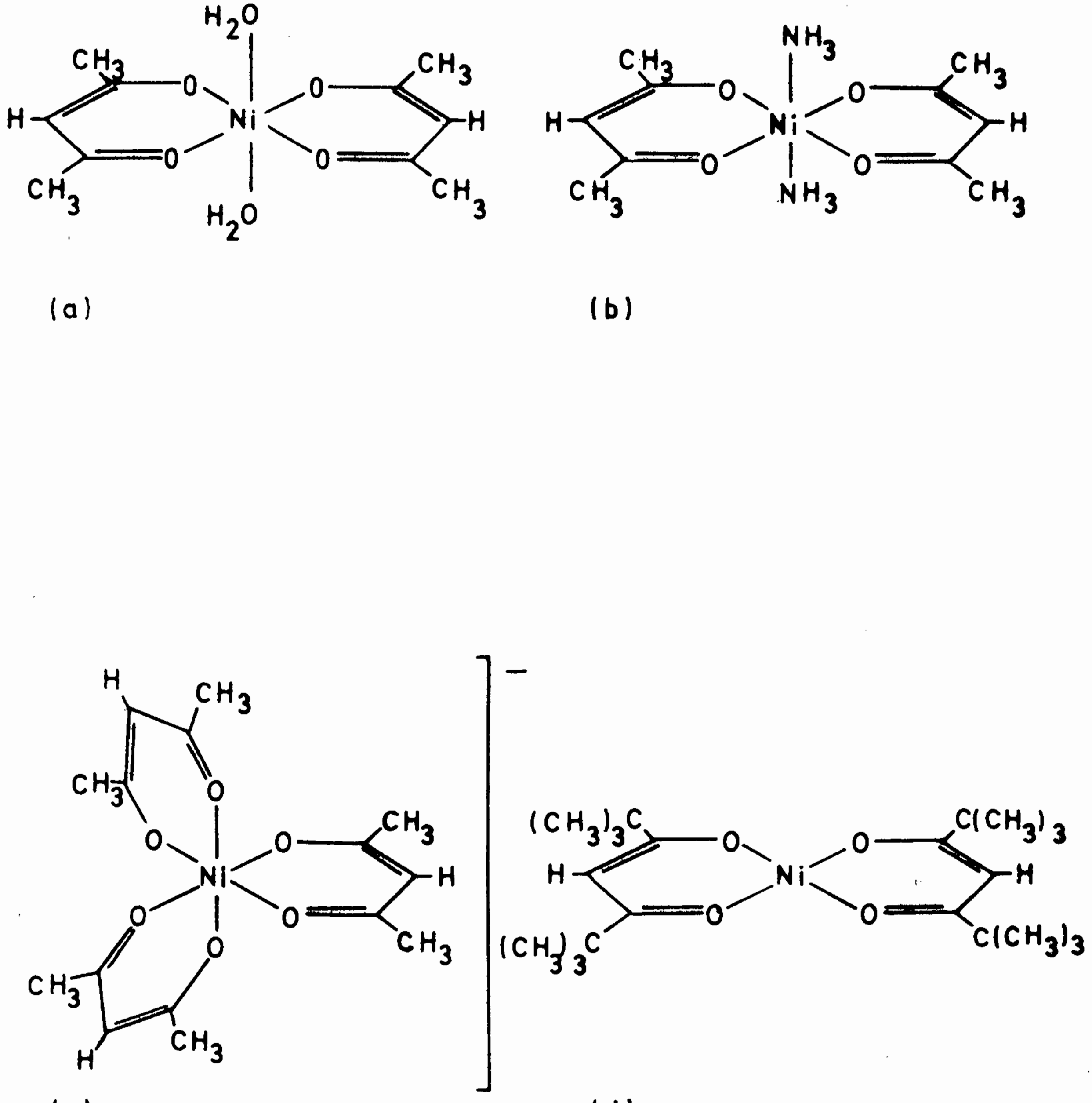


Fig. 14. Spectrum of K[Ni(Acac)$_3$] in the region 200 - 2000 cm^{-1}.



(a) (b)

(c) (d)

Fig. 15. Structures of various Ni(II) β-diketonates.

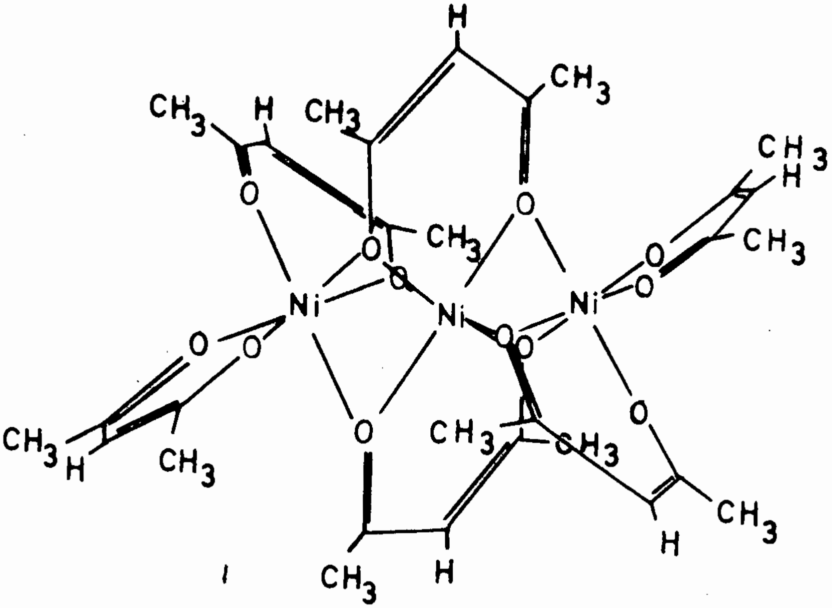


Fig. 16. Structure of $[Ni(acac)_2]_3$

F. The divalent bis(acetylacetonates) of the first transition period

The bis(acetylacetonates) of the divalent ions of the first transition period may be obtained in various forms according to the methods and conditions of preparation. This has led to confusion in the literature, since in many cases the actual preparative methods were not indicated, nor were elemental analyses reported which might have indicated the precise composition of the complexes. For example, the IR spectrum of "nickel acetylacetonate" as reported by Lawson (1) seems from the reported IR data to be that of $[Ni(Acac)_2(H_2O)_2]$, while that reported by Nakamoto (57) would seem to pertain to $[Ni(Acac)_2]_3$, the octahedrally coordinated trimer. (Figs. 15 and 16.)

Considerable care was thus exercised on our own part in the preparative methods employed, and the elemental composition determined by microanalysis for those complexes having any possible uncertainty as to precise composition. (see experimental section.)

The bis(acetylacetonates) of the divalent metals are to be found in two main classes. The simpler structurally are the square-planar acetylacetonates with two molecules of water occupying the fifth and sixth coordination positions (Fig. 15). This configuration has been confirmed by structural determination for the Ni(II) (6) and Co(II) (7) complexes. With these complexes may also conveniently be grouped the octahedrally coordinated nitrogenous base adducts of the bis(acetylacetonates), of the general formula $[M(Acac)_2X_2]$ where X = NH_3 pyridine, etc.

The second general type of bis(acetylacetonate) is the polymeric form of the general formula $[M(Acac)_2]_n$, where n = 3,4 or 6. These initially caused confusion, since from empirical formulae they appeared to be monomeric tetrahedral or square-planar in structure. Unique in structure of the first transition period bis(acetylacetonates is the Cu(II) complex, which is square-planar monomeric, and which forms few isolable adducts. These dissociate readily into the bis-compound and the free base, due to the strong Jahn-Teller distortion associated with the Cu(II) ion.

1. Bis(aquo)- and N-base adducts of the divalent first transition period bis(acetylacetonates)

Octahedrally coordinated bis(aquo)-bis(acetylacetonato)- complexes (Fig 15) are known for Ca(II), Mn(II), Co(II) and Ni(II). Zn(II) bis(acetylacetonate) forms a pentacoordinate square-base pyramidal monohydrate. The(M-O)str. frequency occurs at higher wavenumber in these complexes than in their anionic tris(acetylacetonate) counterparts, but otherwise varies qualitatively across the series as would be expected from CFT. If however, eq. 4 is used for estimating empirical Dq values, smaller values are obtained than for corresponding tris(acetylacetonate) complexes. This is due to the relatively higher frequencies of the (M-O)str. in the complexes of the Ca(II),Mn(II) and Zn(II) (d^0, d^5 and d^{10} ions, used for interpolating E_r across the series) ions in the bisacetylacetonate series.

Corresponding to these diaquo- complexes, octahedrally coordinated N-base adducts of the type $[M(acac)_2(NH_3)_2]$and $[M(acac)_2(pyridine)_2]$ (M = Mn(II), Co(II) and Ni(II)) were prepared. Coordination to the Zn(II) complex was once more square-base pyramidal, giving the complexes [$Zn(Acac)_2(NH_3)$] and [$Zn(Acac)_2py$]. The variation of the (M–O)str. across the series was as expected from CFT. Dq values may be estimated for these and the diaquo- and tris(acetylacetonate) complexes of the divalent first transition period ions using eq. 4. These empirically determined Dq values are indicated in Table 4, together with (M–O)str. for each of the complexes.

Table 4

(M–O)str. frequencies (cm^{-1}) and 10Dq determined using eq. 4, for the bis(acetylacetonates) of the first transition period. The adduct occupying the fifth and sixth coordination positions is indicated for each type of bis(acetylacetonate) complex. 10Dq is in $cm^{-1} \times 10^3$.

Complex	X_2 = Acac$^-$	$X_2 = (H_2O)_2$	$X_2 = (NH_3)_2$	$X_2 = (py)_2$
[$Ca(Acac)_2X_2$]	537[a] (–)[b]	535 (–)	–	–
[$Mn(Acac)_2X_2$]	543 (–)	551 (–)	547 (–)	542 (–)
[$Fe(Acac)_2X_2$]	555 (13·7)	–	–	–
[$Co(Acac)_2X_2$]	561 (10·6)	568 (9·4)	560 (8·1)	563 (10·0)
[$Ni(Acac)_2X_2$]	568 (9·5)	571 (6·3)	572 (10·0)	576 (11·2)
[$Zn(Acac)_2X$]	547 (–)	559 (–)	549 (–)	554 (–)

[a] First figure is (M–O)str. [b] Figures in parentheses = 10Dq.

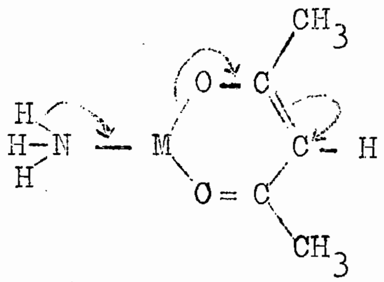
As previously mentioned, Dq may be estimated (20) in terms of a g value associated with the central cation, and an f value associated with the ligands coordinated to it. In complexes where the central cation is coordinated to more than one type of ligand (such as in $[Ni(Acac)_2(NH_3)_2]$) the value of Dq may be estimated in terms of the g value for the cation and the mean of the f values associated with each of the six (in octahedral coordination) ligands coordinated to the central cation. (Thus for example, in $[Ni(Acac)_2(NH_3)_2]$ f for $Acac^- = 1{\cdot}2$, and for $NH_3 = 1{\cdot}25$. Four coordination positions to Ni(II) are occupied by O atoms of the two $Acac^-$ groups, and two positions by NH_3 groups, so that f for the complex = $\frac{4}{6}f_{(Acac^-)} + \frac{2}{6}f_{(NH_3)} = 1{\cdot}216$)

It is therefore predicted that Dq for the complex series $[M(Acac)_2X_2]$ should increase in the order of increase of f for the adducts X. The order of increase of f for the substituents used was $H_2O < Acac^- < NH_3 < Py$. From Table 4 it is seen that the order of increase of Dq for the complexes $[Ni(Acac)_2X_2]$ is also $H_2O < Acac^- < NH_3 < Py$, as predicted by the CFT. In the Co(II) analogues however, the order of Dq for the substituents observed is $NH_3 < H_2O < py < Acac^-$. This effect is possibly associated with changes in affinity for nitrogen as against oxygen donor ligands from one ion to the other. Since (M-N)str. was not observed for these complexes, it is not possible to determine the relative M-N bonding strengths for the two ions, and so resolve the problem.

It is however, possible to gain an indirect indication of the relative magnitude of the M-N bond strenths in the diammine adducts of the bis(acetylacetonates) from the (N-H)def. frequencies of these complexes. The (N-H)def. frequencies associated with the diammine adducts of the bis(acetylacetonates) of the following ions are (cm^{-1})

Ion =	Mn(II)	Co(II)	Ni(II)	Zn(II)
(N-H)def =	1626	1620	1626	1628

If it is supposed that stabilisation of the M-N bond is accompanied by electron shifts such as



then the low (N-H)def. frequency observed in the Co(II) complex is consistent with its having a relatively greater M-N bond strength than observed in the analogous complexes of Mn(II), Ni(II) and Zn(II). The electron shifts indicated suggest further that this relatively greater affinity for nitrogen-donor ligands in Co(II) acetylacetonate should be accompanied by a weakening of the M-O bond. This factor would account for the low Dq values calculated from eq. 4 using (M-O)str. frequencies for the Co(II) bis(pyridine)- and diammine-bis(acetylacetonates). In contrast, the (N-H)def. frequencies of the Ni(II) analogues is at nearly the same frequency as in the Mn(II) and Zn(II) complexes, so that no destabilisation of the M-O bond in the Ni(II) complex relative to the complexes of the latter two ions is anticipated.

2. Polymeric bis(acetylacetonates) of the first transition period divalent metals

By mildly heating, or by subliming the hydrated divalent forms, anhydrous bis(acetylacetonates) of the first transition period ions may be obtained. These are not monomeric, as has often (e.g. ref.1) been previously supposed. The anhydrous bis(acetylacetonates) of Fe(II), Co(II) and Ni(II) have been shown by structural determination to be hexameric (9), tetrameric (2A) and trimeric (2B) respectively, in the solid state. This polymeric structure is brought about by bridging acetylacetonate groups, in which one oxygen atom is shared by two metal atoms. By means of this sharing of oxygen atoms the number of these coordinated to each metal atom is then effectively raised from four to six, so that octahedral coordination to the central ions results (Fig.16a). Thus even in anhydrous forms, no square-planar or tetrahedral structures occur.

Anhydrous Mn(II) acetylacetonate has been shown to be trimeric in benzene solution (9), and it would thus not be unreasonable to suppose that it is also polymeric in the solid state. It has also been reported (9) that Zn(II) acetylacetonate is trimeric in the solid state. Ca(II) bis(acetylacetonate) may be obtained anhydrous in the solid state, but no structural data are at present available. As will be mentioned below, the steric hindrance of the t-butyl groups of DPM^- prevent assumption of the polymeric structure. In contrast to Ca(II) acetylacetonate, Ca(II)dipivaloylmethanate retains the octahedrally coordinated water even when sublimed at 200° C. This suggests that the driving force for the loss of water in the acetylacetonate complex is the assumption of the stable polymeric structure, since $[Ca(DPM)_2(H_2O)_2]$, being unable to form polymers, cannot be readily dehydrated. It is thus possible that Ca(II) acetylacetonate is also polymeric in the solid state when anhydrous.

The IR spectrum of anhydrous Cr(II) acetylacetonate has also been reported (17), and it has been suggested (9, 17) that the structure of this complex is also polymeric octahedral. Band assignments in the reported spectrum (17) were not consistent with those used by ourselves, but the band corresponding to the (M-O)str. in the assignment favoured by us occurs at 590 cm^{-1}.

Polymeric forms of the type $[M(Acac)_2]_n$ where M = Ca(II), Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) are thus known. This is the most complete of the divalent bis(acetylacetonate) series, and should therefore yield useful information in relation to CF parameters.

In dilute solution, smaller oligomers are produced, so that it has been possible to estimate heats of monomerisation, which have been reported (9) as being of the order of 5 kcal/mole. This may account for the generally higher (M-O)str. frequencies in polymeric, as compared with monomeric forms. Using eq. 4 with K adjusted to a best fit, good agreement is obtained with CF predictions (Fig 17). The values of (M-O)str. calcd. using eq. 4, and those actually observed are given in Table 5.

The observed (M-O)str. frequencies are higher than predicted by CFT at the beginning of the series, and lower than predicted by CFT at the end. This may be caused by the decreasing preference of the ions for octahedral coordination across the series, and the resulting lower polymerisation, as illustrated by the sequence $[Fe(Acac)_2]_6$, $[Co(Acac)_2]_4$, $[Ni(Acac)_2]_3$. The high (M-O)str. frequency associated with $[Cr(Acac)_2]_n$ may therefore be due to its being extensively polymerised (9), as suggested by the above sequence.

The qualitative agreement (Fig. 17) with CFT is

Table 5

$-\delta H$ (cm^{-1}), and the observed (M-O)str. ($\nu M\text{-}O_{obs.}$) and (M-O)str. as calculated from eq. 4 ($\nu M\text{-}O_{calc.}$) for the polymeric bis(acetylacetonates) of the divalent ions of the first transition period. (Units are cm^{-1}.)

Ion	$-\delta H$	$\nu(M\text{-}O)_{calc}$	$\nu(M\text{-}O)_{obs}$
Ca(II)	-	-	535
Cr(II)	10,020	576	590[a]
Mn(II)	-	-	545
Fe(II)	5,000	566	558
Co(II)	8,960	583	581
Ni(II)	12,240	597	593
Cu(II)	9,060	590	(615)[b]
Zn(II)	-	-	565

[a] value from ref. 17. [b] The figure is for the monomer [$Cu(Acac)_2$].

otherwise good. An important feature of this trend is the high (M-O)str. for the Cr(II) complex. Irving and Williams explained the order which they had observed for divalent first transition period ions in terms of the variations of ionisation potential and ionic radius across the series (5). Extending this interpretation of the relative stabilities of these complexes to include the Cr(II) ion in the series (It was not included by Irving and Williams in their studies.) we find that the variations of r^+ and I_z across the series predict (13) the sequence Cr(II) > Mn(II), but not the greater sequence Cr(II) > Fe(II), Co(II), which is however predicted by CFT. This indicates that the correct interpretation of the Irving-Williams stability order is in terms of CFT, rather than the variations of r^+ and I_z across the series.

3. Cu(II) bis(acetylacetonate)

Cu(II) acetylacetonate is, as metioned above, unique in the first transition period in having a monomeric square-planar structure. It cannot therefore be compared reliably in relation to CFT with any of the complexes of the other ions in the first period. It is seen however, that Pd(II) and Pt(II) in the second and third series form bis(acetylacetonates) of a comparable square-planar monomeric structure. The IR spectra of these two complexes are reported (52) in the literature, and the (M-O)str. in the two complexes is reported as occurring at 678 and 686 cm^{-1} respectively. Ni(II) forms no complexes with acetylacetone of structure comparable to the square-planar acetylacetonates of its second and third transition period analogues, Pd(II) and Pt(II). An estimate of the (M-O)str. frequency of the hypothetical square-planar complex [Ni(Acac)$_2$] (which is then comparable in structure to [Cu(Acac)$_2$]) may bemade from the M-O str. frequencies of the Pd(II) and Pt(II) complexes as follows.

The extremely high (M-O)str. values in the latter two complexes are associated in the CFT interpretation with the large Dq values (as compared to the first period analogues) observed in second and third transition period ions. An estimate of the CF contribution (K δ H) to the stabilisation of the M-O str. may be made using eq. 4, by subtraction of the E_r contribution (K′n) from the observed (M-O)str. frequencies. The E_r contribution for the (M-O)str. of the Pd(II) complex may be estimated by interpolation between the (M-O)str. frequencies of the Sr(II) and Cd(II) complexes. (This suggests an (M-O)str. frequency of 540 cm^{-1} for the Pd(II) complex in the absence of CF effects.)

The complex [Hg(Acac)$_2$] has a unique structure in

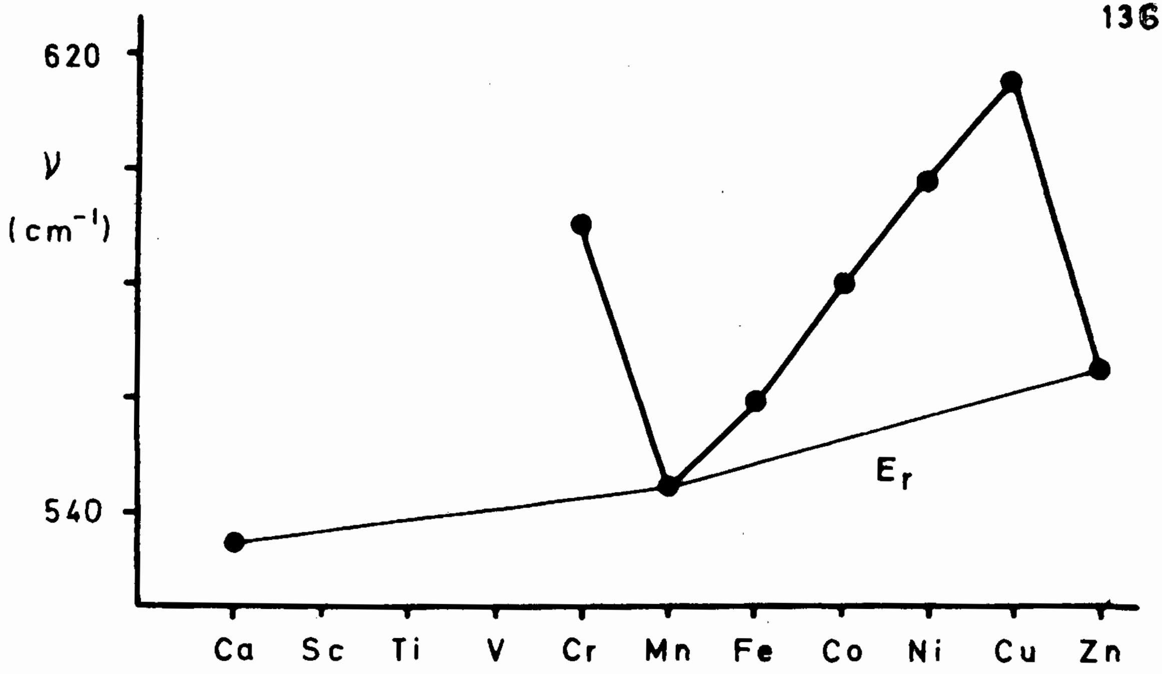


Fig. 17a. Variation of ν(M-O) with at.no. for anhydrous bis-(acetylacetonates) of first transition period M(II) ions.

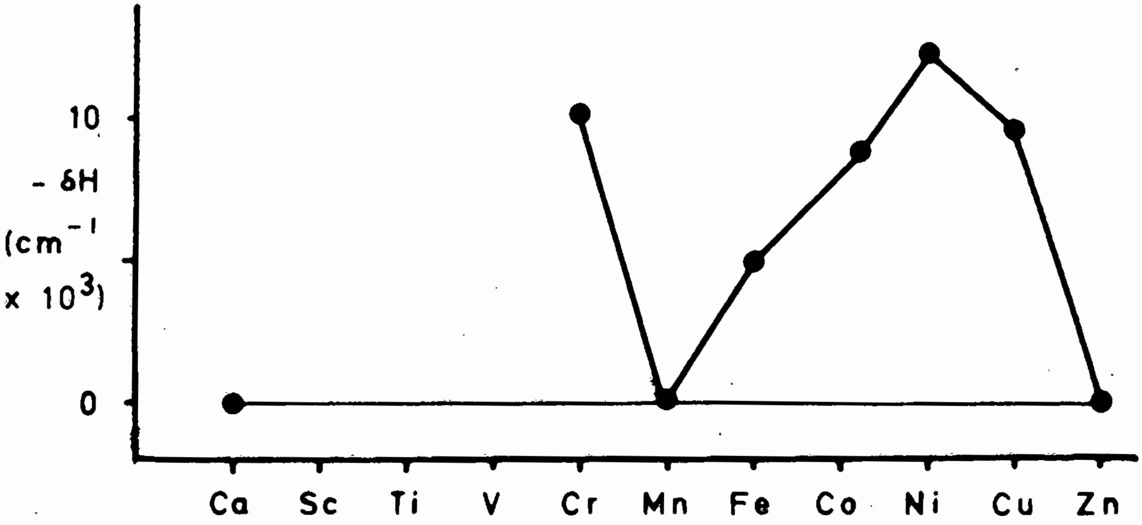


Fig. 17b. Variation of -δH with at.no. for the same series of complexes as above.

which the coordination number of the cation is only two, and a free carbonyl group (as evidenced by the IR spectrum) is left uncoordinated on each Acac$^-$ group. It is thus not possible to estimate E_r by interpolation for the Pt(II) complex. The lanthanide contraction however, causes a decrease in ionic radii in the third transition period ions, such that the expected increase in ionic radius between second and third periods does not occur. It would therefore not be unreasonable to suppose that the E_r contribution to the stability of the complexes of third transition period ions was similar to that of their second period counterparts.(10).

We therefore estimate a CF contribution (= (M-O)str. - E_r) to the (M-O)str. frequency of 138 cm^{-1} for the Pd(II) complex and 146 cm^{-1} for the Pt(II) complex. The following ratios have been estimated (20)

$$\frac{\text{Dq(2nd period)}}{\text{Dq(1st period)}} = 1{\cdot}54 \quad \text{......(5a)}$$

$$\frac{\text{Dq(3rd period)}}{\text{Dq(1st period)}} = 1{\cdot}68 \quad \text{......(5b)}$$

The ratio of K δH in the Ni(II) complex to K δH in the Pd(II) complex suggested by eq. 5 indicates a value of K δH of 89 cm^{-1}, and the ratio to K δ H in the Pt(II) complex suggests a value of K δ H of 87 cm^{-1} in the Ni(II) complex. (The close agreement between these two values of Kδ H calculated for the Ni(II) complex supports the CF interpretation of the values of (M-O)str. for the Pd(II) and Pt(II) complexes.)

(M-O)str. for the hypothetical square-planar complex of Ni(Acac)$_2$ may thus be estimated by addition of the Kδ H contribution, to (M-O)str. due to E$_r$ effects only ((M-O)^o + K′n . K′n is estimated by interpolation between (M-O)str. for Ca(II) complex and Zn(II) complex.). The (M-O)str. frequency for the complex Ni(Acac)$_2$ is thus estimated as 646 cm^{-1}.

This value suggests that the relatively high (M-O)str. frequency in [Cu(Acac)$_2$] (615 cm^{-1}) is thus probably due to its unique structure in the first transition period series of divalent acetylacetonates. It also indicates , that Ni(II) complexes of structures comparable to the Cu(II) complexes in the series should (on a CFT basis) have higher (M-O)str. frequencies than the latter. We may examine this experimentally in the divalent dipivaloylmethanate system, where Ni(II) and Cu(II) form complexes of similar square-planar structure.(18)

G. The divalent bis(dipivaloylmethanates) of the first transition period

Ni(II) dipivaloylmethanate, as precipitated from aqueous solution, is a green paramagnetic solid similar to $[Ni(Acac)_2(H_2O)_2]$. If sublimed at 150°C and 1 mm. Hg the octahedrally coordinated water is lost, and pink diamagnetic needles are obtained in which the coordination to Ni(II) is square-planar (18). (M-O)str. occurs at 636 cm^{-1} in the hydrated form. On assumption of the square-planar configuration, this band increases in frequency to 664 cm^{-1}. The corresponding band in $Cu(DPM)_2$ occurs at 646 cm^{-1}.

These changes in (M-O)str. frequency on change of coordination in $[Ni(DPM)_2]$ indicate that the high (M-O)str. observed in $[Cu(Acac)_2]$ is mainly an effect of lower coordination number, and that Ni(II) will have a higher (M-O)str. frequency than the Cu complex when of comparable structure. It also supports the order of magnitude of (M-O)str. of Ni> Cu as predicted by the CF model.

Since the spin state of Ni(II) changes from high-spin in the octahedrally coordinated DPM complex to low-spin in the square-planar complex, it is possible that the high value of the (Ni-O)str. in $[Ni(DPM)_2]$ as compared with the (Ni-O)str. in the bis(aquo)- complex is due to a change of spin-state rather than a change of coordination number. That this is not the sole effect in increasing the (Ni-O)str. frequency is demonstrated, however, by the fact that similar increases in (M-O)str. frequency are observed in complexes such as $[Zn(Acac)_2(H_2O)]$ on loss of coordinated water, in which no change of spin-state on change of coordination number occur.

Another example of the effect of change of coordination number is found in $[Co(DPM)_2]$. The anhydrous form is tetrahedrally coordinated, and in this form the (Co-O)str. frequency occurs at the same frequency as (Ni-O)str. in $[Ni(DPM)_2(H_2O)_2]$, whereas CFT predicts that it should be considerably lower. This indicates that here again lower covalency has led to higher M-O bond strengths. On the other hand, when compared with the (M-O)str. in [Ni(DPM)$_2$]and [Cu(DPM)$_2$], (M-O)str. for [Co(DPM)$_2$]is very low. This is as would be expected, since Dq for tetrahedrally coordinated complexes are expexted to be lower than for corresponding square-planar complexes.

H. Stability constants, thermochemical data, and the (M-O)str. frequencies in Ni(II) and Cu(II) complexes.

At this stage it might be instructive to compare IR results with the thermochemical and stability constant approach to the stability of Cu(II) and Ni(II) complexes. Even when hexa-coordinate, Cu(II) is highly tetragonally distorted due to Jahn-Teller effects, and will as a result have four short, strong bonds and two long, weak bonds (The reverse is also possible, as in CuF_2 where two Cu-F distances are short, and four are long (19)). Ni(II) complexes on the other hand have regular octahedral coordination to the metal ion.

CFT therefore predicts that the mean bond strengths of Ni(II) will be higher than those of Cu(II) when in an octahedral environment, while the Jahn-Teller theorem predicts that Cu(II) will be tetragonally distorted, so that (Except in CuF_2) the four bonds in the xy plane will be much stronger than the two along the z-axis.

In the thermodynamic approach, the heat of formation of the complexes represents the sum of the thermodynamic stabilisations of each of the six bonds of the octahedron. Therefore tetragonal distortions do not affect the order Ni(II) > Cu(II), as predicted by CFT, even if the species formed in solution are $[Ni(Acac)_2(H_2O)_2]$ and $[Cu(Acac)_2]$, and the distortion of the Cu(II) complex tends to square planar structure. Thus we find that thermochemical data (10) indicate the stability order Ni(II) > Cu(II) in the acetylacetonates.

On the other hand, the step-wise formation constants suggest from K_1 and K_2 for the acetylacetonates the stability order Cu(II) > Ni(II), which agrees with the Irving-Williams stability order (5). This effect is, however, due to the fact that in successive substitions of water molecules by $Acac^-$ groups, H_2O molecules occupy the weakly bound octahedral positions of Cu(II), so that K_1 and K_2 for the $Acac^-$ groups correspond to the four short bonds, and are therefore relatively high.

Thus K_1 and K_2 do not indicate the stability of $[Cu(Acac)(H_2O)_4]^+$ relative to $[Ni(Acac)(H_2O)_4]^+$, or of $[Cu(Acac)_2(H_2O)_2]$ relative to $[Ni(Acac)_2(H_2O)_2]$, but rather only the relative strengths with which the $Acac^-$ groups alone are bound. Stability constant data are thus like the IR approach to stability, since they both indicate the strength of individual bonds in the complex rather than the overall thermodynamic stabilisations of the complex. Thus the high values of K_1 and K_2 for Cu(II) acetylacetonate have, like the high (M-O)str. frequency for the complex, their origin in Jahn-Teller distortion of the molecule, tending towards square-planar structure. Characteristically, K_3,(as is seen in ethylenediammine complexes, as will be discussed in the section on N-donor ligands) because of this distortion, should be extremely small, which agrees with the fact that $Cu(Acac)_2$ does not coordinate with a third $Acac^-$ group to give a stable complex of the type $[Cu(Acac)_3]^-$, as found in all the other divalent metals in the series.

I. Complexes of the first transition period divalent ions with nitrogen-donor ligands

The variation of M-N stretching vibrations on change of central cation (as well as the variation of various vibrations other than the (M-N)str.) has been extensively studied in the literature. In Table 6 are seen reported literature values of various vibrations of series of complexes of first transition period ions from Mn(II) - Zn(II) with nitrogenous bases.

The (M-N)str. (except for a few special cases which will be mentioned) follows the order of increasing frequency Mn $<$ Fe $<$ Co $<$ Ni $\lesssim$ Cu $>$ Zn across the series, as is observed for the (M-O)str. of the acetylacetonates of these ions. In several of the series, however, Cu(II) has a tetragonally distorted structure rather than the square-planar coordination found in the acetylacetonate, which is of interest in relation to the the four short and two long bonds, which should be observable as a splitting of the (M-N)str. in the IR spectrum.

In Cu(II) complexes such as $[CuCl_2.py_2]$, which have tetragonal coordination to the Cu(II) ion, structural determination shows that there are two Cu-N bond-distances at 2·02 Å, two Cu-Cl bond-distances at 2·28 Å, and two Cu-Cl bond-distances at 3·05 Å, whereas the structure of the rest of the members of the series is regular, with all four Cu-Cl bond lengths the same (19). It is thus seen that the two pyridine groups and two of the Cl^- ions occur in the xy plane at short bond-distances, and two of the Cl^- ions (these are each coordinated to two Cu atoms) occur on the z-axis at longer distances. It would thus be expected that the (M-N) str. for Cu(II) would be higher than that for Ni(II). This is observed. However, where one (Cu-CL)str. is expected in other complexes of the series, two would be expected for the Cu(II) complex, one higher than for the complexes of the other ions and one much lower. From Table 6 it is seen that this is also observed. Thus we see that the IR data agrees for Cu(II), both with the predictions of the CFT, and also with the requirements of Jahn-Teller distortion. In that the two short M-N and M-CL bonds may be regarded as representing K_1, K_2, K_3, and K_4 for the Cu(II) complex, the IR spectrum is also in agreement with the predicted stabilities of the Irving-Williams stability order.

Further indications of the correctness of this idea are found in the series $[M(py)_2(NCS)_2]$(M = Mn, Fe, Co, Ni, Cu, Zn.), which have polymeric octahedral structures. Whereas other members of the series have two bonds in the metal to ligand vibration region, due to (M-N) and (M-NCS)str., Cu(II) has three bands in this region, with the lowest being much lower than the lower band of the Ni(II) complex, and the highest being much higher than the higher in the Ni(II) complex. In $[M(aniline)_2Cl_2]$no third band is reported for the Cu(II) complex, which may, however, be due to its being below the frequency range of the instrument used.

As previously mentioned, the phenomenon of increasing complexity of the spectrum in the (M-L)str. region due to Jahn-Teller distortion is also observed in Mn(III) beta-diketonates. Two bands in the region where only one occurs in the other, undistorted, members of the series. A simple procedure for the estimation of the thermodynamic stability of the complex, would be to take the mean of the frequencies associated with each of the six bonds, corresponding to the vibration observed for undistorted complexes. This was not, however, done for the Mn(III) beta-diketonates, since the separation between the two bands was small, the lower band due to the two long bonds being generally only 10 cm^{-1} lower than the band due to the four short bonds. In $[Cu(py)_2Cl_2]$ on the other hand, the separation is 57 cm^{-1}, and in $[M(py)_2(NCS)_2]$ it is 63 cm^{-1}. This agrees with the smaller distortions of d^4 as opposed to d^9 ions.

While we may ignore the small dostortions of Mn(III) without altering its position in the stability order of the trivalent ions, or affecting the degree to which (M-O)str. frequencies predicted on a CF basis agree with the observed (M-O)str. frequencies, the much larger distortions in Cu(II) do, however, lead to an erroneous picture of its relative thermodynamic stability, and so must be taken into account in the IR approach.

The effect of Jahn-Teller distortion on the stability constant (which, as we have mentioned, like (M-L)str. frequencies, indicate the bond-strength of specific bonds) is well illustrated for the d^4 and d^9 configurations by stability constants of, for example, the ethylenediamine complexes. The data below represents the CF contribution to the logarithm of the stepwise formation constants, corrected (by interpolation between the values for the Mn(II) and Zn(II) ions)for

for ionic contraction across the series.

Table 8

CF contributions to the logarithms of the stepwise formation constants (L_n) of first period divalent tris(ethylenediamine) complexes.

	Cr(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
L_1	3·00	-	0·94	1·94	2·85	5·43	-
L_2	2·55	-	0·60	1·59	2·42	4·77	-
L_3	-1	-	0·94	1·88	2·98	-2·7	-
ΣL	4·55	-	2·48	5·41	8·20	7·50	-

For L_1 and L_2, the order of stability is Mn<Fe<Co<Ni<Cu>Zn, which agrees with the Irving-Williams stability order, the high position of Cu(II) being due to its Jahn-Teller distortion. When L_3 is taken into account, the total CF stabilisation (ΣL) indicates the order of stability of Mn<Fe<Co<Ni>Cu>Zn, which agrees with CF predictions.

As in the tetrahedral Co(DPM)$_2$, some complexes in the series are known to be tetrahedral. Where these occur in a series, it is found that the (M-N)str.II for the Co(II) complex (when Co(II) is tetrahedrally coordinated) is higher than for the corresponding Ni(II) complex. Zn(II) is also often tetrahedral in structure, but it is found that the (M-N)str. is not particularly high in these cases. However, in the two cases where the (M-Cl) and (M-NCS)str. frequencies are reported, these are found to occur at exceptionally high values for the tetrahedral Zn(II) complexes. This suggests that the Zn(II) ion has a greater affinity for the Cl^- and NCS^- ions than for the bases coordinated to it. A further peculiarity is that in these cases, a doubling of the (M-Cl) or (M-NCS) vibrations occurs, which may, like the tetragonal distortion in Cu(II) producing a splitting of the M-L vibration, be a symmetry effect.

If we use an equation of the same form as eq. 4 used for the acetylacetonates, a quantitative examination of the agreement of the (M-N)str. frequencies with CF predictions may be made. Since only the (M-N)str. frequencies are generally observed, these may not be truly representative of the relative stability of the complex in the absence of knowledge of the variation of other (M-L)str. frequencies. In complexes of the type

$[M(NH_3)_6]X_2$ this problem does not arise since only NH_3 is directly coordinated to the metal.

Table 7.

(M-N)str. frequencies (cm^{-1}) of complexes of the type $[M(NH_3)_6]X_2$, where X = Cl, Br, I., M = Mn, Fe, Co, Ni, Cu and Zn. ν(M-N) observed, and as calcd. from eq. 4.

Ion	X = Cl		X = Br		X = I		$-\delta H$[b] (cm^{-1})
	(calc)	(obs)	(calc)	(obs)	(calc)	(obs.)	
Mn(II)	-	307	-	299	-	295	-
Fe(II)	320	321	312	315	306	306	5,200
Co(II)	325	327	318	318	311	312	8,080
Ni(II)	337	334	330	327	321	322	13,000
Cu(II)	325	420[a]	-	-	-	-	9,000
Zn(II)	-	300	-	294	-	282	-

[a] Square planar. Frequency is from ref.35. [b] − H values calcd. from Dq values quoted in ref. 19 for divalent hexammines.

$[Cu(NH_3)_4]^{++}$ cannot be included in the study, since like $[Cu(Acac)_2]$ it is not really comparable with the hexacoordinate members of the series. The (M-N)str.

frequencies of the hexammine complexes of the divalent ions , together with their frequencies calculated using a value of K in eq. 4 of 0.0026, where $-\delta H$ is expressed in cm^{-1}, are given above. Dq values for the hexammines of Co(II), Ni(II) and Cu(II) are reported in the literature (19), while Dq for Fe(II) was calculated using f and g values, taking NH_3 to have an f value of 1.25 (19).

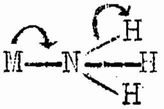
The agreement with CF expectations is seen to be good. As would be expected, since the coordinated ligand is NH_3 in all cases, K has the same value for all three sets of complexes (X = Cl, Br, I.) but is slightly larger here than it is in acetylacetonates (0.0020), which is possibly a mass effect.

The variation of ligand vibrations with at. no. in these series is of great interest (Table 6). One might expect from the principle of constant summation of bond order about an atom, which argument has been heavily relied on in IR studies of transition metal complexes, that ligand vibrations would decrease with increasing (M-N)str. frequency. From Table 6, however, it is seen that in fact precisely the opposite is true.

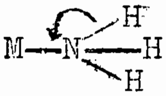
Thus, (N-N)str. in hydrazine complexes, (C-N)str.

in pyridine thiocyanate complexes, (N-H)def. in ammines and the (C-C) in-plane-def of heterocyclic aromatic nitrogenous bases, as well as various other vibrations which might be expected to vary inversely with the (M-L)str., all show parallel variations with the latter. The paralleling of the frequency trends of the (M-N)str. extends even to increasing at Co(II) (as (M-N)str. does) when the latter is tetrahedrally coordinated. This is demonstrated by the complexes $[Co(py)_2Br_2]$ and $[Co(\gamma\text{-picoline})_2Cl_2]$, where the coordination to Co(II) is tetrahedral.

This indicates that CF stabilisation in these molecules cannot be interpreted as a simple process of electron-flow from the metal ion into the M-N bond, with a flow of electrons away from the bonds adjacent to the (M-N) bond, as envisaged in the principle of constant total bond summation about any one atom . This simple mechanistic interpretation may be represented as



or



It would seem that CF stabilisation should rather be interpreted as a thermodynamic effect which stabilises bonds throughout the molecule as a whole. As will be seen later, the principle of total bond summation does not apply to the M-O and C-O vibrations in the IR spectra of the beta-diketonates with change of CF stabilisation of the molecules, but does hold for non-transition metal beta-diketonates on change of metal, and for all beta-diketonates on change of the 1,3- substituents. Further, bonds not adjacent to the M-O bond in beta-diketonates do show inverse relationships with adjacent bonds (as indicated by their str. frequencies) as evidenced by the (C-O) and (C-C)str. frequencies, whether accompanied by CF effects or not.

From this discussion on nitrogen-donor ligands, it is seen that the interpretation of the variations of the (M-N)str. frequencies in the spectra of their complexes with the divalent first period transition metals Mn(II) - Zn(II) is, as might be expected, very similar to the interpretation of the (M-O)str. frequencies in the beta-diketonate complexes of these ions. The trends observed in both series are in good agreement with CF predictions. The high (M-L)str. frequency observed for the Cu(II) complexes of both types of ligand is due to a highly distorted structure, and is not a realistic picture of its thermodynamic stabilisation. Reduction of coordination number in other ions of the series of complexes of both types of ligand also leads to relatively high (M-L)str. frequencies, as in $[Co(DPM)_2]$, $[Ni(DPM)_2]$, or $[Co(aniline)_2Cl_2]$, $[Co(py)_2Br_2]$. We thus see that the conclusions reached regarding the interpretation of the IR spectra of the oxygen-donor complexes in relation to the CFT are amply confirmed by the IR spectra of the nitrogen-donor complexes.

Table 6

Frequency data for complexes of transition metal(II) ions with nitrogen donors. (cm^{-1})

Complex	Vibrn.	Struct.	Mn	Fe	Co	Ni	Cu	Zn	ref.
M-N vibrations									
$[M(NH_3)_2Cl_2]$	ν(M-N)	p.o.[b]	-	415	423	435	480	421^t	
$[M(NH_3)_2Br_2]$	ν(M-N)	p.o.	-	424	432	434	486	414^t	
$[M(NH_3)_6]Cl_2$	ν(M-N)	p.o.	307	321	327	334	420^c	300	
$[M(NH_3)_6]Br_2$	ν(M-N)	m.o.	299	315	318	327	-	294	
$[M(NH_3)_6]I_2$	ν(M-N)	m.o.	295	306	312	322	-	282	
$[M\ hy_2Cl_2]^a$	ν(M-N)	p.o.	343	369	388	409	440	385 345	25
$[M\ hy_3](NO_3)_2$	ν(M-N)	p.o.	-	-	393	417	-	359	26
$[M\ an_2Cl_2]$	$\nu(M-N)^d$	p.o.	386	-	415^t	388	430	402^t	27
$[M\ an_2Br_2]$	$\nu(M-N)^d$	p.o.	367	-	412^t	386	424	400^t	27
$[M\ an_2I_2]$	$\nu(M-N)^d$	p.o.	361	-	410^t	361	424	396^t	27
$[M\ py_2Cl_2]$	$\nu(M-N)^{ef}$	p.o.	212	219^g	224^g	239^g	268	220^t	28
$[M\ py_2Br_2]$	ν(M-N)	p.o.	212	-	250^t	237^g	269	220^t	28
$[M\ py_4Cl_2]$	ν(M-N)	m.o.	-	-	225	242			29
$[M\ py_2(NCS)_2]$	$\nu(M-N)^e$	p.o.	200	200	213	229	256 214	227^t	30
	ν(M-NCS)	p.o.	254	261	268	280	319	312 268^t	30
$[M\ py_4(NCS)_2]$	ν(M-N)	m.o.	195	203	212	233	245	-	29,30
	ν(M-NCS)	m.o.	253	267	270	285	311	-	30
$[M(quin)_2Cl_2]$	ν(M-N)	p.o.	196	-	226^t	223	259	205^t	29
$[M(alan)_2]$	ν(M-N)	p.o.	-	-	322	328	335	305	31
$[M(leucine)_2]$	ν(M-N)	p.o.	-	-	312	323	400 388	314	32

Table 6 (contd.)

Representative M-sensitive ligand vibrations (cm^{-1})

Complex	Vibn.	Mn	Fe	Co	Ni	Cu	Zn	ref.
$[M(NH_3)_2Cl_2]$	NH_3rock	-	624	645	676	716	685	23
$[M(NH_3)_2Br_2]$	NH_3rock^h	-	617	639	670	720	680^t	23
$[M(NH_3)_6]Cl_2$	δNH_3deg.	1592	1597	1602	1607	-	1596	24
"	δNH_3sym.	1134	1151	1163	1175	-	1145	24
"	δNH_3rock	617	641	654	680	709^c	645	24
$[M(NH_3)_6]Br_2$	δNH_3deg.	1589	1595	1600	1603	-	1592	24
"	δNH_3sym.	1145	1159	1174	1188	-	1156	24
"	δNH_3rock	606	625	647	672	-	636	24
$[M(NH_3)_6]I_2$	δNH_3deg.	1582	1592	1595	1597	-	1594	24
"	δNH_3sym.	1155	1182	1189	1205	-	1179	24
"	δNH_3rock	592	617	626	654	-	621	24
$[M\ hy_2Cl_2]$	(N-N)str.	960	964	974	978	985	976	25
"	NH_2as.rock	590	607	625	649	682	625	25
"	NH_2sym.rock	518	553	582	613	658	580	25
$[M\ hy_3](NO_3)$	N-Nstr.	-	-	964	973	-	972	26
$[M\ an_2Cl_2]$	M-Clstr.	227	-	318 299^t	238	306	294^t	27
$[M\ py_2Cl_2]$	ligand^{ij}	627	629	631	634	644	639^t	28
"	ligand^{kl}	419	424	429	439	441	422^t	28
"	M-Clstr.	231	-	234	264	294 237	331 298^t	29
$[M\ py_2Br_2]$	ligand^i	628	-	642^t	634	644	639^t	28
"	ligand^k	422	-	422 416^t	442	441	422^t	28
$[M\ py_4Cl_2]$	ligand^i	-	-	623	627	-	-	29
$[M(\gamma pic_2Cl_2]$	ligand^i	535	-	554^t	546	550	555 550	33
$[M\ \gamma pic_4Cl_2]$	ligand^i	533	-	538	541	-	-	33
$[M\ \gamma pic_4Br_2]$	ligand	542 535	536	539	541	-	-	33

Table 6 (contd.)

Complex	Vibn.	Mn	Fe	Co	Ni	Cu	Zn	ref.
[M $py_2(NCS)_2$]	ligand[ie]	627	629	628	630	640	-	20
"	N-Cstr[n]	-	2062	2088	-	2096	2075^t	24
[M $py_4(NCS)_2$]	ligand[ie]	625	623	625	627	636	-	30
"	C-N str.	2066	2068	2072	2079	2080	-	30
[M$(quin)_2Cl_2$]	ligand[i]	621	-	635^t	631 621	637	635^t 623^t	29
"	M-Cl str.	246	-	312^t	263	332	316^t 300^t	29
[M$(alanine)_2$]	NH_2 rock	-	-	565	641	665	635	31
[M$(leucine)_2$]	NH_2 rock	-	-	579	625	655^s	645	32

[a] ligand abbreviations; hy = hydrazine ; an = aniline; py = pyridine ; quin = quinoline; pic = picoline

[b] p.o. = polymeric octahedral; m.o. = monomeric octahedral. Exceptios (other than tetragonal Cu(II)) are indicated by suffixes: t = tetrahedral; s = square-planar

[c] $[Cu(NH_3)_4]Cl_2$. Frequency from ref 35.

[d] assignments of M-N frequencies in an complexes are by no means certain. A lower frequency band also quoted as M-N str. exhibits a roughly inverse relationship to that quoted here.

[e] frequencies are in good agreement with those in ref.29.

[f] frequency for Cr(II) complex = 219 cm^{-1}

[g] assignment on the basis of ref. 29

[h] a lower frequency NH_3 rocking frequency exhibits the same trends.

[i] C–C in-plane bend of heterocyclic ring (29).

[j] frequency for Cr(II) complex = 640 cm^{-1}.

[k] C–C out-of-plane bend of heterocyclic ring (29).

[l] frequency for Cr(II) complex = 440 cm^{-1}

[m] frequencies are not in good agreement with those in ref 30, but appear to have been determined with greater precision.

J. Complexes with mixed donor-atom ligands of Nitrogen and Oxygen

Beta-imino ketones may be reacted with Cu(II) and Ni(II) to form compounds analogous to the beta-diketonates of these ions. (Fig. 18) However, the Ni(II) complex differs from Ni(II) acetylacetonate in that it has a square-planar structure (as in $Ni(DPM)_2$) analogous to that of the Cu(II) complex, and so presents another example with which to test the CF prediction of stability Ni(II)>Cu(II).

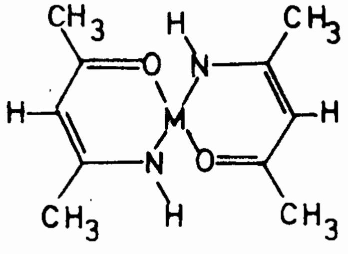
The spectra (Fig. 19) of the two complexes are rather similar to that of Cu(II) acetylacetonate, and the bands in them may be assigned by direct comparison with the spectra of the latter. A set of bands corresponding to the metal-sensitive bands in the spectrum of Cu(II) acetylacetonate in the region 300 - 700 cm^{-1} are observed, and the frequencies are as follows

$Cu(Acac)_2$	655	615	-	455	431	
$Cu(AAI)_2^a$	650	620	580	466	437	
$Ni(AAI)_2$	685	661	630	486	458	448

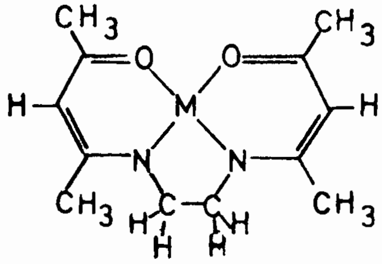
[a] AAI = Acetylacetone imine (4-imino-2-pentanone)

It is seen that in all of these bands, the frequency for the band in $Ni(AAI)_2$ is higher than in $Cu(AAI)_2$, as predicted from CFT. It is possible that the low intensity 580 and 630 cm^{-1} bands in the Cu(II) and Ni(II) beta-imino-ketone complexes respectively, are associated with M-N vibrations, since they are not present in the spectrum of $Cu(Acac)_2$. Similarly, in the region 500 - 300 cm^{-1}, extra bands are observed in the spectra of the $M(AAI)_2$ complexes, which are also possibly due to M-N vibrations. These also indicate the order of stability of Ni(II) Cu(II).

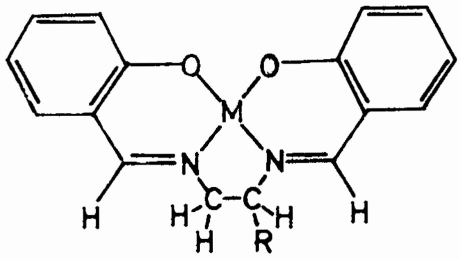
In $Ni(Acac)_2$, (M-O)str. (647 cm^{-1}) was calculated, using eq.4 and (M-O)str. frequencies of Pd(II) and Pt(II) acetylacetonates, as being 32 cm^{-1} higher than in Cu(II) acetylacetonate. The difference in (M-L)str. observed for $Ni(AAI)_2$ (661 cm^{-1}) and $Cu(AAI)_2$ is 41 cm^{-1}, which agrees fairly well with the value predicted for the acetylacetonate complexes. The greater difference in frequency, as well as the higher M-L frequencies in the AAI complexes, may be associated with the generally higher Dq values associated with nitrogen-donor, as compared with oxygen-donor ligands.



M(AAI)$_2$

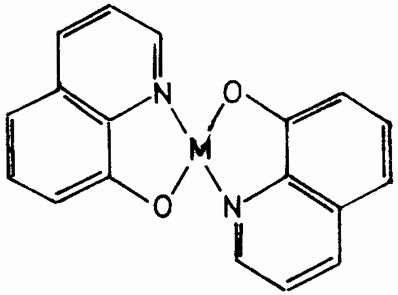


M(EDDAA)



R= H = M(EDBSA)

R = CH$_3$ = M(PDBSA)



M(OX)$_2$

Fig. 18. Structures of complexes of mixed-donor-atom ligands.

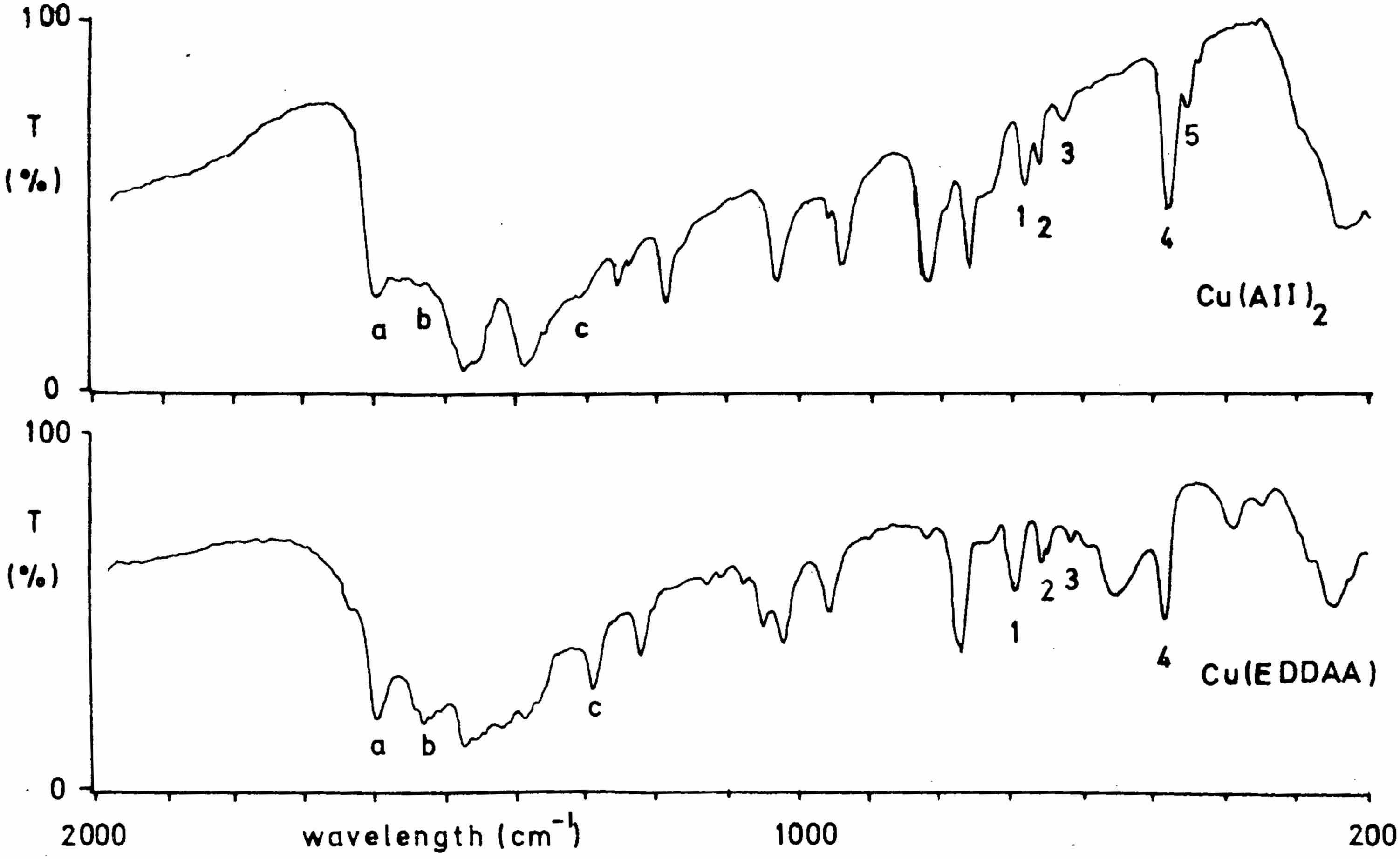


Fig. 19. Spectra of Cu(AII)$_2$ and Cu(EDDAA) in the region 200 - 2000 cm^{-1}.

On condensation with ethylenediamine, acetylacetone and salicylaldehyde form tetradentate ligands which also react with Ni(II) and Cu(II) to yield square - planar complexes. The spectra of the bis(acetylacetone) ethylenediamine (4,4'-(ethylenediamino)di-3-penten-2-one, abbreviated as EDDAA) complexes are similar to those of the beta-imino ketone complexes. In these, the order of stability indicated by the (M-L) band frequencies is Ni(II) Cu(II), as predicted by CFT. Extra bands, corresponding to those at 580 and 630 cm^{-1} in the Cu(II) and Ni(II) AAI complexes, are also observed, but are broadened compared to those in AAI complexes, and are shifted to lower wavenumber. This supports the idea that these bands in both types of complex are largely associated with the (M-N) vibration, since the exchange of the single proton for a bulky methylene group on the nitrogen atom would be expected to have just such an effect on M-N frequencies.

In the complexes of bis(salicylaldehyde)ethylenediamine (1,1'-(ethylenediamino)di-o-hydroxyphenylmethane, abbreviated to EDBSA) with divalent metals, the Co(II) complex is of interest in that it has a low-spin configuration, and is therefore thought to be square planar (22). The Zn(II) complex is mono-hydrated and therefore of a square-base-pyramidal structure, as observed in other of its complexes, which were discussed earlier. The frequencies for this complex will however serve as a rough guide to the magnitude of CF effects across the series.

The spectra of the EDBSA complexes resemble those of their EDDAA analogues in that there are low-intensity bands in the region 500 - 600 cm^{-1} which are sensitive to change of metal, and thus correspond to those tentatively assigned as M-N frequencies in the spectra of the latter. There are also higher intensity bands in the regions 400 - 500 and 600 - 700 cm^{-1}, which are highly sensitive to change of metal, and therefore correspond to the M-O bands observed in the spectra of analogous EDDAA complexes.

Complexes of the ligand propylenediamine-bis(salicylaldehyde)(1,1′-(propylenediamino)di-o-hydroxyphenylmethane, abbreviated to PDBSA) were also prepared with the ions Ni(II) and Cu(II). The frequencies for the metal sensitive bands in the region 400 - 700 cm^{-1} in the spectra of these and the EDBSA complexes are (cm^{-1})

as follows

	M(EDDAA)		M(EDBSA)				M(PDBSA)	
	Cu(II)	Ni(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)
M-O	687	696	650	662	662	654	677	663
	650	–	625	637	628	615	627	627
	611	617	599	615	607	–	614	609
M-N	572[a]	591	560	555	576	550	558	555
	554	551	510	523	530	505	535	535
M-O	462	484		470	462		466	

[a] many of the bands in this region are broad and of low intensity, so these figures may not be completely reliable.

Square-planar structure may be thought of as an extreme case of tetragonal distortion of an octahedral structure. From the splitting of the d-orbitals in square-planar environments, it is possible to predict that the $d_{x^2-y^2}$ orbital must be more unstable than the other orbitals. Thus, we are definitely able to predict from CFT the order of stability Ni>Cu in square-planar environments, since this orbital is not, as in Cu, electronically occupied in Ni square-planar complexes.

However, the relative stability of the d_{xy}, and the d_{xz} and d_{yz} orbitals (these two are of equal stability) varies from one complex to another (19), so that it is difficult to predict the stability of square-planar Co(II) complexes relative to square-planar Ni(II) complexes on a CF basis.

The order of stability indicated by the IR data is $Co < Ni > Cu > Zn$. This suggests that electronic occupation of the orbital, or orbitals, immediately below the $d_{x^2-y^2}$ level is energetically favourable, since the order of stability Ni(II) > Co(II) is indicated. (Ni(II) has one electron more than Co(II) has in the d_{xy}, d_{xz} and d_{yz} levels.) The explanation of the stability of these orbitals, as indicated by the IR data, is possibly (as will be discussed in the section on MOT) in the participation of the electrons in these orbitals in π-bonding with the orbitals of the ligand.

The spectra of the 8-hydroxyquinoline complexes of Ca(II), Mn(II), Co(II), Ni(II) and Cu(II) have been reported (36) in the literature, as far as 400 cm^{-1} into the far infra-red. No bands were assigned to M-L vibrations, but by their metal-sensitivity, it appears that

that the band occuring in the 480 - 525 cm^{-1} range in the spectra of these complexes must contain a fairly high degree of M-L character, and is possibly, by analogy with other complexes containing M-O bonds (in which M-O vibrations occur in the range 500 - 700 cm^{-1}), an M-O band. The order of stability indicated by this band is Ca < Mn < Ni < Co < Cu > Zn, as is seen below

Ion:	Ca	Mn[a]	Fe	Co	Ni	Cu	Zn
(M-L):	489	492	-	513	505	525	494

[a] Frequency from ref. 36.

The variation of the M-L str. frequency across the series is consistent with CFT expectations. No structural data is available for the Co(II) complex, but from the fact that the M-L str. frequency for this complex is higher than in the Ni(II) complex, it would appear that it has the tetrahedral structure.

K. The CF approach to the thermodynamic stabilisation of the beta-diketonates of the first transition period trivalent ions

Wood and Jones (38, 39) have undertaken oxygen-bomb-calorimetric studies of the heats of combustion of the first transition period trivalent tris(acetylacetonates) and tris(dibenzoylmethanates) for the ions Sc(III), V(III), Cr(III), Mn(III), Fe(III) and Co(III). The heats of combustion and heats of volatilisation of the complexes were determined, and used in constructing a Born-Haber cycle from which heterolytic bonding energies for the complexes were estimated.

As was previously mentioned, the heterolytic bonding energies may be divided into a CFSE contribution ($-\delta H$), and an ionic contraction contribution (E_r). $-\delta H$ for each complex was thus derived by subtraction of the ionic contraction energy of each ion from the heterolytic bonding energy of the complex. E_r for the CF stabilised ions was determined by interpolation between the $-\Delta H$ values of the Sc(III) and Fe(III) complexes, for which $-\delta H = 0$. ($-\Delta H$ being plotted against at. no. for the series.)

In both the series $M(Acac)_3$ and $M(DBM)_3$, thermodynamic 10Dq values agree reasonably well with those determined spectroscopically (11) for M = Cr, Mn and Co. However, for the ions of lower at. no. (M = Ti, V) the thermodynamic 10Dq values were severalfold as large as those determined spectroscopically.

A simple explanation for this observation is found in the suggestion (10) that the $-\Delta H$ values for Sc(III) complexes are too low, since the phenomenon of 10Dq being too high for Ti(III) and V(III) is almost invariably observed in series of complexes of the first transition period trivalent metals. The erroneous $-\Delta H$ values for Sc(III) complexes are attributed to the fact that some of the thermodynamic data on Sc(III) such heats of solution in acid, rely on single reported determinations in the early literature (10) which have not been rechecked. It is generally considered that heats of formation of Sc(III) compounds are low by some 40 kcal/mole (10). This error in $-\Delta H$ was estimated by subtraction of spectroscopically determined $-\delta H$ from thermodynamically determined $-\Delta H$ for the complexes of each of the ions Ti(III), V(III), Cr(III), Mn(III) in the series in order to obtain empirical E_r energies for them. Extrapolation of these empirically determined E_r values for a number of series of complexes suggested the higher values for Sc(III) for each of them.

Extrapolation of the heats of hydration of the trivalent ions of the first transition period indicates that $-\Delta H$ for Sc(III) is here also 40 kcal/mole too low. Since the metal ions are in an octahedral oxygen environment, as is found in the acetylacetonates, it would not be unreasonable to suggest this figure as the correction to $-\Delta H$ for Sc(III) acetylacetonate. This lowers 10Dq for V(III) to 69·8 kcal/mole. The uncorrected value is 100 kcal/mole. while that found spectroscopically is 51·5 kcal/mole (11). The agreement is most certainly improved by this correction, and it is possible that this correction to $-\Delta H$ of Sc(III) is still larger.

Wood and Jones (38) were unsuccessful in preventing partial oxidation of the Ti(III) acetylacetonate complex, so that 10Dq for this complex is not considered reliable. The correction of $-\Delta H$ for Sc(III) does not, however, solve the problem of the very low Dq value observed for Mn(III) (only 14·7 kcal/mole as against a spectroscopic value of 48·6 kcal/mole (11)). As will be discussed later this, like the high M-Ostr. for Ru(III), Rh(III) and Co(III), is possibly a π-bonding effect.

For the Co(III) ion, raising $-\Delta H$ for Sc(III) is expected to raise Dq. In their first paper on this subject (38) Wood and Jones neglected to correct P for the solid state (the quoted values are for the gaseous ion) and obtained a value of 10Dq higher than that determined spectroscopically. Further, it seems that their value for the P term in eq. 3 is in error. The spin-pairing energy (P) is the energy required to change ~~of~~ the spin-state of the ion from high-spin to low-spin. In high-spin Co(III) there is one pair of spin-paired electrons, while in low-spin Co(III) there are three. Thus, the difference in energy corresponds to the pairing of two pairs of unpaired electrons (and not of three, as intimated by these authors). Thus, from their literature source, where the energy of spin-pairing of d-orbital electrons in Co(III) is quoted as 60 kcal/mole per pair, they calculated a value of P = 180 kcal/mole instead of 120 kcal/mole. (Using P = 180 kcal/mole actually suggests that $Co(Acac)_3$ should be high-spin if we use Dq determined spectroscopically for calculating $-\Delta H$.)

Taking into account the corrections for the solid state (using P = 90 kcal/mole) 10Dq for Co(III) acetylacetonate is calculated as 49 kcal/mole from the thermodynamic data of Wood and Jones, instead of 83·3 kcal/mole as reported by these authors. 10Dq determined spectroscopically is 60 kcal/mole. Using the above-mentioned corrections to P has thus brought about better agreement between spectroscopic and thermodynamic data than was suggested by previous work.

In Table 9 a comparison of the 10Dq values for the series $M(Acac)_3$ (M = Sc(III), Ti(III), V(III), Cr(III), Mn(III), Fe(III), Co(III), Ga(III)) as determined from IR spectra, electronic spectra, calorimetric studies, and from f and g values, is seen. It is observed that, in general, closer agreement is found between 10Dq values determined from IR spectra and electronic spectra, than between the latter and those determined thermodynamically. This is only to be expected since IR determined Dq values are derived from a single precise determination, whereas the calorimetric determinations of 10Dq rely on a large number of separate experimental determinations.

Table 9

Comparison of Dq values (kcal/mole.) determined from UV-visible spectra (Dq_{uv}), lattice energies (Dq_H. Dq_{ha} = ref. 38, Dq_{hb} = corrected as in text.), infrared data (Dq_{ir}) and f and g values (Dq_{fg}).

Ion	Dq_{uv}	Dq_{ha}	Dq_{hb}	Dq_{ir}	Dq_{fg}
Sc(III)	-	-	-	-	-
Ti(III)	40·0	(270)[a]	(135)[a]	44·4	58·0
V(III)	51·5	100 0	47·0	47·8	50·6
Cr(III)	51·8	52·1	41·0	57·5	49·7
Mn(III)	48·6	25·8	10·5	36·0	60·0
Fe(III)	46·9	-	-	-	39·1
Co(III)	60·0	83·3	50·0	79·5	53·1

[a] data unreliable.

Comparisons of the Dq values obtained by all three methods for each of the acetylacetonate complexes with those determined spectroscopically for the corresponding hexaquo ions (i.e. the f and g values.) show two salient changes. Whereas in the hexaquo ions, 10Dq for Mn(III) is higher than that for any other ion, in the acetylacetonates it is lower than for any other ion, except Fe(III). Furthermore, for Co(III), 10Dq in the hexaquo ions is of the same order of magnitude as in the other ions, while in the acetylacetonates it is appreciably latger. The significance of these differences is possibly attributable to effects which are not taken into account in the CF model.

L. Transition metal complexes bonded to carbon

The only extensive series of metal complexes bonded/ to carbon (other than the zero-valent metal carbonyls) which are of comparable structure throughout the series are the hexacyano complexes. The IR spectra of these from 300 - 600 cm^{-1} in aqueous solution have been reported (4), and agree reasonably well with our own, recorded in the solid state as nujol mulls and KBr pellets. The frequencies of the absorption bands occurring in this region are seen in Table 10, as well as the $(C\equiv N)$str.

frequencies of the complexes. The spectra were recorded as the potassium salts, $K_3[M(CN)_6]$.

Table 10

Frequency data for the potassium hexacyano complexes of first transition period metals, and $-\delta H$ for these complexes as calculated from spctroscopic Dq values (19).

Complex	ν C≡N (cm^{-1})	ν M–C (cm^{-1})	δ M–C≡N (cm^{-1})	$-\delta H^a$
$K_3[Cr(CN)_6]$	2131	345	465	91·6
$K_3[Mn(CN)_6]$	2112	361	485	103·0
$K_3[Fe(CN)_6]$	2119	389	512	42·0
$K_3[Co(CN)_6]$	2131	413	566	139·7
$K_4[Fe(CN)_6]$	2044	416	583	132·2

[a] kcal/mole.

All ions in the series are low-spin so that, neglecting P for the moment, the order of M–C expected from CFT is that observed, namely Cr < Mn < Fe < Co. Dq values are reported for the ions Cr(III), Co(III) and Fe(II) (19), and may be estimated for Mn(III) and Fe(III) using an f value for 6 CN^- of 1·7 (19). The values of P for these ions were as calculated for the corresponding acetylacetonates using the available Racah parameters for their determination.

From these $-\delta$ H energies (Table 10), it appears that a cusp is predicted in the frequency trend at Fe(III) due to its large pairing energy (130 kcal/mole). νM-C for the Fe(III) complex does occur at lower frequency than would be expected by interpolation between the frequencies for Cr(III) and Co(III), but the drop is not as large as predicted by CFT. Further, contrary to the predictions of CFT, M-C in Fe(III) occurs at a substantially higher frequency than in Cr(III) and Mn(III), which is also not as would be expected, unless we suppose that the rise of E_r effects across the series is inordinately large.

The small drop in the M-L frequency trend at the d^5 configuration is in fact rather similar to that observed in the second period trivalent transition metal tris(acetylacetonates) (page 103). This therefore suggests that the apparent lowering of P indicated by the IR data for these complexes is better interpreted as an extra stabilisation of the M-L bond due to π-bonding, rather than a lowering of P.

As was mentioned earlier, Jones (4) has made a convincing interpretation of the integrated band intensities of $\nu(C{\equiv}N)$ for the different hexacyano complexes in terms of the ability of the metal to form π-bonds with the CN^- ions. νM-N increases in the order suggested by the amount of π-bonding estimated from the integrated band intensities for each of the complexes (viz. $Cr < Mn < Fe < Co$), rather than that predicted by CFT (viz. $Cr \sim Mn > Fe < Co$), suggesting that the π-bonding contribution to the stabilisation of metal-ligand bonds is of great importance here.

We see therefore that CFT provides a satisfactory approach to the problem of bonding in transition-metal complexes as evidenced by their IR spectra. It does, however, have shortcomings in dealing with complexes where π-bonding is thought to be strong, particularly those of low-spin ions (viz. Co(III), Ru(III) and Rh(III), as evidenced by their tris(acetylacetonate) complexes, and Mn(III) and Fe(III) in their hexacyano complexes.) It would therefore be of interest to examine the MOT and LFT approaches to this problem, since these approaches take the phenomenon of π-bonding into account.

It is worth mentioning in passing that, as previously found for the nitrogen-donor complexes, νC≡N does not show an inverse relationship with νM-C, but rather parallels its shifts, with the exception of the band in the Cr(III) complex, which is higher than that in the Mn(III) complex, showing that the principle of constant summation of bond-order, even about the C-atom, is not always applicable.

II. π-Bonding: The Ligand Field and Molecular Orbital Theories

CFT provides an interpretation of the thermodynamic stabilisation of TM complexes in terms of the splitting of the d-orbital shell. (Fig. 20a). The MOT approach, wherein molecular orbitals are formed by overlap of metal atomic and ligand molecular orbitals of suitable geometry, gives the same result. This is illustrated by the CFT and MOT approaches to the splitting of the d-shell in octahedral environments . In CFT, the energy of the e_g level is raised relative to that of the t_{2g} level because of the closer proximity of the ligands to, and hence greater electrostatic repulsion on, the electrons occupying the e_g level. This results in the greater stability of the orbitals of the t_{2g} level.

In MOT, the origin of the splitting also lies in the different spatial relationships between the orbitals of the t_{2g} and the e_g levels with those of the ligand. However, the difference in energy is attributed not to electrostatic effects, but rather to the σ-bonding characteristics of the e_g, and π-bonding characteristics of the t_{2g} level. We thus see that (Fig. 20) transitions from the t_{2g} level are to the antibonding e_g level, formed by overlap of the ligand σ-orbitals with the e_g orbitals of the metal.

It is observed that in the spectrochemical series, the order of increasing Dq associated with the different ligand types is for the different donor-atoms $F < O < N < C$, which in MOT has a ready explanation in terms of the covalency of the bond formed between the donor-atom and the metal. (Increasing covalency leads to greater raising of the antibonding and lowering of the bonding

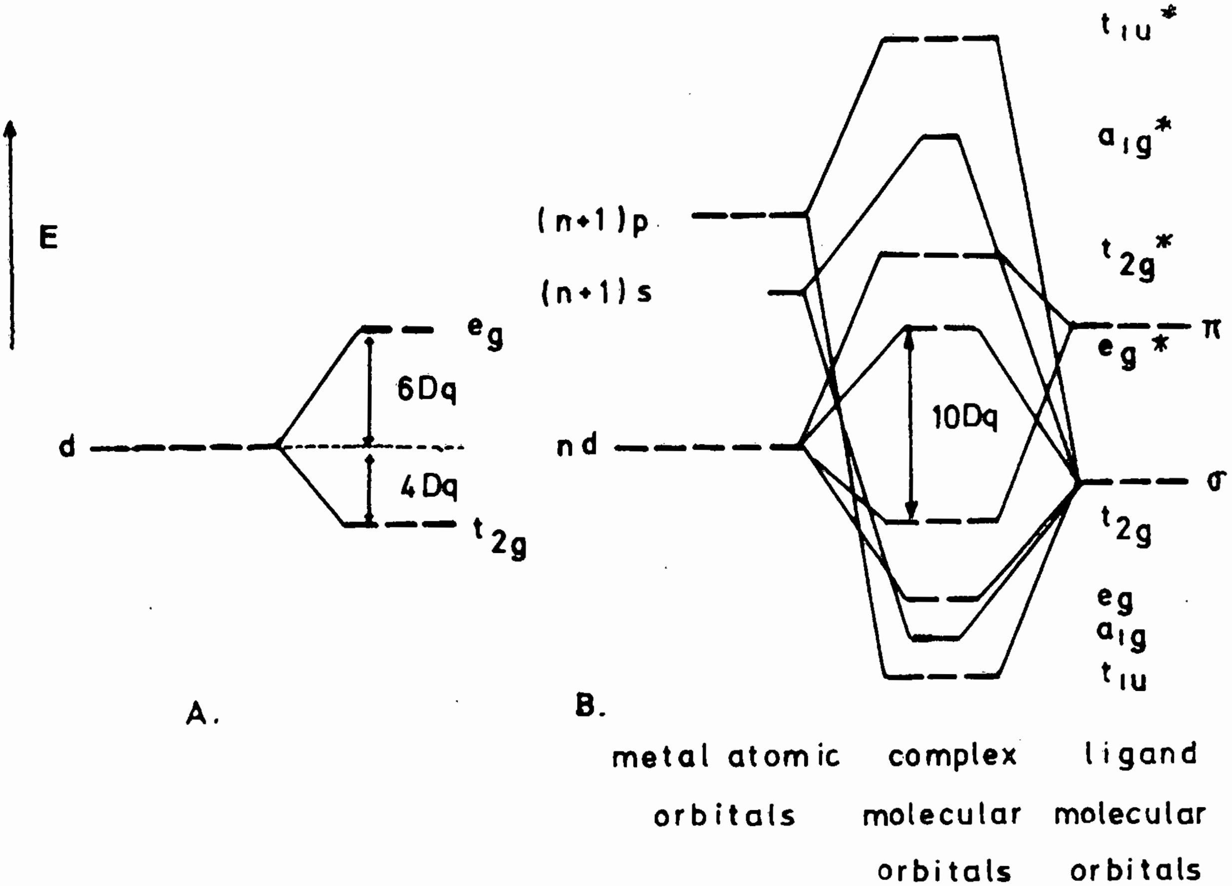


Fig. 20. Origin of the splitting of the d-shell in octahedral environment in (A) CFT (B) MOT.

levels in bond-formation.) The phenomenon of the stabilisation across transition metal series due to ionic contraction is also readily explained in the MOT view in that covalency increases across the series due to the increase of ionisation potentials.

The t_{2g} orbitals interact with ligand orbitals of suitable symmetry to form π-bonds. These are of two types. In ligands with electronically unoccupied orbitals, overlap may occur with electronically occupied metal t_{2g} orbitals, resulting in metal to ligand π-bonding ($M-\pi^*$), or electronically occupied ligand orbitals may overlap with electronically unoccupied metal t_{2g} orbitals, resulting in ligand to metal π-bonding ($\pi \rightarrow M$). Depending on the energies of the ligand orbitals relative to the t_{2g} level, two different effects on the value of 10Dq for the complex are observed. In complexes with π-orbitals of energy higher than the t_{2g} level, overlap causes an increase in 10Dq, while overlap with orbitals of lower energy causes a decrease in 10Dq. These two effects may be equated with $M-\pi^*$ and $\pi-M$ π-bonding respectively.

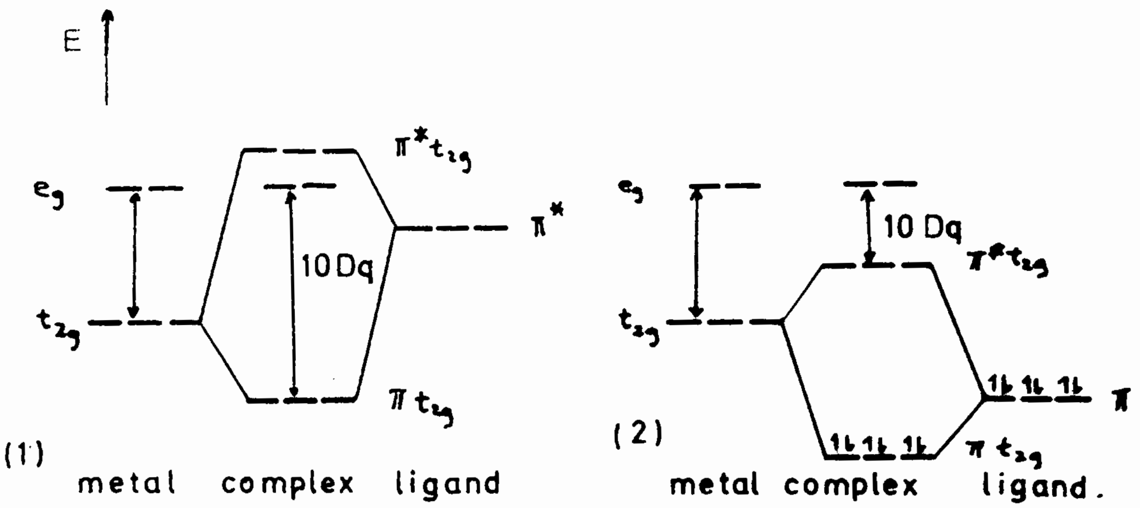
From this, it is seen that the simple CFT approach will give a fairly accurate measure of the stabilisation of the molecule as far as π-bonding goes if the degree of π-bonding is negligible, or does not vary much across the series. This erroneous picture presented by CFT possibly also accounts for the observation that thermodynamically determined 10Dq values are usually larger than those determined spectroscopically (10).

Since CFT is fairly satisfactory as far as giving an account of the σ-bonding aspects of the complex, the LFT has been developed, in which the general CFT approach is preserved, but allowance is made for π-bonding effects. LFT, because of its much greater simplicity, is much easier to apply than MOT, and so will be used in our discussion.

A. π-Bonding effects in the UV spectra of metal beta-diketonates, and their significance in the stabilisation of metal to ligand bonds

There is a fairly extensive literature at present on the UV-visible spectra of the acetylacetonates. Holm and Cotton (40) have reported the UV spectra of thirty metal acetylacetonates in solution, while Barnum (41) has reported the solution spectra of the acetylacetonates of the first transition period trivalent series and performed Hückel LCAO-MO calculations for these complexes (42). Solid state spectra have been reported for the series Ti(III) - Co(III), in which Dq values were obtained (11, 43, 44). A certain amount of work has also appeared on the effect of change of the 2- and 1,3- substituents (45,46) on the UV spectra of Cu(II) beta-diketonates, with particular reference to ligand π - π^* transitions.

The π-molecular orbital energy levels of the acetylacetonate ion are shown in Fig. 21. The energy of these is such that the electronically occupied π_3 and the antibonding π_4 levels are close enough energetically to the t_{2g} level of the metal ion for appreciable overlap to occur. In the spectra of all acetylacetonate complexes an intense band is observed at about 35,500 cm^{-1}. This has been assigned to the π_3-π_4^* transition of the acetylacetonate anion (40). At shorter wavelength (about 48,000 cm^{-1}), a second band may be observed, which has been assigned (46) to the π_3 - π_5^*



Effect of (1) M → π^*, and (2) π → M, π-bonding on 10 Dq.

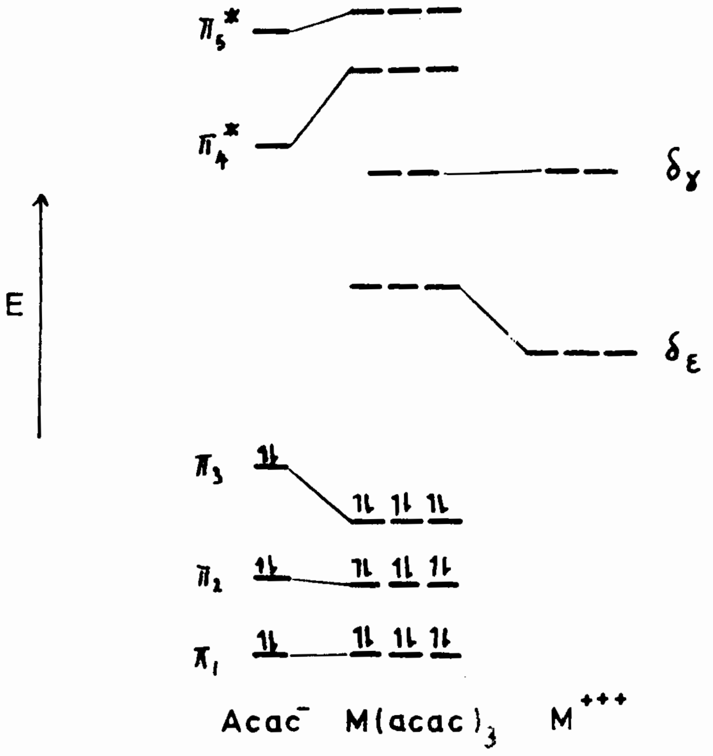


Fig. 21a

combination of Acac⁻ π-orbitals with those of M^{+++} to produce M(Acac)$_3$

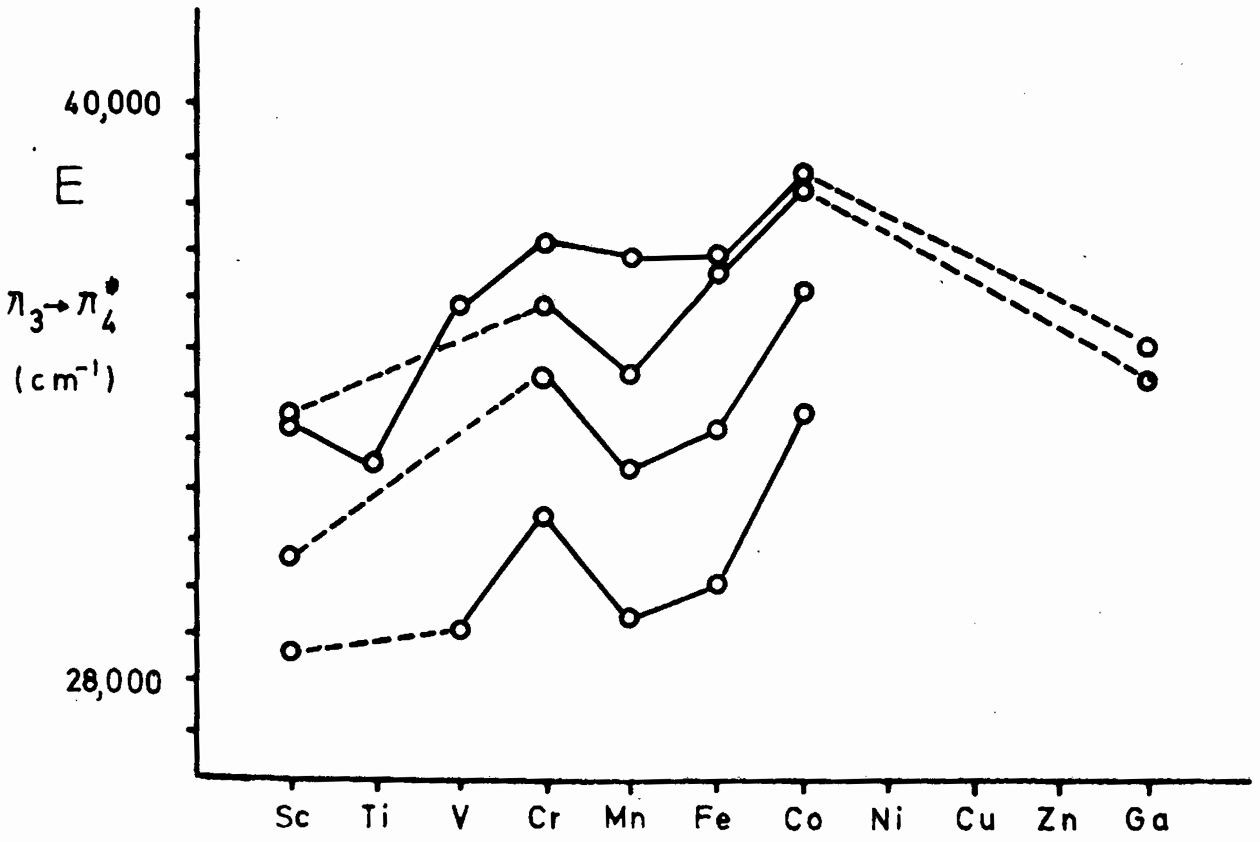


Fig. 21b. Variation of $\pi_3 - \pi_4^*$ with at.no. in M(III) β-diketonates.

transition.(46). In addition, in transition metals with electronically occupied t_{2g} levels only, an intense band at lower frequency than the $\pi_3 - \pi_4^*$ transition is found. This has been assigned to the $\delta_\varepsilon - \pi_4^*$ transition (41).

Barnum (42) has suggested that increasing π-bonding in these complexes will lead to increased $\pi_3 - \pi_4^*$ transition energies. As seen in the simplified MO diagram of Fig. 21 this is a very logical interpretation. It has been suggested, however, that increasing π-bonding will increase the resonance paths of the electrons in these orbitals, so that these bands should shift to longer wavelength on increase of π-bonding (40). Both of these interpretations suffer from various difficulties.

That the shifts observed in $\pi_3 - \pi_4^*$ are actually due to π-bonding is apparent from the fact that this band does not vary much from a mean position in non-transition metal acetylacetonates, whereas it is highly metal-sensitive in the transition metal complexes. This mean value of 35,500 cm^{-1} in non-transition will thus be taken as a guide to the value of the $\pi_3 - \pi_4^*$ transition in the absence of π-bonding. One difficulty id that Sc(III) has $\pi_3 - \pi_4^*$ at much longer wavelength than found in other non-transition metals, while that in Co(III) is at much shorter wavelength. If we suppose that the first interpretation is correct, it cannot account for the shift of Sc(III) to longer wavelength, while the second cannot account for the extremely high position of this band in Co(III).

However, the π-bonding effect is not the only factor governing the energy of the $\pi_3 - \pi_4^*$ transition. Belford, Martell and Calvin (47) have made a simple MO calculation which predicts a red shift for the $\pi_3 - \pi_4^*$ transition with increasing charge on the central cation. This offers a possible explanation for the position of $\pi_3 - \pi_4^*$ in Sc(III) acetylacetonate. Since Sc(III) is more electropositive than the other metals in the series, accounting for the lower $\pi_3 - \pi_4^*$ band frequency for Sc(III) acetylacetonate. The interpretation of Barnum thus seems to be correct, with the modification that higher electropositivity will cause a shift of $\pi_3 - \pi_4^*$ to longer wavelength. The latter seems to be a smaller effect on $\pi_3 - \pi_4^*$ than the effect of π-bonding. Therefore, for the purposes of a general discussion, the latter consideration only, will be taken into account.

The variation of $\pi_3 - \pi_4^*$ with at. no. across the first transition period trivalent acetylacetonate series is shown in Fig. 21, which also illustrates the variation of this band in 1,3- and 2- substituted beta-diketonates. The same general trends hold for all the beta-diketonate series studied. The salient feature of these plots is the extremely high position of this band in the Co(III) beta-diketonates, suggesting a high degree of π-bonding in this ion.

This is in good agreement that the fact that a simple CF approach predicts an M-O frequency lower than actually observed in Co(III) beta-diketonates. The extra stability is accounted for by π-bonding. For the acetylacetonates of the second period ions Ru(III) and Rh(III), and also the trifluoroacetylacetonate of Rh(III), $\pi_3 - \pi_4^*$ occurs at high frequencies, as found in the Co(III) complexes. In our IR study on second period complexes, although Racah parameters were not known for Ru(III) and Rh(III) (and also in our calculations of P for TcO) it was suggested that they would possibly not be lowered by the large fraction which the (M-O)str. implied. The position of $\pi_3 - \pi_4^*$ supports the idea that the high M-L str.'s observed in these molecules are due ~~due~~ to the extra stabilisation of π-bonding, rather than a lowering of the pairing energy. (We may of course interpret this as π-bonding lowering the pairing energy, since the electrons are partly transferred to ligand orbitals.)

In addition, π-bonding in low-spin Co(III) complexes between the t_{2g} and the ligand π-orbitals can only be of the M-π^* type. Since this leads to increased 10Dq, this accounts for the change in relative magnitude of 10Dq in $[Co(H_2O)_6]^{+++}$ in the hexaquo series as compared with $[Co(Acac)_3]$ in the acetylacetonate series. In $[Co(H_2O)_6]^{+++}$, where no M-π^* bonding is possible, 10Dq is not significantly larger than that of other ions in the series. In $[Co(Acac)_3]$, where a considerable degree of M-π^* bonding occurs, 10Dq is much larger than that of other ions in the series. (see Table 9.)

Another important feature of the plot of π_3- π_4^* against at. no. is the low position of the Mn(III) point in all of the beta-diketonate complexes. Since Mn(III) is less electropositive than the other ions in the series, this cannot, therefore, as in the case of Sc(III), be an effect of increased charge on the central cations. It must therefore be taken to indicate only a very small amount of π-bonding. This agrees with the observation that 10Dq for $[Mn(H_2O)_6]^{+++}$ is larger than that for any other ion in the series, while in the acetylacetonate series 10Dq for $Mn(Acac)_3$ is smaller than that of all other ions in the series, with the exception of Fe(III). The change of 10Dq of the Mn(III) complexes relative to those of other ions in passing from the hexaquo to the acetylacetonate series is thus explicable in terms of the poor π-bonding ability of the Mn(III) ion in both of these environments. In the hexaquo environment, where L-M π-bonding only is possible, 10Dq for the Mn(III) ion is larger than for any other ion because L-M π-bonding is weak for $[Mn(H_2O)_6]^{+++}$. (L-M π-bonding lowers the energy of 10Dq) On the other hand, in the acetylacetonate environment, M-π^* π-bonding is weak in the Mn(III) complex, resulting in a lower 10Dq value.

From the relatively low position of $\pi_3 - \pi_4^*$ in Fe(III) beta-diketonates, it might be supposed that π-bonding in its complexes was weak. However, this need not necessarily be so, since Fe(III) is fairly electropositive. The low position may thus be due to the latter effect, as is also likely with Ti(III) and V(III).

The energy of $\pi_3 - \pi_4^*$ has been found (46) to vary with changing of the 1,3- substituents in Cu(II) beta-diketonates. A red shift is observed on substitution with more electron withdrawing substituents, suggesting that in these π-bonding is weakened by electron withdrawal. The slopes of $\pi_3 - \pi_4^*$ versus IP of the 1,3-substituents of the ligand are seen to fall into two series, depending on the nature of the substituent. The first series is that in which successive substituents are phenyl groups, and the second is the series of non-aromatic substituents. The slope of this plot is much steeper for the aromatic substituents, $Acac^- > Bzac^- > DBM^-$, than for the non-aromatic substituents $Acac^- > TFA^- > HFA^-$. This is presumably related to the increase of the resonance path of the electrons in phenyl substituted forms, and need not necessarily indicate weakened π-bonding. It is even possible that the opposite is true, that phenyl substitution enhances π-bonding

In both series changes of slope are observed, which are qualitatively the same in both series, on

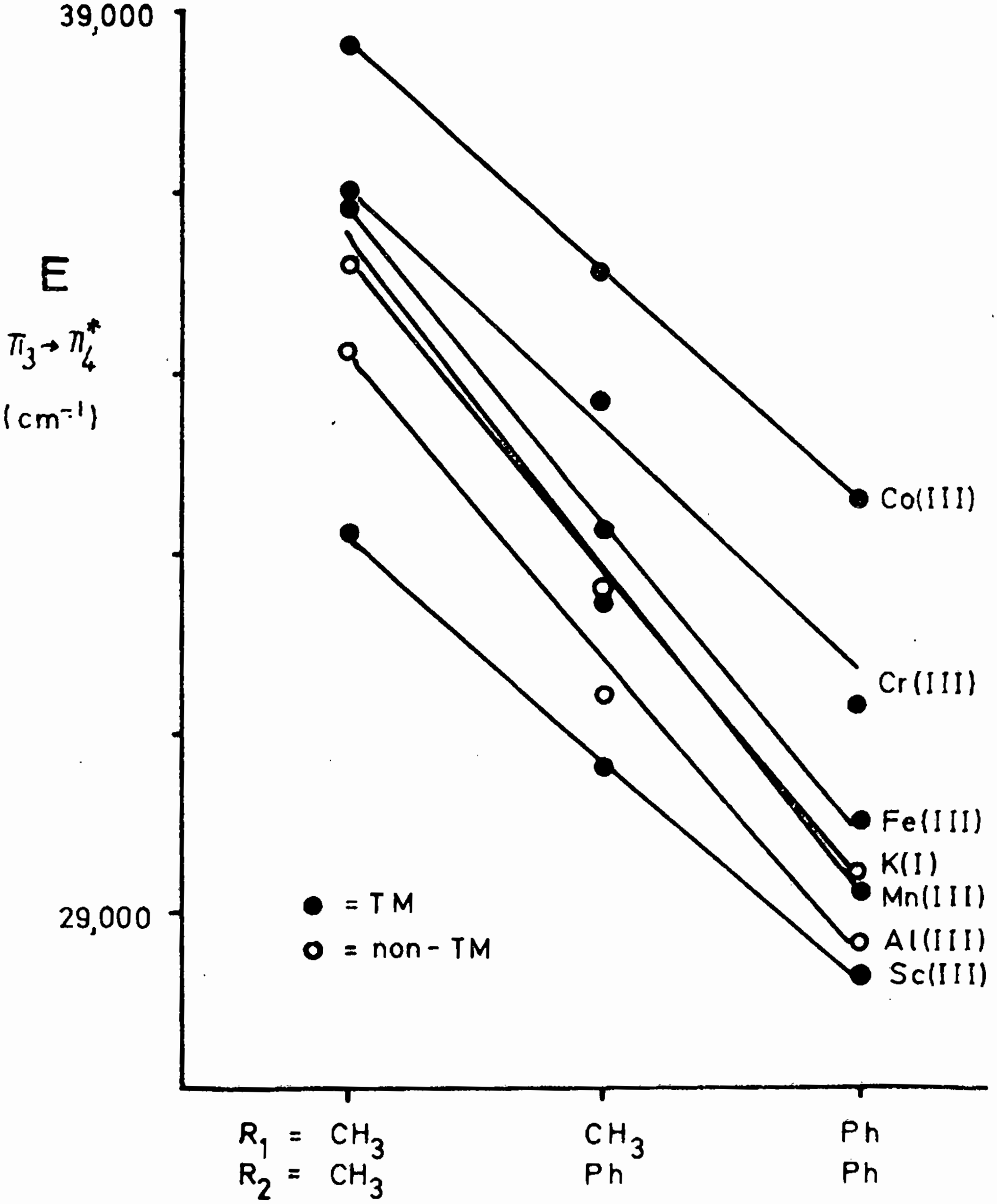


Fig. 22. Variation of $\pi_3 - \pi_4^*$ on change of 1,3-substituent.

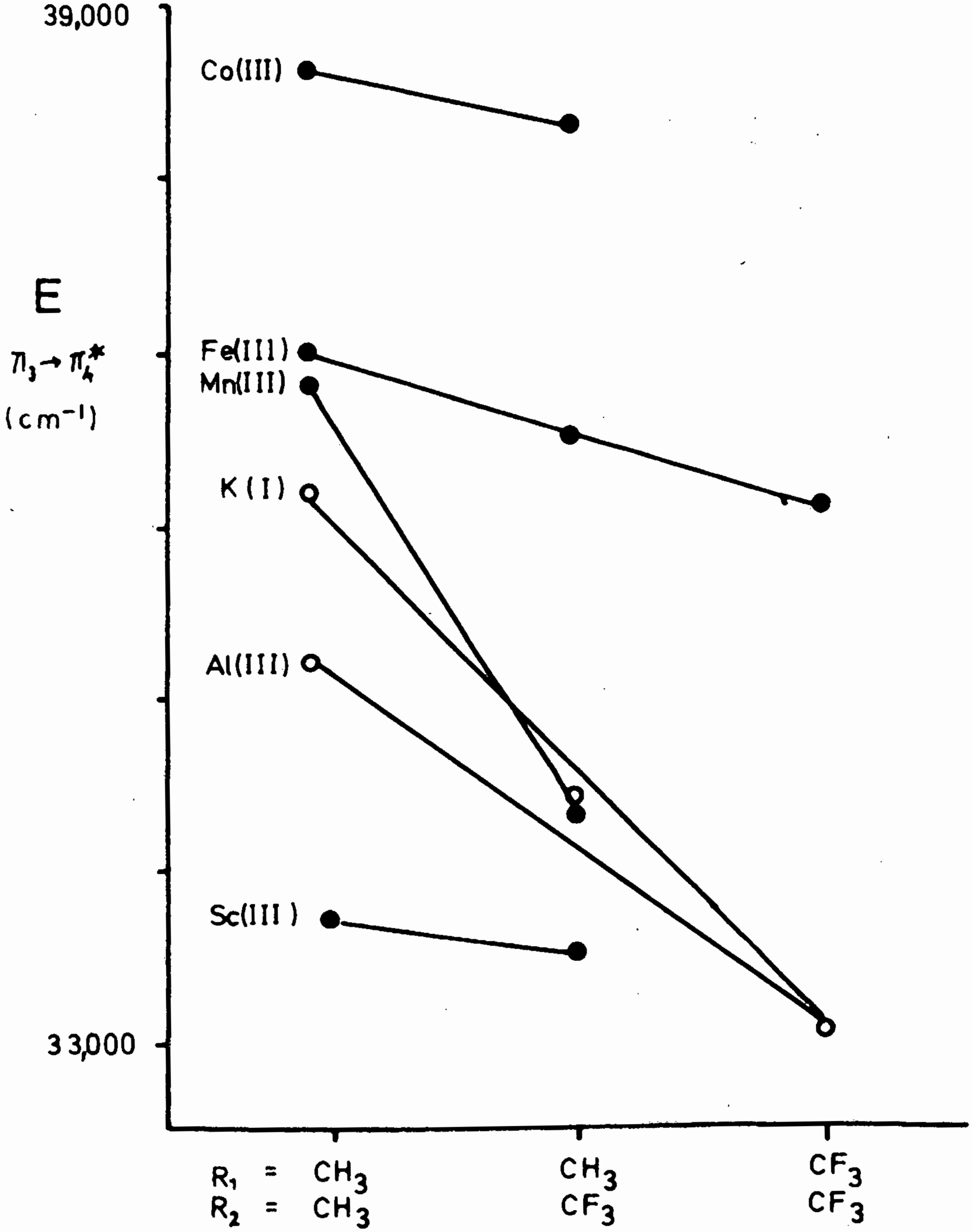


Fig. 22b. Variation of $\pi_3 \rightarrow \pi_4^*$ on change of 1,3-substituent.

change of one particular cation for another. Since comparable changes of slope occur in both series on change of cation, either may be used for the purposes of discussing this effect. The UV spectra of the complexes of Acac$^-$, DPM$^-$, DBM$^-$, Bzac$^-$, TFA$^-$ and HFA$^-$ with the cations K$^+$, Cu^{++}, Al^{+++}, V^{+++} and Fe^{+++}, as well as all of these except the HFA$^-$ complex for the ions Sc^{+++}, Cr^{+++}, Mn^{+++} and Co^{+++} were recorded. The series of substituted beta-diketonates of K$^+$ and Al^{+++} were included so as to obtain a measure of the value of $\pi_3 - \pi_4^*$ for each ligand type in the absence of any possible π-bonding effects. The small difference between the plots for K$^+$ and Al^{+++} was taken as being due to the increased cationic charge of Al^{+++} relative to K$^+$, as expected from the work of Belford et. al. (47).

As previously mentioned, the decrease in energy of $\pi_3 - \pi_4^*$ on increasing electron withdrawal by the 1,3-substituents need not necessarily indicate a decrease in the amount of π-bonding. Thus, we may regard the slopes of the plots ~~of~~ for K$^+$ and Al^{+++} as $\pi_3 - \pi_4^*$ in the absence of π-bonding effects. Any change in slope (the slopes of the K$^+$ and Al^{+++} series are the same) from the slopes of the latter two ions observed in the series of substituted beta-diketonates of other ions must therefore be regarded as being due to π-bonding effects. Thus a less steep slope on increasing electron withdrawal could be taken as evidence of enhanced π-bonding due to electron-withdrawal by the 1,3- substituents. Similarly, a steeper slope could be regarded as evidence of destabilisation by electron withdrawing substituents. The same observation could also be interpreted as the reverse, i.e. stabilisation by electron-donation.

In Fig. 22 are seen the plots of $\pi_3 - \pi_4^*$ versus the electronegativity of the substituents at the 1,3- positions, for the aromatic and non-aromatic series with the previously mentioned cations. The salient feature of these plots is the small slope of that for the Co(III) ion. This is, as seen from the above discussion, in good agreement with our suggestion that the Co(III) ion is able to undergo considerable $M \rightarrow \pi^*$ π-bonding with beta-diketonate ligands. The Cr(III) series have a slightly steeper slope than the Co(III) series, but are not nearly as steep as observed in the Al(III) and K^+ series, suggesting that in this ion a considerable amount of M-π^* π-bonding occurs. The slopes of the plots become steeper in other transition metals, and finally, in Mn(III), the slope is the same as observed in non-transition metal ions. This indicates that very little π-bonding occurs in this ion, which agrees with our earlier observations on the poor π-bonding ability of the Mn(III) ion, as evidenced by the low Dq values (as compared with Mn(III) in the hexaquo system) found for Mn(III) in the beta-diketonate system.

The spectra of the divalent acetylacetonates were also recorded, both for the type $[M(Acac)_2(H_2O)_2]$ and $[M(Acac)_3]^-$. The π_3- π_4^* transition in the spectra of the former type are at fairly long wavelengths, and so at best, only very weak π-bonding is expected in them. This is in agreement with the fact that CF predictions for the M-O frequencies in the IR spectra indicate no additional stabilisation which can be attributed to π-bonding. In the second type, slight shifts to shorter wavelengths are observed, which are probably associated with the increased delocalisation caused by the negative charge on the complex.

B. Evidence from NMR for π-bonding effects in transition metal beta-diketonates

The NMR spectrum of the acetylacetonate anion is very simple, and consists of a band at -331 c.p.s. from TMS. due to the ring proton, and one at -120 c.p.s. due to the methyl group protons. In diamagnetic forms, the position of these bands does not vary very much with change of metal ion, except for the acetylacetonates of Co(III), Rh(III), and Be(II), in which the methyl group protons shift downfield to about -130 c.p.s.. In the NMR spectra of TFA$^-$ and Bzac$^-$ complexes of Co(III) and Sc(III), and in the TFA complex of Rh(III), the same downfield shift of the band due to the methyl group protons is also observed, relative to the position of this band in the Al(III) complexes. The unique spectra of the Be(II), Sc(III), Co(III) and Rh(III) beta-diketonates thus suggest a difference in electron distribution in the ring, as compared with other metal beta-diketonates.

This difference is presumably due to the higher covalency found in the complexes of these ions, the higher covalency in the Be(II) complex being due to more covalent σ-bonding, and the higher covalency in the transition metal complexes being due to π-bonding. The latter observation is in complete agreement with the greater degree of π-bonding character predicted for the complexes of these ions by their UV and IR spectra. The frequency data for the diamagnetic beta-diketonates is as in Table 11 below.

Table 11

NMR of diamagnetic acetylacetonates,[a] benzoylacetonates, and trifluoroacetylacetonates. In $CDCl_3$, shifts in c.p.s. at 60 Mc.p.s. (shifts for CH_3 and ring protons only.)

Acac⁻	Zn(II)	Al(III)	Co(III)	Sc(III)	Rh(III)
CH_3	-120	-117	-133	-130	-128
H	-328	-327	-331	-330	-328
Bzac⁻	**Al(III)**	**Co(III)**	**TFA⁻**	**Al(III)**	**Rh(III)**
CH_3	-130	-144	CH_3	-137	-151
H	-372	-372	H	-355	-357

[a] Data on the diamagnetic acetylacetonates of Be(II), Zn(II), Al(III), Ga(III), In(III), Sc(III), Y(III), Zr(IV), Th(IV), and Co(III) are reported in ref. 40.

The NMR spectra of paramagnetic acetylacetonates have been studied in detail by Eaton (48), and the paramagnetic shifts recorded for the acetylacetonates of Ti(III), V(III), Cr(III), Mn(III), Fe(III), Mo(III), Ru(III), Mn(III), Fe(III) and Co(III). The observed large shifts of the $-CH_3$ and -H protons were explained in terms of the contact mechanism, in which electron spin is delocalised from the metal ion onto the ligands.

For metal to ligand charge transfer, a large positive spin-density is expected to result on the C-atom bearing the methyl group, resulting in large downfield shifts of these protons. For ligand to metal charge transfer, two differing effects may result. If ligand α-electrons (i.e. those having spins parallel to the inpaired d-orbital electrons of the metal ion) are transferred to the metal, a large downfield shift is expected. If ligand β-electrons (i.e. those of opposite spin to the d-orbital electrons) are transferred, an upfield shift of the ring proton is expected. The abrupt change from low downfield s ift to high upfield shift on passing from Mn(III) to Fe(III) is explained in terms of a crossover from α-electron donation to β-electron donation to the metal d-orbitals.

Apart from this feature, the increasing downfield paramagnetic shifts obtained for the CH_3 protons along the series indicated (48) a steady drop in $M \rightarrow \pi^*$ π-bonding with increasing at. no. from Ti(III) down to Fe(III). Unfortunately, the data on the shifts of the ring proton is not complete, but suggets strong $\pi \rightarrow M$ π-bonding for V(III) and Fe(III), with the π-bonding of the $\pi \rightarrow M$ type being very weak for Mn(III). The important feature of these results in the paramagnetic forms is the weak π-bonding indicated for Mn(III), and the strong π-bonding indicated for the Sc(III), Co(III) and Rh(III) diamagnetic forms, supporting our interpretations of the UV and IR spectra of these compounds.

3. The beta-diketonate IR spectrum

A. The region 2000 - 1350 cm^{-1}

As was previously mentioned, most earlier work on the IR spectra of these complexes has centred around the C=O str. and C=C str. vibrations. Further, the assignment of the highest frequency band below 2000 cm^{-1} in the IR spectra of acetylacetonates to the C=O str. and the second highest to the C=C str. by Nakamoto (53) and the confirmation of his assignment by Pinchas et. al. in their studies of the IR spectra of ^{18}O- substituted acetylacetonates was discussed (page 11).

In phenyl-substituted beta-diketonates (Bzac and DBM) another difficulty of band assignment has arisen. Some aromatic C-Cstr. vibrations are expected to occur in the region 1500 - 1600 cm^{-1}, making distinction between C-C str.(phenyl), C=Cstr. (ring) and C=O str. difficult. Nakamoto (55) performed pertubation calculations for the DBM complexes of Cu(II) and Ni(II), based on his previous NCT for Cu(II) acetylacetonate. He concluded that the first band below 1600 cm^{-1} in the DBM and in the Bzac complexes was the ring C=C str., and that the second was C=O str.

This result is not, however, consistent with our own findings (56). The C=O str. in the IR spectra of the series $M(Acac)_3$, M = Sc, Ti, V, Cr, Mn, Fe, Co, Ga, has been found to be fairly sensitive to change of metal. The variation of the C=O str. with at. no. across this series is seen in Fig. 23. The C=C str. exhibits an inverse relationship to the frequency trend observed for the C=O band. In the analogous phenyl-substituted series ($M(DBM)_3$, $M(Bzac)_3$, M = Sc, V, Cr, Mn, Fe, Co.) the first band below 1600 cm^{-1} (assigned to ring C=C str. by Nakamoto) is almost insensitive to change of metal, while the second (assigned to C=O str. by Nakamoto) and third (assigned to C=O str. + C-H bend) exhibit the degree of sensitivity to change of metal displayed by the C=O str. and C=C str. of the acetylacetonate series. Furthermore, the frequency trends in C=O str. and C=C str. of the acetylacetonate series on change of metal with increasing at. no. across the series are reproduced almost exactly by the second and third bands below 2000 cm^{-1} of the Bzac and DBM series (Fig. 23). It was therefore concluded that the correct assignments for these bands was that, in phenyl-substituted ligands, the highest band below 1600 cm^{-1} was the aromatic C–C str., while the second and third of these bands were the C=O str. and C=C str. respectively.

These assignments are consistent with other observations on the effect of phenyl conjugation on the spectra of ketonic compounds. Phenyl conjugation is found (58) to lower the C=O str. to lower wavenumber than found in aliphatic ketonic compounds. If the C=O str., as assigned by Nakamoto in DBM, is compared with that assigned by him to the C=O str. in the corresponding Acac complexes (57), it is found to be at higher wavenumber than the latter. (e.g. C=O str. in $Cr(DBM)_3$ = 1540 cm^{-1}, C=O str. in $Cr(Bzac)_3$ = 1555 cm^{-1}, C=O str. in $Cr(Acac)_3$ = 1524 cm^{-1}.) Using the ammended assignments however, the C=O str. in phenyl substituted forms now occur at much lower wavenumber than in corresponding aliphatic complexes. (e.g. the C=O str. in $Cr(DBM)_3$ = 1540 cm^{-1}, $Cr(Bzac)_3$ = 1555 cm^{-1}, $Cr(Acac)_3$ = 1574 cm^{-1}).

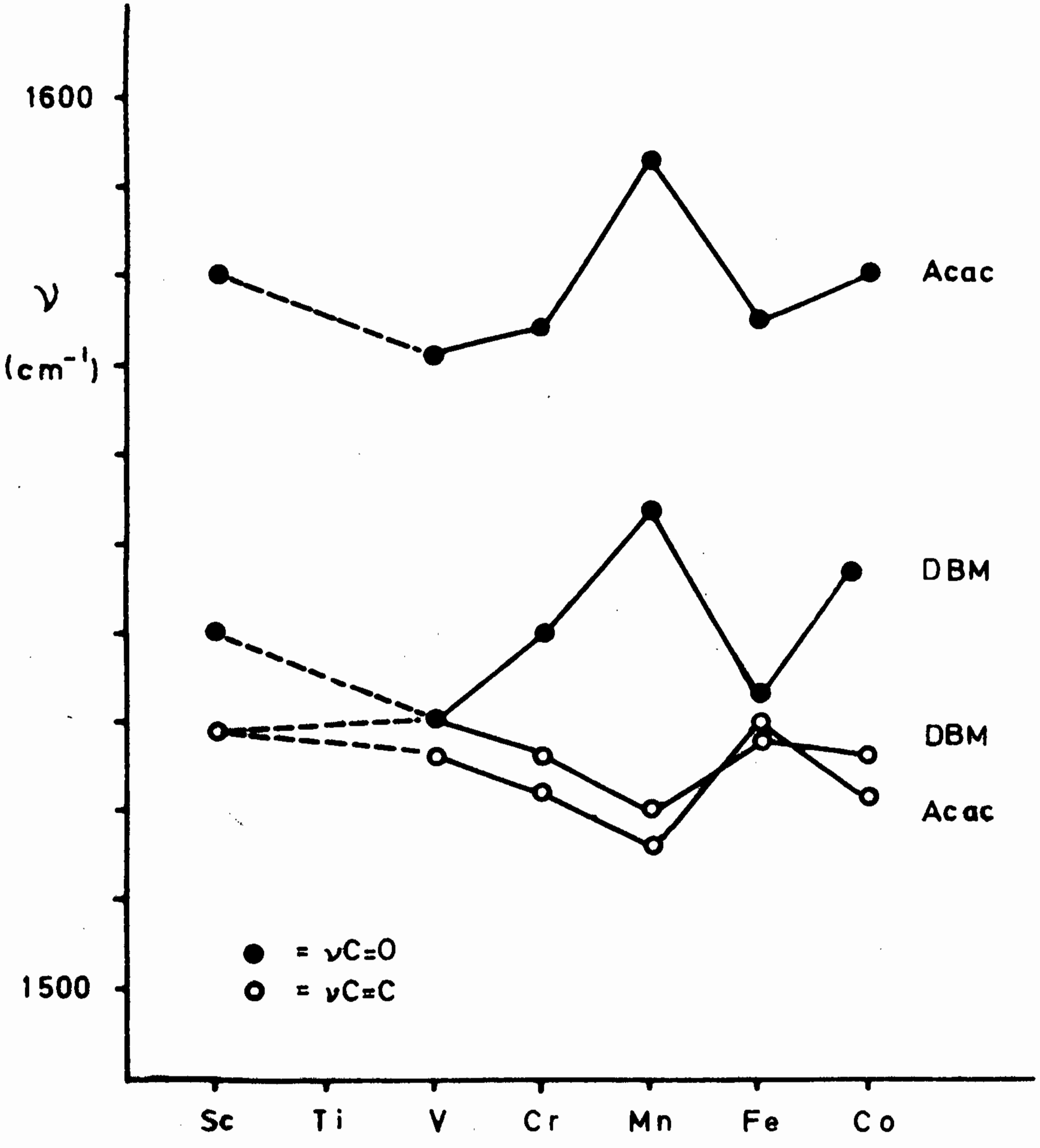


Fig. 23. Variation of νC=O and νC=C with at.no. in M(III) β-diketone complexes.

Further, in Bzac and DBM complexes, the first band occurs at 1591 ± 2 cm^{-1} in all transition metal complexes, whereas the second band in Bzac complexes (with one phenyl group on exch chelate ring) occurs at frequencies intermediate to that of the second band in DBM complexes (with two phenyl groups on each chelate ring), and the first band in Acac complexes (with no phenyl groups on the chelate ring). If we suppose the effects on the C=O str. of successive substitution of phenyl groups for methyl groups to be additive, as is found in substitution of trifluoromethyl groups for methyl groups (the C=O str. in $Fe(Acac)_3$ = 1575 cm^{-1}, in $Fe(TFA)_3$ = 1616 cm^{-1}, and in $Fe(HFA)_3$ = 1647 cm^{-1}), this assignment is more logical than the earlier assignment of Nakamoto, where the effect of successive substitution of phenyl groups is not additive.

In trifluoromethyl- substituted beta-diketonates (TFA and HFA) both C=O str. and C=C str. are raised to higher wavenumber on substitution of trifluoromethyl for methyl groups. The frequency trends in these across the series do not parallel those observed in the spectra of the analogous Acac complexes, and do not exhibit an an inverse relationship with each other. However, if we examine the effects on these of change of metal in non-transition metal series, it is seen that the trends parallel those in similar Acac series, so that we are able to assign the higher band to the C=O str. and the second band to the C=C str. in TFA and HFA complexes. (the difference observed between the trends in Acac, Bzac and DBM complexes on the one hand, and the trends of C=O str. and C=C str. in TFA complexes on the other hand, will be discussed in relation to the π-bonding properties of TM complexes at a later stage.)

B. The beta-diketonate IR spectrum 1350 - 800 cm^{-1}.

The assignment of bands in this region is substantially the same as given in the literature (55) for the IR spectra of the complexes of Acac, Bzac, DBM, TFA and HFA. (these are seen in Tables I - XX, pages 46 - 65.) A band of particular interest in terms of its metal sensitivity is that occurring in the region 1320 - 1230 cm^{-1} in the spectra of beta-diketonate complexes, which has been assigned as the coupled vibration C=C + C-R str. (where R = substituents at the 1,3- positions of the chelate ring). Its shifts parallel those of the C=C str. on change of metal but it is, however, more metal sensitive than the latter, and has thus been used extensively in interpreting the effects of change of metal.

It has been possible to check the assignment of bands to this vibration in differently substituted beta-diketonate complexes by the fact that the frequency trends on change of metal displayed by the band so assigned is the same for the series ML_3,(M = Sc, V, Cr, Mn, Fe, Co) irrespective of whether L = Acac, Bzac, DBM, DPM or TFA. In a similar fashion, we have been able to check that the bands assigned to C=O + C-R str. and C-H out-of-plane bend, in differently substituted complexes are correctly assigned.

C. The beta-diketonate IR spectrum 800 - 200 cm^{-1}

So far we have used band assignments of M-O str. in the IR spectra of the beta-diketonates, without discussing the reasons for the assignments themselves. The question of M-O band assignments in the spectra of the beta-diketonates has no bearing on the question of the validity of the CFT interpretation of IR frequency trends on change of metal across series of TM complexes, since all reasonably metal-sensitive vibrations below 800 cm^{-1} in these series exhibit at least reasonable qualitative agreement with CFT predictions. This is illustrated by the six metal-sensitive bands observed in the 800 - 300 cm^{-1} region of the spectrum of the first transition period trivalent acetylacetonates (Figs. 2, 3, 7, 24) which all exhibit frequency trends across the series which are consistent with the CFT interpretation.

It seems improbable that any one of the bands in the 800 - 200 cm^{-1} region of the beta-diketonate spectrum can alone be assigned to the pure M-O str. vibration. Firstly, any vibration will contain at least a fair percentage of ligand vibration coupled to it, and secondly, the complexity of the M-O octahedra, tetrahedra, *etc.* is such that M-O vibrations of different symmetries are expected to occur. (*e.g.* in octahedral tris(acetylacetonates, three infrared-active M-O str. vibrations are expected to occur (52), one belonging to the A_2 species, and two belonging to the E species.)

Three bands only are observed in this region in the spectrum of $K(Acac)(H_2O)_2$, at 655, 522 and 412 cm^{-1}. In octahedrally coordinated acetylacetonates, two groups of bands are observed which, from the ranges over which their frequencies vary on change of metal, (520 -700 and 410 - 520 cm^{-1}) appear to be derived from the bands occurring at 522 and 412 cm^{-1} in potassium acetylacetonate.

The 655 cm^{-1} band of potassium acetylacetonate (assigned by Nakamoto (55) to M-O + $C-CH_3$ str.) is one of the most insensitive to change of metal in the whole acetylacetonate spectrum, and occurs in the range 654 - 663 cm^{-1} (in most cases it occurs at, or close to 655 cm^{-1}) in the spectra of all sixty-nine of the different acetylacetonate complexes examined (including polymeric forms, hydrates, amine and pyridine adducts, and mixed complexes such as $[Pb(CH_3)_2(Acac)_2]$). In the ^{18}O- studies of Pinchas _et.al._ (54) this band was also found to be insensitive to increase in mass of the oxygen atoms of the chelate ring, and was thus assigned to the out-of-plane ring deformation vibration. We have thus adopted this assignment, since it is consistent with the insensitivity of the band to change of metal.

The number of bands in the two groups corresponding to the 412 and 520 cm^{-1} bands of potassium acetylacetonate is characteristic of the metal. In beta-diketonates of octahedrally coordinated (symmetry = D_3) trivalent metals of the first transition period, there are three metal sensitive bands in both the 500 - 700 cm^{-1} region (corresponding to the 520 band of potassium acetylacetonate) and 410 - 520 cm^{-1} (corresponding to the 412 cm^{-1} band of potassium acetylacetonate) region of the spectrum, irrespective of the nature of the 1,3- or 2- substituents.

Further, in complexes of C_{2v} and D_{2h} symmetry, for example, the number of bands in each of these regions is lowered in many cases. (e.g. in $Cu(Acac)_2$, $Pd(Acac)_2$ and $Pt(Acac)_2$ one of the bands in the 500 - 700 cm^{-1} region is lost, while in $Ca(Acac)_2$, $Sr(Acac)_2$, $Ba(Acac)_2$, two bands in both the upper and lower region are lost.)

The phenomenon of reduction in the number of bands does not, however, seem to be related to change of symmetry so much as to the covalence of the M-O bond. In group IA and 2A acetylacetonates, for example, three bands (corresponding to those observed in octahedral complexes) are observed in the upper group 500 - 700 cm^{-1} in the spectra of the Li, Be and Mg complexes. In members of higher atomic number in the series, however, there is a lowering of intensity and eventual complete disappearance (at K^+ in group IA, and Sr^{++} in group IIA) of the two bands of higher frequency in the 500 - 700 cm^{-1} group of bands. This reduction of the number of bands with increasing at. no. is accompanied by an increase in ionic character of the M-O bond, so that it is possibly related to this phenomenon. It might also be supposed that this was an effect of increasing mass with increase of at. no. The increasing mass of the central cation on descending a non-TM group should cause a lowering of the M-O str. frequency, and hence a lowering in frequency and convergence of the higher with the lower vibrations. That this is not so, however, is illustrated by the fact that in the corresponding TFA and HFA series, it is the lower frequency band in each group which disappears with increasing at. no., which is contrary to the expectations of the effects of increasing mass of the central cation.

Further, in the spectra of the octahedrally coordinated $K[M(Acac)_3]$ complexes of first transition period M(II) ions, a reduction in the number of bands in the 500 - 700 cm^{-1} region occurs, in spite of the fact that there is no change in the mass of the central cation compared with their trivalent $M(Acac)_3$ counterparts. Moreover, although the number of bands in this region is reduced in the octahedrally coordinated trivalent rare-earth tris(acetylacetonates), it is not reduced in complexes such as $UO_2(Acac)_2$, $MoO_2(Acac)_2$ or $Th(Acac)_4$, where the high oxidation state of the central cation leads to greater polarising power, and hence greater covalency, even though the masses of the central cations are large.

Nakamoto, in his NCT of $Cu(Acac)_2$ (51), and of $Al(Acac)_3$, $Fe(Acac)_3$, $Cr(Acac)_3$ and $Co(Acac)_3$ (57), assigned the bands at 455, 495, 437, and 466 cm^{-1} respectively in these complexes to a nearly pure M–O str. The bands of the upper group were either assigned to a coupled M–O str. + ring def. vibration, or else were not assigned at all (the lower two bands, in the range 520 – 675 cm^{-1}.))

As was mentioned earlier, ^{18}O isotope studies (54) indicated that the bands at 595 and 570 cm^{-1} in the spectra of $Cr(Acac)_3$ and $Mn(Acac)_3$ respectively had more M–O character than those at 462 cm^{-1} in these complexes (assigned by Nakamoto (51, 57) to M–O str.). This agreed with the greater sensitivity of the 520 – 650 cm^{-1} bands to change of metal, so that this assignment was adopted for the purposes of our CFT study.

We shall in future refer to the three metal-sensitive bands in the 500 - 700 cm^{-1} region as bands 1, 2 and 3, in order of decreaing frequency. The bands in the region 300 - 500 cm^{-1} will be referred to as bands 4, 5 and 6, in order of decreasing frequency. This corresponds with the labelling of bands in the 200 - 700 cm^{-1} region of the spectra of beta-diketonate complexes reproduced in this study.

It does not seem that the corresponding bands in this sequence of six all have the same assignments for all the differently substituted beta-diketonates. The phenomenon of disappearance of bands in the 300 - 700 cm^{-1} region on change of metal from covalently to ionically bound types is encountered generally with all the differently substituted beta-diketonates. However, it is not always the same band in the series of six which remains in the potassium complex, suggesting that the assignments for bands which correspond in position in the sequence is different with different beta-diketonates.

Thus, while in Acac complexes, it is band 3 which persists in the potassium complex, in TFA complexes it is band 2, and in HFA complexes it is band 1 which remains. In phenyl-substituted ligands, the picture is confused by the occurrence of several ligand vibrations in the 500 - 700 cm^{-1} region, but it would appear that band 2 persists in potassium benzoylacetonate, and band 1 in potassium dibenzoylmethanate. In all cases, band 4 persists in the potassium salt. (Fig. 25)

The nature of the two bands which remain (one corresponding to bands 1,2 and 3, and one corresponding to band 4, of octahedral complexes) in the spectra of the potassium complexes is uncertain. A clue as to their nature may be found in the fact that they exhibit an inverse relationship with each other on change of 1,3- substituent. (Fig. 26) This is consistent with the assignment of Pinchas et.al. of the higher bands to M-O str. + ring def., and band 4 to M-O + C-R str.. The ring def. vibration may be thought of as a C=O + C=C deformation vibration, and since C=O and C=C increase simultaneously on change of 1,3- substituent, we should expect the order of increase of the C=O str. and C=C str. to be the same as the order of increase of the ring def. vibration. We thus find that for both the

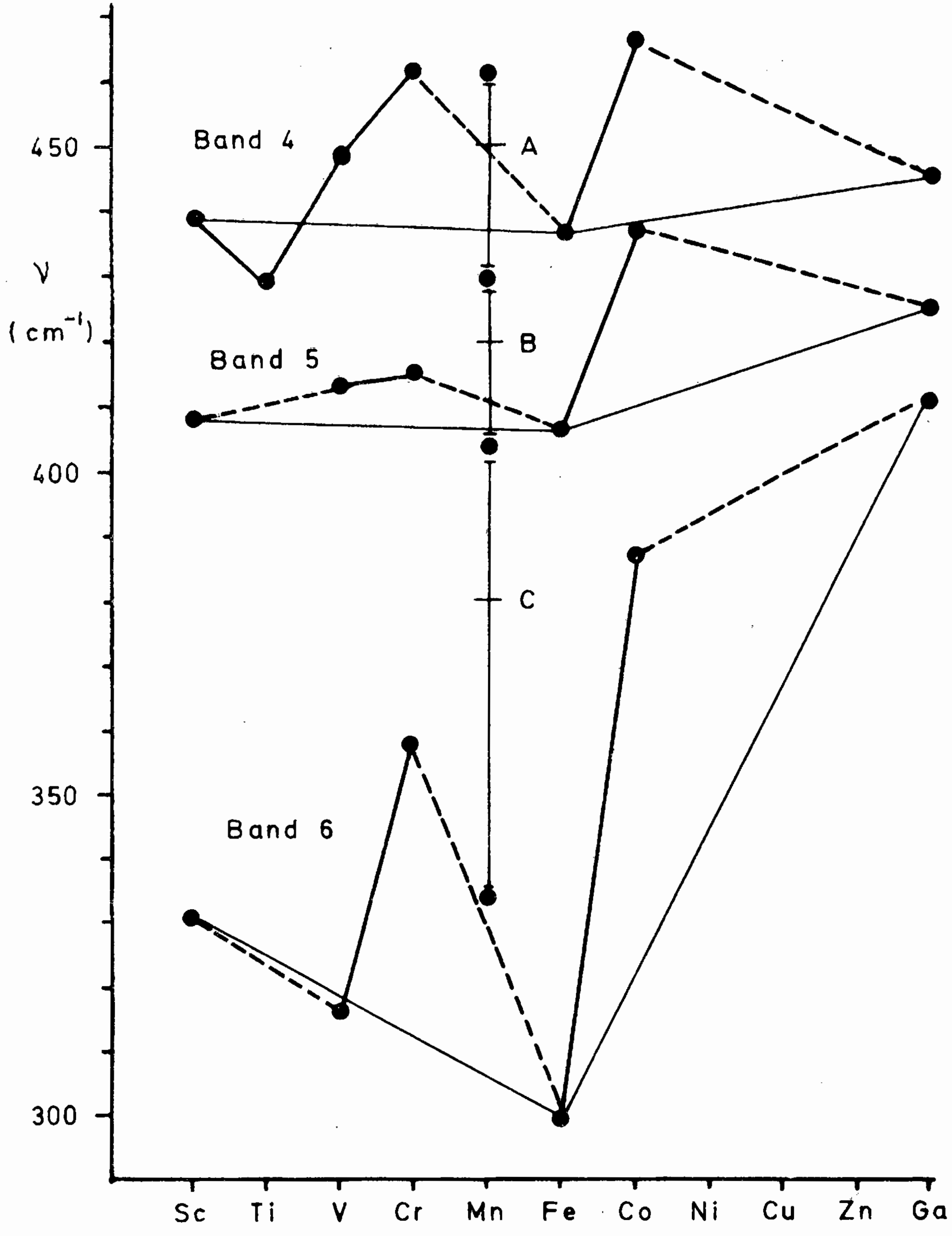


Fig. 24. Variation of bands 4,5 and 6 with at.no. in first transition period $M(Acac)_3$ complexes

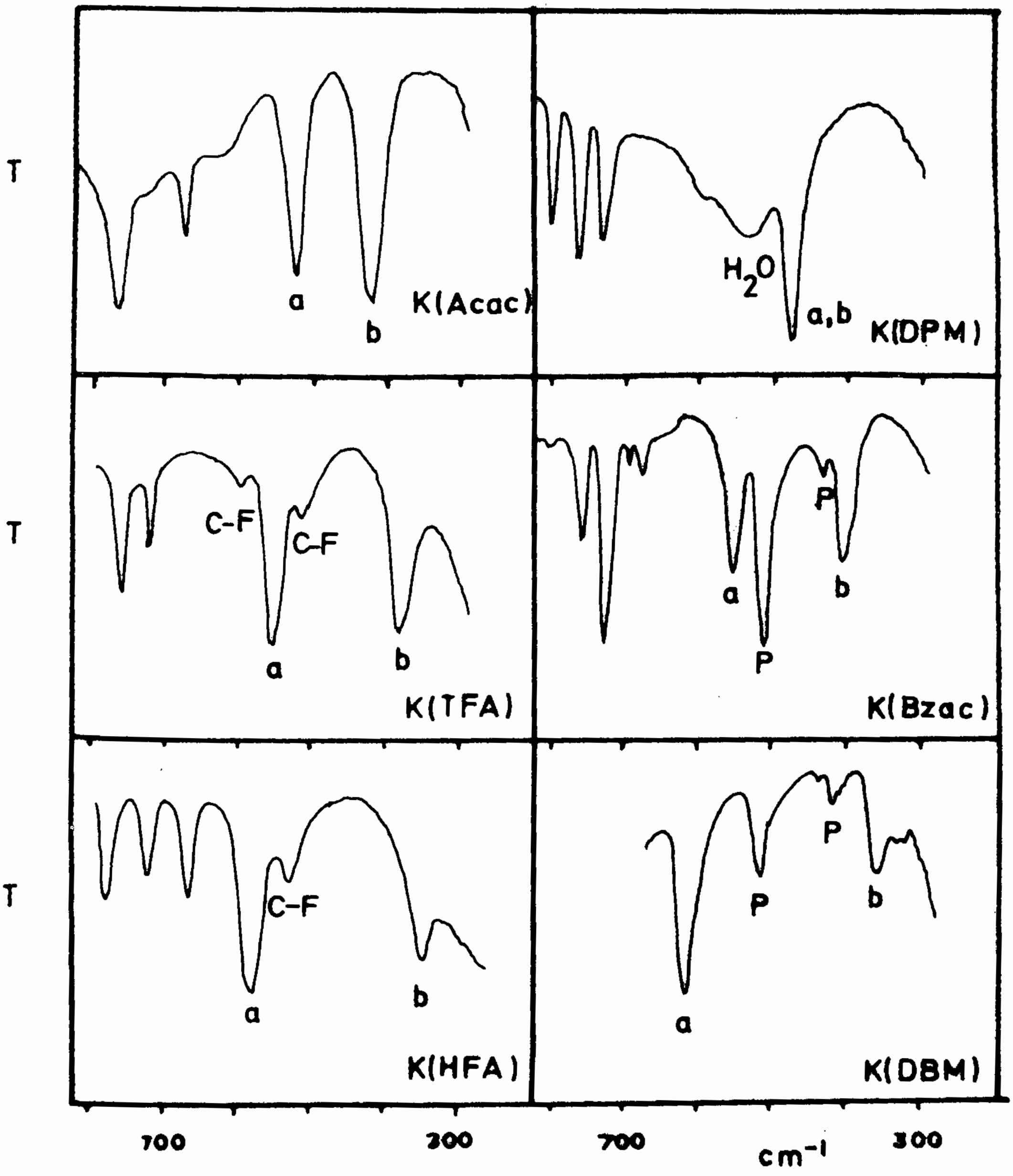


Fig. 25. IR spectra 200-800 cm^{-1} of K$^+$ β-diketonates.

(a = (νM O + ring det.), b = ν(M-O + C-R), P = phenyl.)

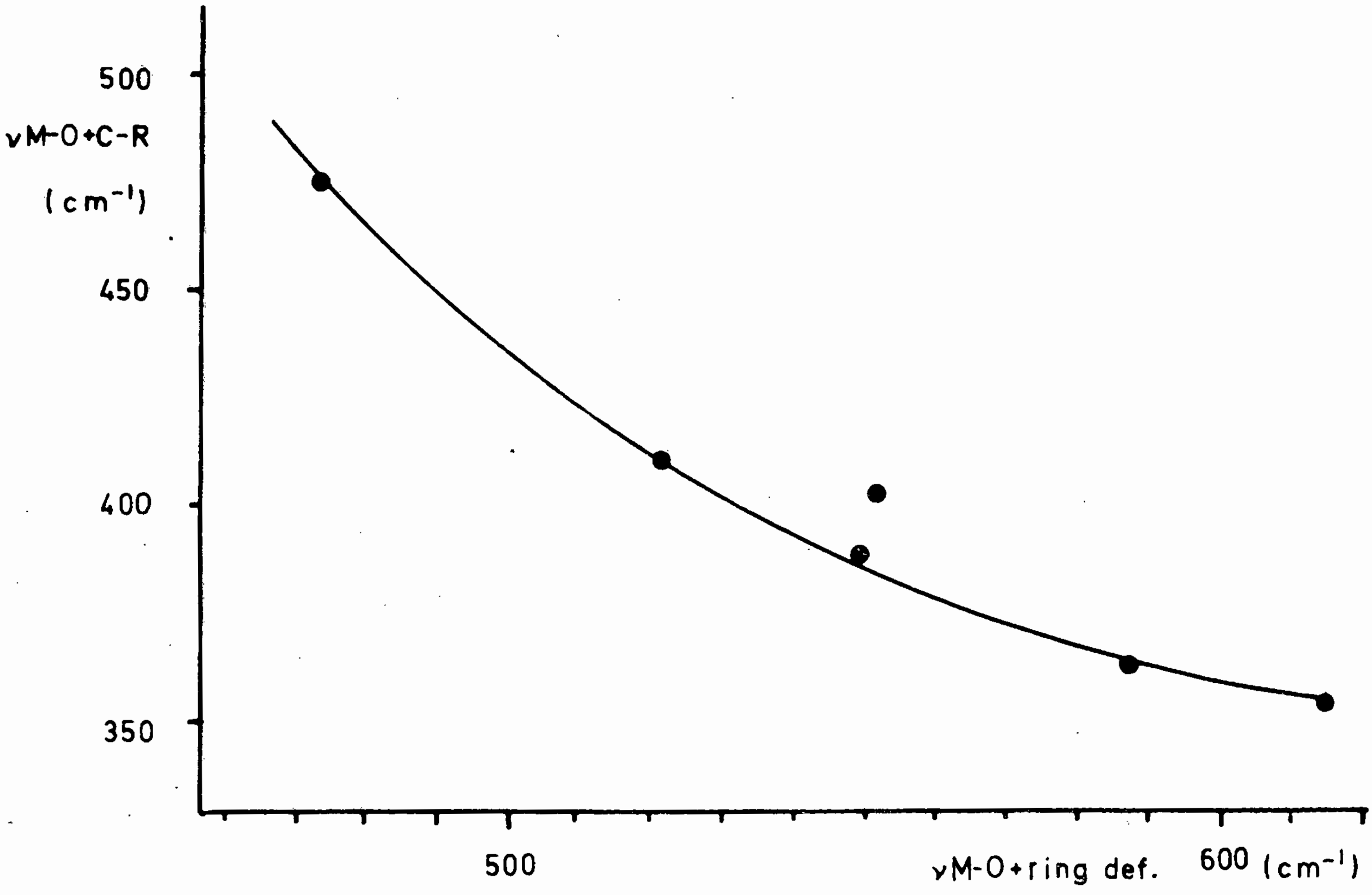
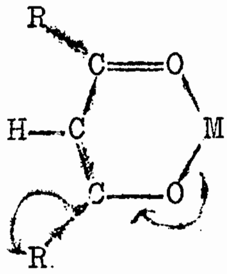


Fig. 26. Variation of νM-O + C-R with νM-O + ring def. for K^+ β-diketonates.

C=O str. and C=C str., and the ring def. vibrations, (i.e. the band observed in the 500 - 700 cm^{-1} region of the spectrum of the potassium salt) the order of increase in frequency is DPM< Acac< TFA<HFA. (The phenyl substituted ligands do not follow this trend, as will be discussed in the section on substituent effects.)

On the other hand, the order of increase of the frequency of the C-R str. vibration should be the reverse of the order of increase of the C=O str. vibration, if we suppose that electron shifts occur as follows on change of 1,3- substituent



which would account for the inverse relationship exhibited by the M-O + ring def. (since ring def. = C=O def. + C=C def.) with the M-O + C-CH_3 str. (since C-CH_3 exhibits an inverse relationship with C=O str.)

This may be summarised in the form of a Table:

Compound	C=O str. (cm^{-1})	M-O str + ring def. (cm^{-1})	M-O str. + C-R str. (cm^{-1})	C-R str.
K(HFA)	1677	580	364	should
K(TFA)	1661	550	387	decrease
K(Acac)	1619	522	412	as C=O str.
K(DPM)	1581	474	474	increases

These frequency shifts thus support the assignments of Pinchas <u>et.al.</u>(54) of band 4 to M-O + C-R str., and the higher bands to M-O str. + ring def..

A further point of interest is that the relative metal-sensitivity of bands 1,2 and 3 alters on change of 1,3- substituent. Thus, for example, in Bzac complexes, it is band 2 which exhibits the greatest sensitivity to change of metal, while in DBM it is band 1, and in TFA complexes it is band 3. This is illustrated in Table 12 below, in which the sensitivity to change of metal of any particular band is represented by the range over which it varies in the first transition period trivalent beta-diketonate in question.

The first point which is noticed about Table 12 is that the frequency range of the band of greatest metal-sensitivity in the spectra of each differently substituted beta-diketonate series rises in the order TFA < Acac ~ 3-MeA ~ 3-EtA < Bzac < DBM ~ DPM. This may be interpreted as a raising of the M-O str. frequency, and hence the occurrence of the band containing the most M-O character in the spectra of the complexes of each ligand type at successively higher frequencies.

The second point which may be raised is that in band 4 (M-O + C-R str.), the range of variation of frequency on change of 1,3- substituent is virtually the same in all cases, so that it is possible that in this band, which contains less M-O str. character (as indicated by ^{18}O studies (54), and its low metal-sensitivity) the amount of M-O str. character is the same for all the differently substituted beta-diketonates.

Further, band 4 increases in frequency in the order HFA < TFA < Acac < Bzac < DBM < DPM, which is the order of increase of M-O str. indicated by the shifts in greatest metal sensitivity from band 1 to 2, and from 2 to 3. This is as would be expected from the fact that

Table 12

Range (in cm^{-1}) over which bands 1, 2, 3 and 4 vary on change of metal in the differently substituted beta-diketonate series of complexes with first transition period trivalent metal ions.

Complexes	Range of variation (cm^{-1}) Band 1	Band 2	Band 3	Band 4
M(TFA)$_3$	47[a]	24	50[b]	19
M(Acac)$_3$	30	110	95	27
M(3-MeA)$_3$[c]	8	62	67	22
M(3-EtA)$_3$[c]	11	67	54	24
M(Bzac)$_3$	10	106	22	33
M(DBM)$_3$	43	36	15	36
M(DPM)$_3$	44	16	-	29

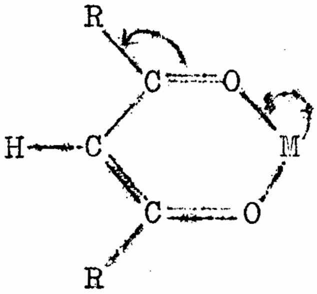
[a] This range is unrepresentative of the sensitivity of this band to change of metal, since the Co(III) complex, for which M-O str. is the highest in each range, had an exceptionally high frequency. Neglecting the frequency for the Co(III) complex, the order of metal sensitivity indicated for TFA complexes by the variations of these bands is seen in the ranges over which they vary in the remaining complexes; Band 1 = 16 cm^{-1}, Band 2 = 18 cm^{-1}, Band 3 = 38 cm^{-1}.

[b] Underlined ranges indicate the most metal- sensitive band, or bands, in the spectra of each of the series of differently substituted beta-diketonates.

[c] These ranges are unrepresentatively small, since the points for the Co(III) complexes are unknown.

the M-O str. remains coupled to band 4 throughout all the series of 1,3- substituted ligands, instead of there being an increase of M-O character in successively higher bands, as in bands 1,2 and 3, on increase of the M-O str. frequency.

The extent to which band 4 reflects the electron shift (band 4 = M-O + C-R str.)



on change of substituent is seen in Fig. 27, in which the C=O str. is seen to exhibit an inverse relationship with band 4 on change of 1,3-substituent in series of beta-diketonate complexes with any one metal. The M-O str. (the most metal-sensitive of bands 1,2 or 3 for any particular beta-diketone ligand) yields a similar inverse relationship. (Fig. 28).

In studying the effect of change of metal, it is

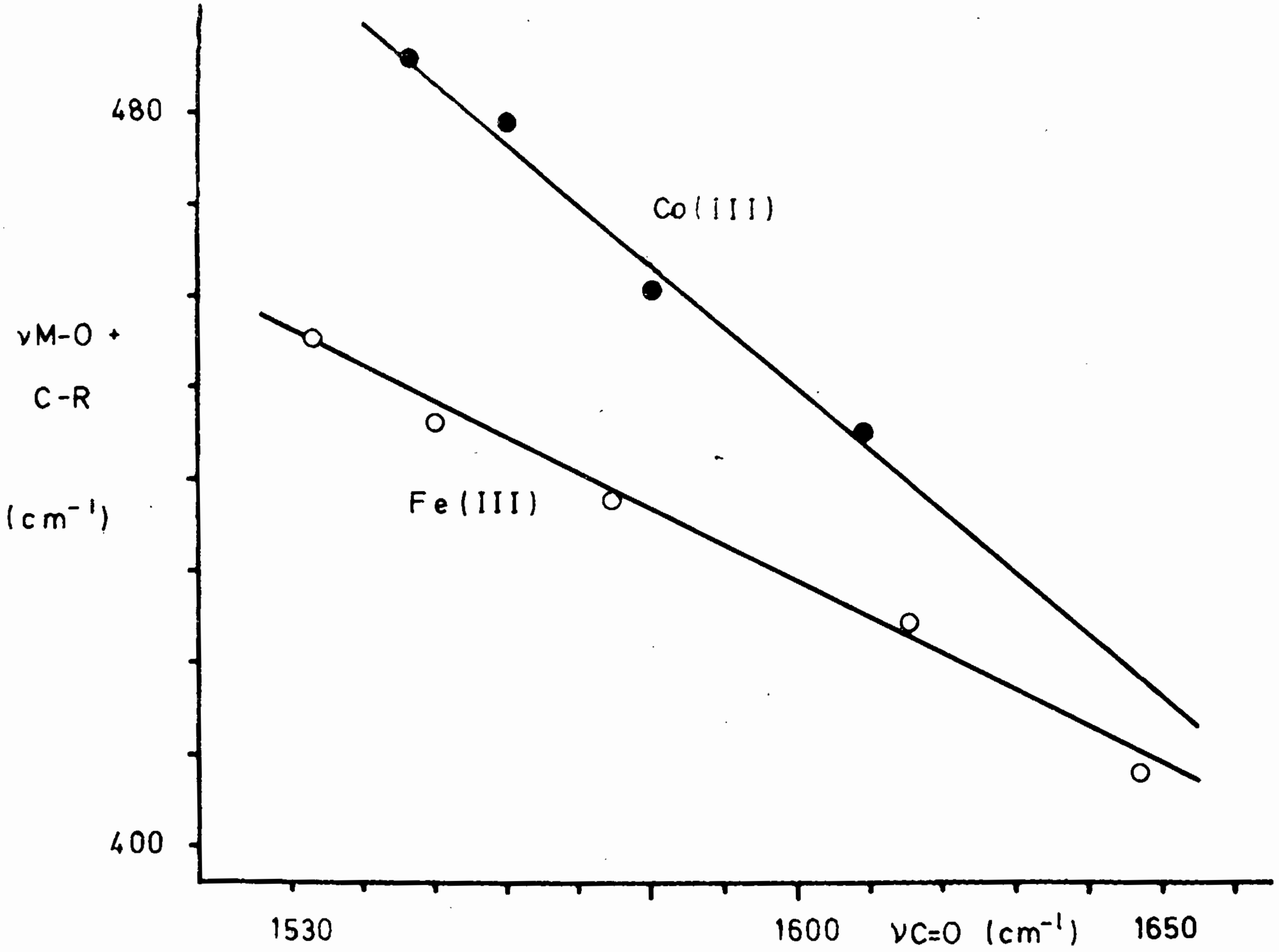


Fig. 27. Variation of νM-O + C-CH_3 with νC=O on change of 1,3 substituent.

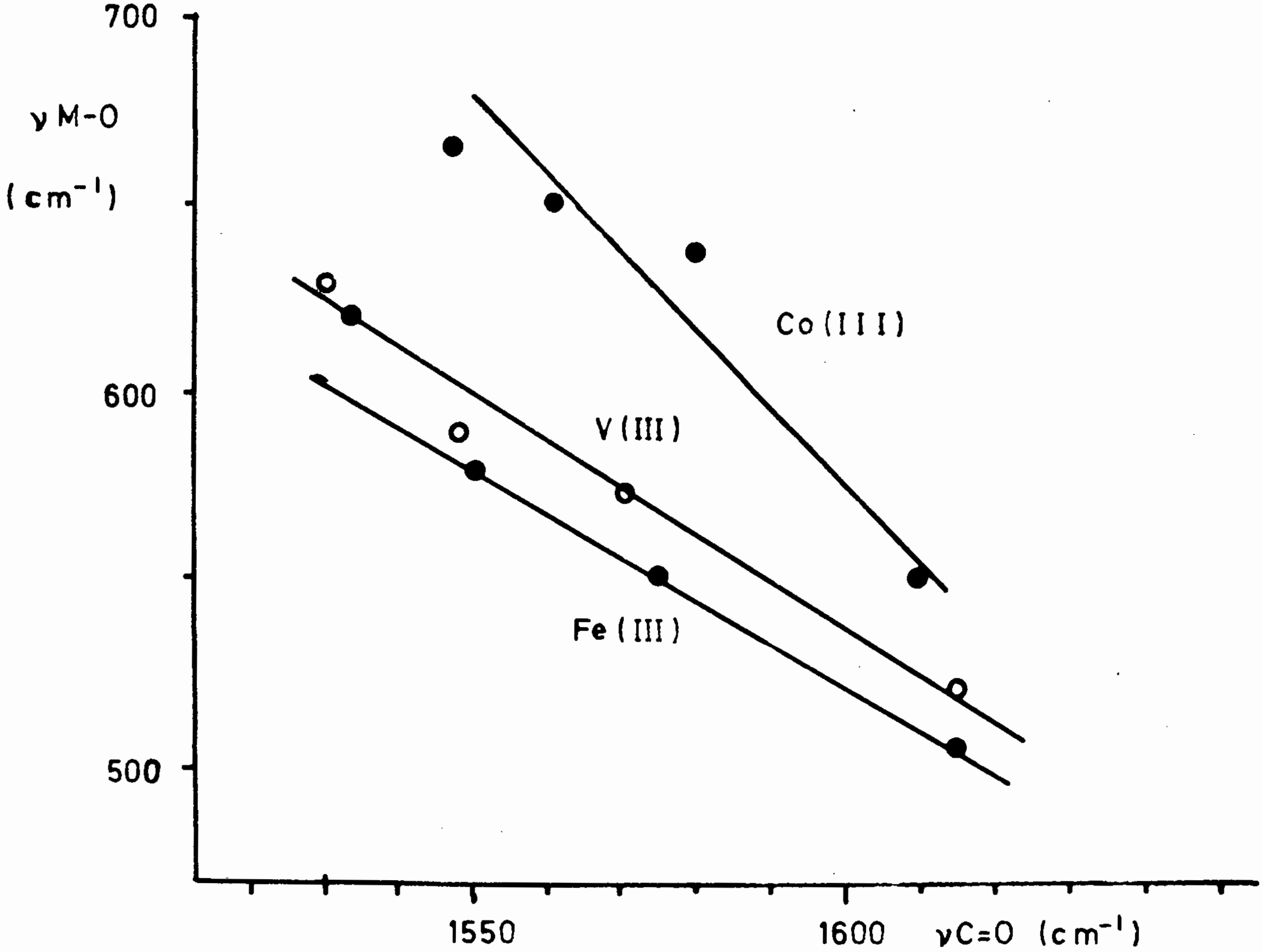


Fig. 28. Variation of νM-O with νC=O on change of 1,3-substituent.

convenient to use M-O str., this being assigned as the most metal sensitive of bands 1,2 or 3. This is a valid procedure, since the trends displayed by Bands 1,2 and 3 are essentially the same for all the differently substituted beta-diketonates on change of metal.

However, using bands 1,2 or 3 in studying effects of change of 1,3 substituent presents various difficulties. In many cases, there are two bands of similar metal-sensitivity, in which case it is difficult to decide which band to use, or else involves the unreliable procedure of attempting to estimate intermediate frequencies which will be representative of the stability of the complex. Further, the actual strength of the M-O bond may be greater, or smaller than, is represented by the frequencies at the extremes of each range. (i.e. HFA complexes at one extreme may be relatively less stable than indicated by the lowest band in the series of three in the upper region, and DPM at the other extreme may be relatively more stable than indicated by the highest bands in the upper region.)

On the other hand, band 4, assigned to the M-O +

C-R str., should yield a reliable estimate of M-O band shifts, since, as seen from the electron shifts which occur on change of 1,3- substituent (page 225), both the M-O str. and C-R str. should increase simultaneously. Therefore, keeping in mind that band 4 represents change in the C-R bond strength as well as of the M-O bond strength, we shall use this band in interpreting the effects of change of 1,3- substituent at a later stage.

In addition to bands 1,2,3 and 4 (and a low intensity band about 30 cm^{-1} below band 4, further referred to as band 5), low intensity bands may be observed in the region 400 - 200 cm^{-1} of the beta-diketonate spectrum. The nature of these is uncertain, but it has been reported (52) on the basis of a NCT that the highest of these is a M-O str. vibration. This is reasonable in that this band is highly sensitive to change of metal. The range over which it varies is 93 cm^{-1} on change of metal in the first transition period trivalent tris(acetylacetonates), as compared with 95 cm^{-1} for band 3, and 110 cm^{-1} for band 2.

Moreover, if we examine structurally simpler complexes, such as the $[M(CN)_6]^{n-}$ and $[M(NH_3)_6]^{n+}$ ions, we find that the ranges over which the M-L str. frequencies vary where M are also first transition period ions is approximately 340 - 420 cm^{-1} and 300 - 400 cm^{-1} respectively. By comparison then, we might also expect the M-O str. frequencies in oxygen - donor complexes to occur in similar ranges (i.e. 290 - 400 cm^{-1}), since the masses of the C, N and O atoms which are coordinated to the metal in each particular case are similar.

However, this is not necessarily so, in that force constants are not reliably known for any of these molecules, and further, the beta-diketonates are chelate complexes, and so may not be directly comparable with monodentate forms. In addition, the range over which band 6 varies is not larger than the ranges over which bands 2 and 3 vary in the acetylacetonate spectrum, so that there is no basis for assigning a greater M-O character to this vibration on the grounds of metal sensitivity.

The variations of band 4, 5 and 6 with at. no. in the first transition period trivalent tris(acetylacetonates) are seen in Fig. 24 (page 218). It is observed that in passing from bands 4 to 5, and from bands 5 to 6, a large increase in the frequencies for the Sc(III) and Ga(III) complexes is observed, relative to those of the complexes of the other ions in the series.

Four bands instead of three are present in this region in the Mn(III) complex, presumably due to Jahn-Teller distortion. A mean frequency between each of these may be estimated which roughly corresponds to the four short, and two long, M-O bonds. (These are points A, B and C in Fig. 24.) This must be higher than the lower of two successive bands by two thirds of the difference between them, since each higher band corresponds to four short bonds, and each lower band corresponds to two long bonds. These rough estimates indicate that the frequency of band 6 for the Mn(III) complex, as with the Sc(III) and Ga(III) complexes, is higher than would be predicted by CFT. It may be observed (Fig 23) that the C=O str. for the same three ions, Sc(III), Mn(III) and Ga(III) occurs at significantly higher wavenumber than for the other ions in the series. If we suppose that band 6 contains a high percentage of C=O character, this would then account for the observation that band 6 for Sc(III), Mn(III) and Ga(III) is significantly higher than would be predicted by CFT.

On the basis of these arguments, we therefore suggest the following assignments for the more metal-sensitive bands observed in the spectra of beta-diketonate complexes in the region 200 - 800 cm^{-1}.

	Band	Assignment	
Upper region	1	M-O str. + ring def.	The most metal-sensitive of these = M-O str.
	2	M-O str. + ring def.	
	3	M-O str. + ring def.	
Lower region	4	M-O str. + C-R str.	
	5	M-O str. + C-R str.	
	6	M-O str. + ring def.	

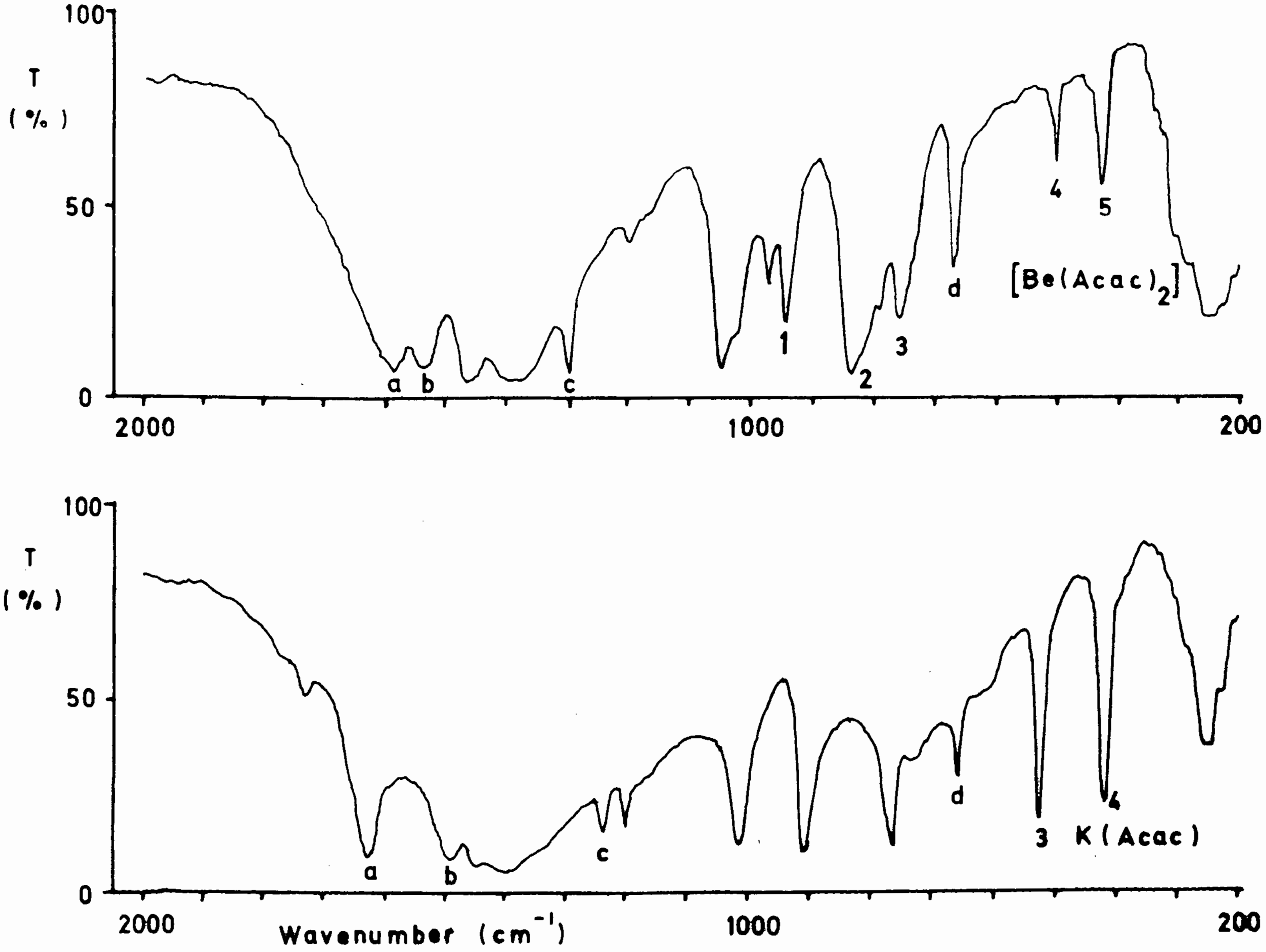


Fig. 29. Spectra of Be(Acac)$_2$ and K(Acac) in the region 200 - 2000 cm^{-1}.

4. The non-transition metal acetylacetonates

There is an extensive literature on the interpretation of frequency trends in the IR spectra of acetylacetonates on change of central cation, but in these studies distinction between the complexes of TM and non-TM metal has not usually been made. Earlier studies have been concentrated on the C=O str. and C=C str. vibrations, because of limitations in relation to instrumentation in the far IR (the range of many of the instruments used was only 4000 - 625 cm^{-1}, which does not extend far enough into the far IR to detect M-O str. vibrations in most compounds.).

In discussing the C=O str. and C=C str. vibrations, band assignments used by other authors will be altered to agree with those used by ourselves, so as to avoid confusion. Correlations of frequency trends on change of central cation have been found with parameters such as stability constants for the complexes themselves, and with ionisation potentials and ionic radii of the central cations of the complexes.

A. Correlations of frequency trends with stability constant data

Holtzclaw and Collman (59) found an inverse relationship between the C=O str. and stability constants of the series of acetylacetonates $M(Acac)_2(H_2O)_n$, where M = Mn, Co, Ni, Cu, Pd, Mg, and Cd, and $M(Acac)(H_2O)_2$ where M = Na. This is as would be expected if we suppose that strengthening of the M-O bond causes a weakening of the C=O bond.

However, the reliability of such correlations is dubious, in that change of structure in the Ni(II) complex above from n = 2 to n = 0 causes an increase in the frequency of the C=O str. of 22 cm^{-1}. Thus, depending on which complex was used, the position of the ion in the series varies. This makes comparison with data derived from stability constant studies difficult, since the identity of the species in solution is unknown.

Further, in complexes such as the trivalent beta-diketonates of first transition period ions, the C=O str. does not exhibit an inverse relationship with the M–O str. on change of metal, so that it would not be possible to infer the relative strengths of the M–O bonds from the variation of the C=O str. The frequency of the M–O str. does, however, appear to reflect the relative stability of the complex, as indicated by stability constant data for both divalent and trivalent ions (66). This is as seen in Table 13 below. The stability constant data are from the literature (66)

Table 13

Stability constant and IR data for acetylacetonate complexes. Frequencies are in cm^{-1}.

		$M(Acac)_2$		$M(Acac)_2(H\ O)_2$	
Metal	$\log K_1K_2$	M–O str.	C–O str.	M–O str.	C–O str.
Mn	7·25	545	1611	551	1616
Fe	8·67	558	1581	–	–
Co	9·51	581	1591	568	1612
Ni	10·38	593	1620	571	1598
Cu	14·95	612	1580	–	–
Zn	–	565	1586	559	1604
	$\log K_1K_2K_3$	$M(Acac)_3$			
La	11·9	527	1594		
Ce	12·6	529	1608		
Nd	13·1	531	1605		
Al	22·3	580	1597		
Ga	23·6	584	1586		

B. Ionisation potentials and ionic radii

West and Riley (60) observed a relationship between the C=O str. and ionisation potential (I_z) for eighteen metal derivitives of acetylacetone. The C=O str. was found to decrease with increasing I_z of the central cation. (For comparison with the C=O str., 1st ionisation potentials for the complexes of monovalent metals, 2nd ionisation potentials for the complexes of divalent metals, and third ionisation potentials for the complexes of trivalent metals were used.)

This work was supported by Lawson (1), who also observed a similar relationship for the C=C str.. This moved to higher wavenumber with increasing I_z of the central cation, exhibiting an inverse relationship with the C=O str.. Lawson also observed an inverse relationship between the M-O str. and the ionic radius (r^+) of the central cation on change of metal in acetylacetonate complexes.

The significance of these correlations of IR frequencies with I_z and r^+ values is to be found in the relationship between the covalent (as opposed to ionic) nature of any particular bond and the ionic radii of the atoms forming the bond. Covalency arises out of the ability of the ability of the cation to attract electrons (or lose electrons to the cation in the case of the anion) from the anion with which it is forming the bond, so that the two atoms forming the bond are held together by electron-sharing, rather than electrostatic forces alone, as in the case of ionic bonding. The ability of the cation to attract electrons from the anion to which it is bonded is dependent on the charge density on the cation, which is in turn dependent on two factors; first, the charge on the cation (the greater the charge, the greater the attracting power, so that attracting power should increase $M^{+} < M^{2+} < M^{3+} < M^{4+}$ etc.) , and second, the radius of the cation (the smaller r^{+}, the greater the charge density on the cation) (62). Other factors which also (62) play a part in determining the covalent nature of the bond are the existence of d-orbitals energetically available for π-bonding, and the size of the anion (the larger the anion, the more easily is it polarised by the cation).

The effect of increasing ionic charge on the frequencies of the M–O str., the C=O str., and the C=C + C–CH_3 str. for complexes of ions from the same period (the ions are therefore of comparable mass) of the periodic system is seen in Figs. 30, 31 and 32 respectively (pages 239 – 241). The typical and A subgroup elements are classified separately from the B subgroup elements from the same group . *e.g.* Al(III) is classified with Sc(III), Y(III) and La(III), rather than with Ga(III) and In(III)), since B subgroup elements have undergone the d-orbital contraction which results in smaller ionic radii than found in A subgroup elements from the same period. This accounts for the greater resemblance of the properties of the typical elements of group III and IV to their B rather than their A subgroups. Thus we find that the M–O str. Ga(III) and In(III) is very much closer to that for Al(III), whereas the M–O str. for Sc(III), Y(III) and L (III) is very much lower than observed in the Al(III) complex.

The effects of change of ionic radius are illustrated by trends observed within a single group of the periodic table where ionic charge remains constant, *e.g.*

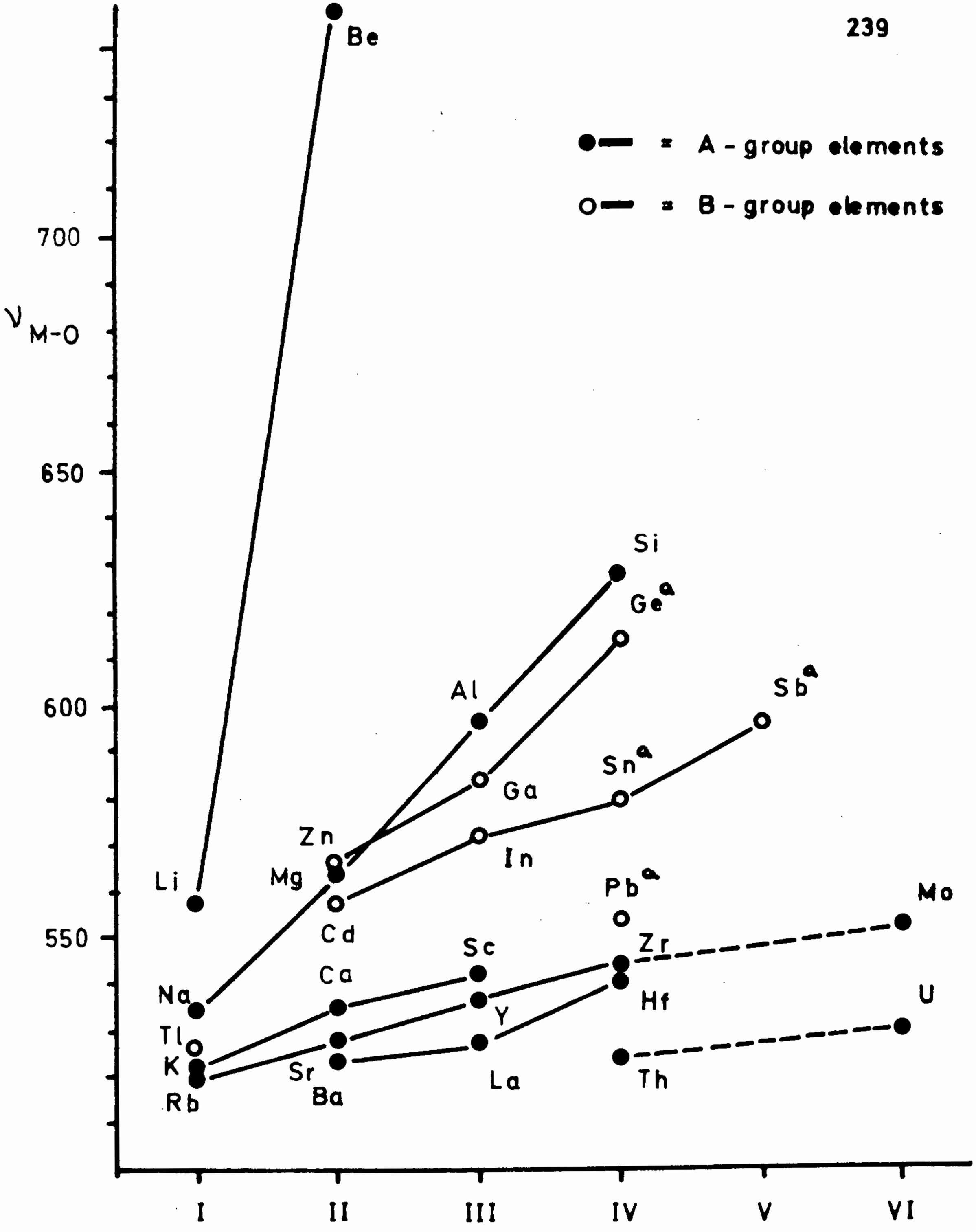


Fig.30. Effect of increasing ionic charge on νM-O across non-TM periods. ([a] = ref. 105)

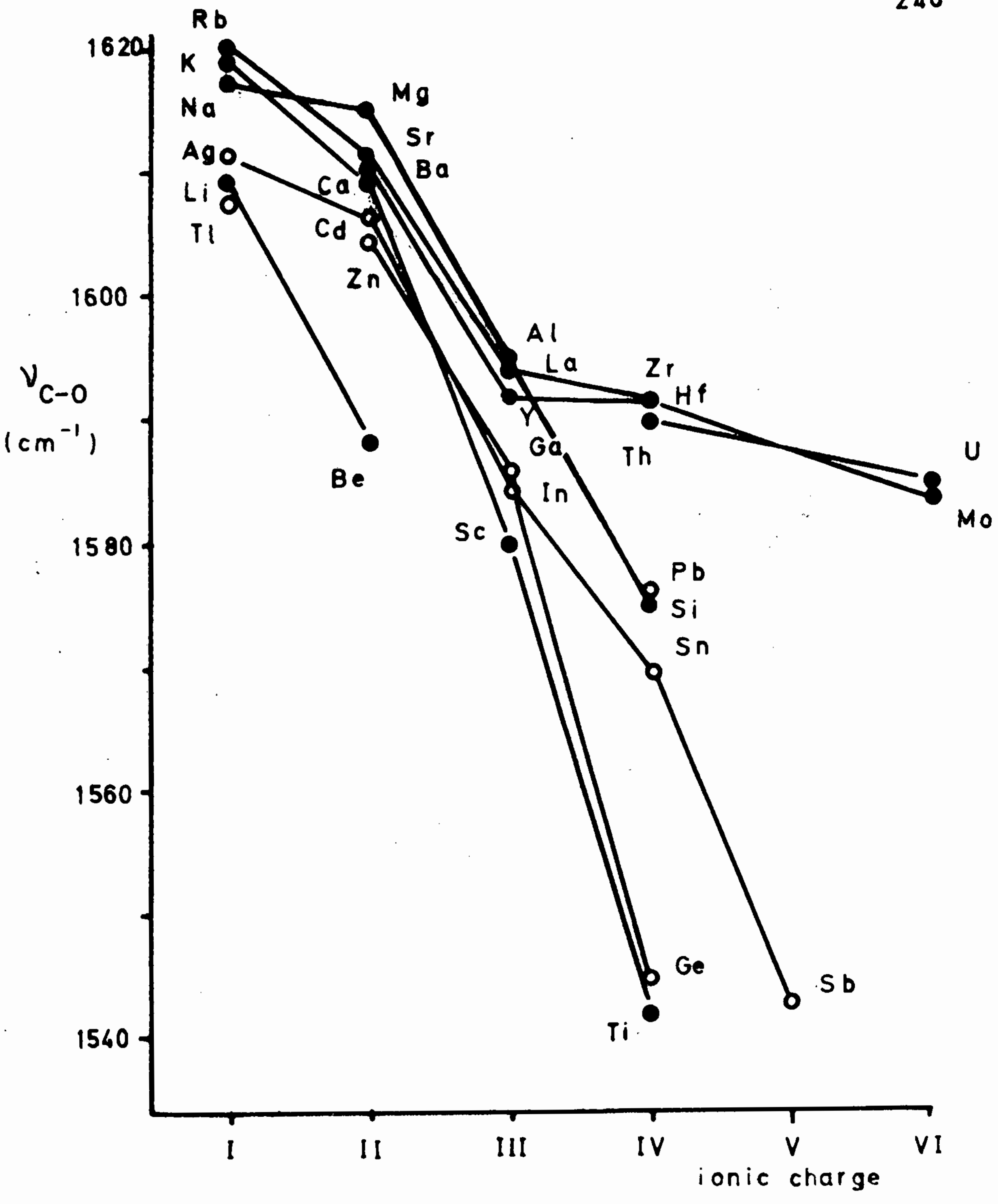


Fig. 31. Effect of inceasing ionic charge on νC=O across non-TM periods.

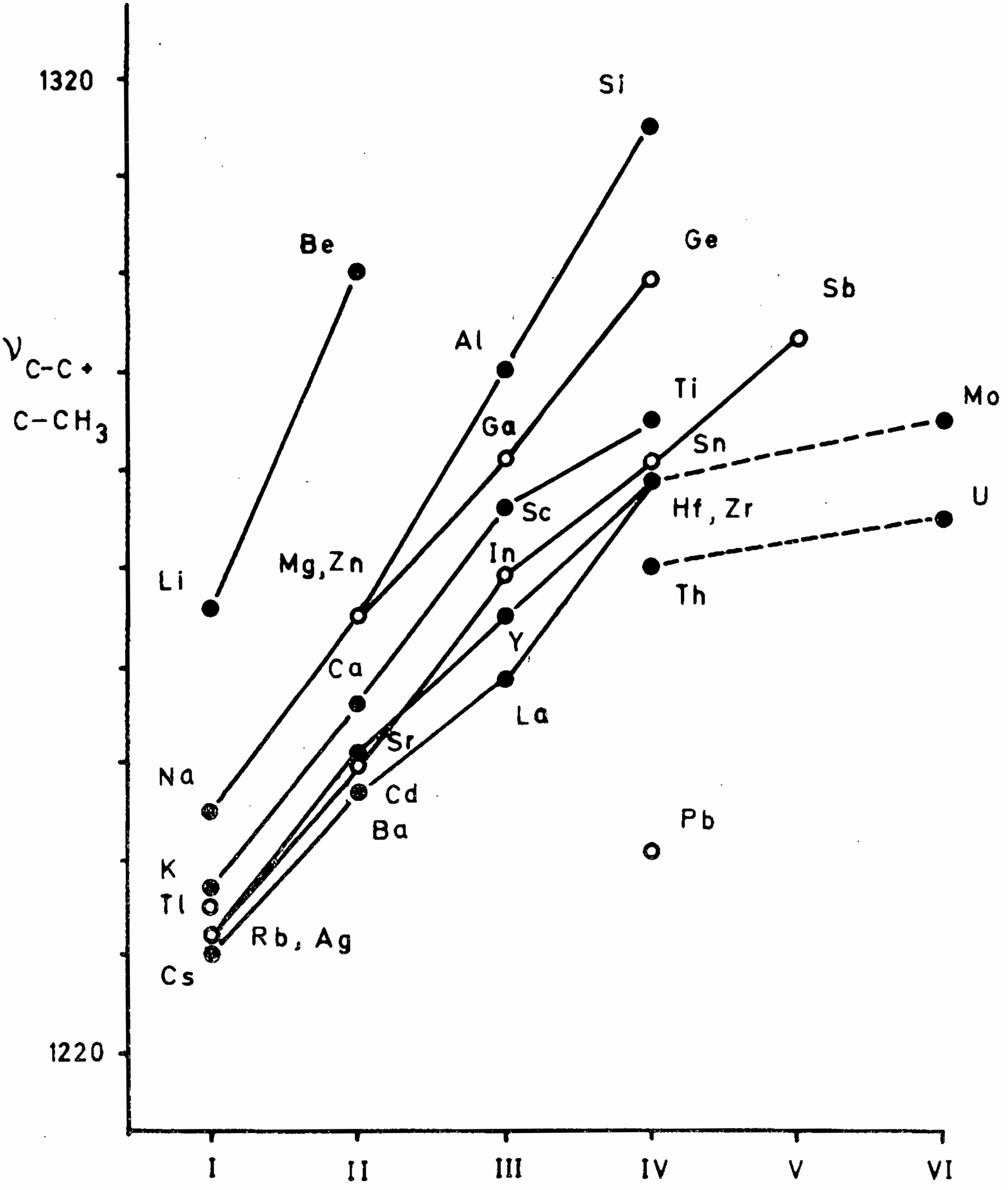


Fig. 32. Effect of increasing ionic charge on $\nu(C=C+C-CH_3)$

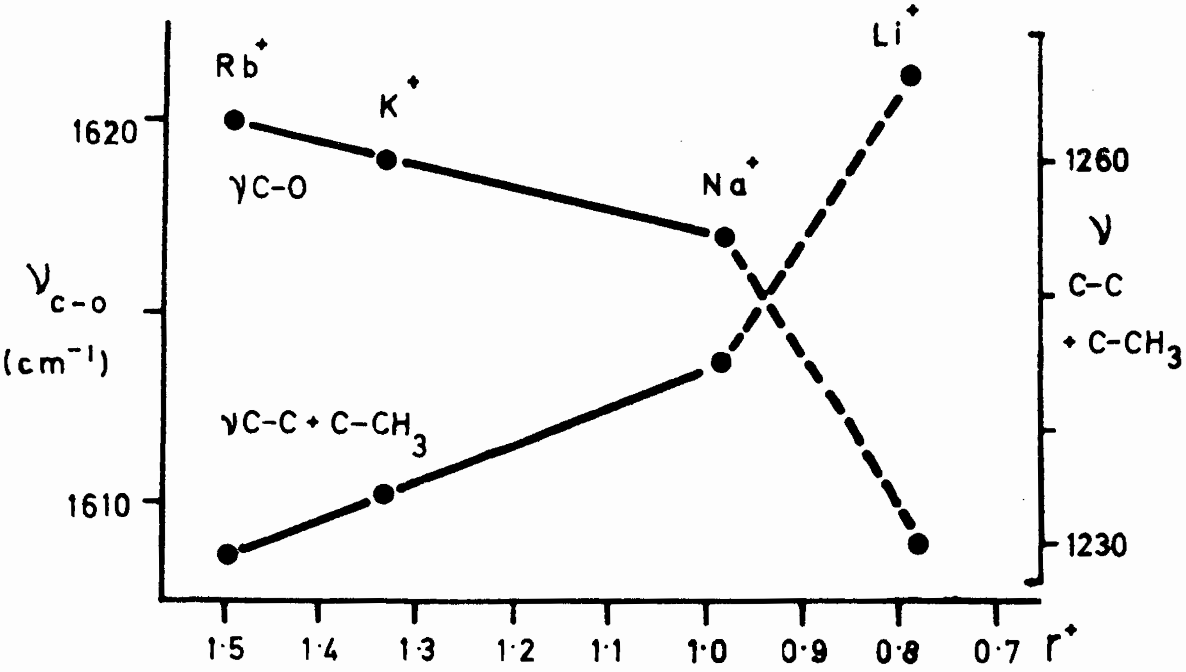
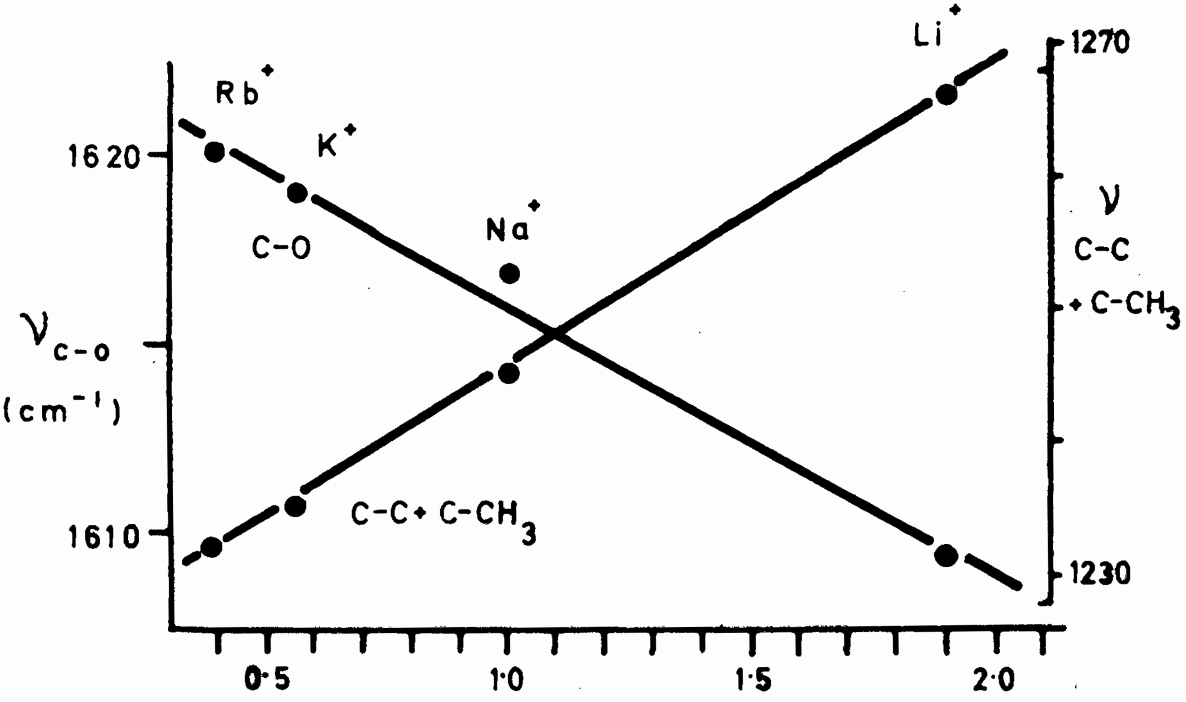


Fig 33a Variation of IR frequencies in spectra of group IA acetylacetonates with (above) r^+ and (below) C.



Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$. , where the M-Ostr. and C=C + C-CH$_3$ str. decrease, and the C=C str. increases, with increasing ~~increasing~~ r$^+$, as seen in the Table below

Table 14

IR frequency data (cm^{-1}) and r$^+$(Å) for the acetylacetonates of various non-TM ions.

Ion	r^{+} [a]	M-O str.	C=O str.	C=C str.	C=C + C-CH$_3$
Li$^+$	0·68	557	1609	1523	1266
Na$^+$	0·98	534	1617	1515	1245
K$^+$	1·33	522	1619	1511	1237
Rb$^+$	1·49	520	1620	1510	1232
Cs$^+$	1·65	–	–	1506	1230
Be^{++}	0·30	748	1588	1535	1300
Mg^{++}	0·65	563	1615	1528	1265
Ca^{++}	0·99	535	1609	1522	1256
Sr^{++}	1·10	528	1611	1522	1251
Ba^{++}	1·29	524	1610	1514	1247
Al^{+++}	0·45	580	1597	1535	1290
Sc^{+++}	0·78	542	1580	1529	1276
Y^{+++}	0·93	536	1592	1530	1265
La^{+++}	1·22	527	1594	1527	1257
Si^{++++}	0·28	628	1575	1555	1320
Ti^{++++}	0·64	596	1544	1527	1284
Zr^{++++}	1·48	545	1591	1540	1281
Hf^{++++}	1·48	542	1593	1539	1279
Th^{++++}	1·65	524	1590	1538	1270

[a] From references 62 and 67.

The polarising power of cations (which we shall call C) is related to the square of the ionic radius of the ion (62). Taking into account the ionic charge (I) we arrive at the expression

$$C = \frac{I}{(r^+)^2}$$

In previous work on the correlation of IR frequency trends with ionic radii, correlations with r^+ itself were sought. However, as can be seen in Fig. 33, linear relationships with M-O str., C=O str., C=C + C-R and C=C str. are not observed with r^+, but rather with C on change of central cation in group IA acetylacetonates, benzoylacetonates and dipivaloylmethanates.
In both the group IA and IIA series, the values for the lightest elements, Li and Be, in each series are too high in the case of the M-O str., C=C str., and C=C + C-R str., and too low in the case of the C=O str., to yield linear correlations with r^+. (Fig. 33)

This might be explained in terms of a mass effect, since r^+ and the mass of the central cation both increase on descending these groups, and both effects are expected to lower the M–O str. Thus, a relationship of the M–O str. with both mass and ionic radius would result, which could be expressed as

$$\text{M–O str.} \propto \frac{1}{mr^{+}} \quad (\text{where } m = \text{the mass of the ion of radius } r^{+}.)$$

However, the C=O str. for the Li^+ and Be^{++} complexes, as previously mentioned, are lower than would be expected from interpolation of the best straight line through the frequencies for the complexes of the other ions in the series, as plotted against r^+, and a mass effect would be expected to have the opposite effect, since Li^+ and Be^{++} are the lightest members of each of their respective series.

C. The effect of mass of the cation on IR frequencies in beta-diketonate complexes

The actual part played by mass effects in the spectra of these complexes does not appear to be very large. If we compare the M–O str. for the tetrakis-(acetylacetonates) of the two ions Zr(IV) and Hf(IV), where the ionic radii are identical, we see that a lowering of the M–O str. of only 3 cm^{-1} is produced by an increase in mass of 97%. Other examples of this effect are seen below

Ion	r^+	M–O str. (cm^{-1})	At. Wt.
Al^{+++}	0·65	580	26·97
Ga^{+++}	0·62	584	69·72
Zr^{++++}	0·87	545	91·22
Hf^{++++}	0·87	542	178·6
Rb^{+}	1·49	520	85·48
Tl^{+}	1·49	526	204·39
Ca^{++}	1·06	535	40·08
Cd^{++}	1·03	556	112·41
Mg^{++}	0·78	563	24·32
Zn^{++}	0·83	565	65·38
Co^{+++}	0·65	637	58·94
Rh^{+++}	0·69	650	102·91

Djordjević (63) has calculated the relative bond strengths of Al(III), Ga(III) and In(III) tris(acetylacetonates) using the equation for the isolated oscillating dipole

$$\nu = \frac{1}{c}\left(\frac{K}{4\pi^{2}\mu}\right)^{\frac{1}{2}}$$

where ν is the frequency of the vibration in cm^{-1}, c is the velocity of light, and μ the reduced mass of of the two atoms, A and B, forming the dipole, such that

$$\mu = \frac{M_A \times M_B}{M_A + M_B}$$

where M is the mass of each of the atoms A and B constituting the dipole, and is expressed in c.g.s. units. K is the force constant of the bond, and is the force tending to restore the atoms when displaced to their equilibrium positions.

Use of this model, however, disregards the fact that the change of mass of the central cation is very small when one considers the mass of the beta-diketonate molecule as a whole. The application of the simple diatomic model is particularly erroneous when one considers that the metal atom may be joined to as many as eight oxygen atoms, instead of one as implied by use of the diatomic model.

We may construct a simple model for the octahedral case to illustrate this point, in which it is assumed that a single oxygen atom constitutes one of the atoms in a diatomic molecule, while a metal atom and the other five oxygen atoms of the octahedron, held together by infinitely strong bonds, constitute the other atom. (In other words, we suppose that each oxygen atom vibrates against the mass of the metal atom plus the mass of the other five oxygen atoms.) This then should take into account the fact that the metal atom is joined to more than one oxygen atom, although of course, we do not suppose that it predicts accurately the shifts which would be observed in real beta-diketonates, rather illustrating only qualitatively the point that mass effects are probably smaller than indicated by the diatomic model.

Thus, for example, the effect of change of metal from Al(III) to Ga(III) in the diatomic molecule model should be accompanied by a decrease of 12·6%, with unchanged M-O force constants, while the model in which a single oxygen atom vibrates against the mass of the metal atom plus the other five predicts a drop due to the increased mass of the metal atom of only 1·8%. From the table on page 245, it is seen that the effect of increase of mass probably causes a decrease in the M-O str. frequency of pairs of ions of similar radius of less than 1%.

On the other hand, the effect of increase of mass of the oxygen atoms is much larger. In the ^{18}O studies of Pinchas _et. al._ (54), a decrease in the frequency of the M-O str. of 3·2% was observed on substitution of the heavier oxygen atoms (mass 18) for the lighter (mass 16) atoms. We find that our crude model correctly predicts that the change of mass of the oxygen atoms should have a greater effect than the effect of change of mass of the central cation, while the diatomic molecule predicts that the effect of change of mass of the metal atom should have a greater effect. This may be summarised in the form of a table

% decrease in the M-O str.

	predicted		observed
	M-O	O-(MO$_5$)	
A. On change from Al to Ga	12·6%	1·8%	less than 1%
B. On change from 16-O to 18-O	4·3%	5·5%	3·2%

It therefore seems probable that we may ignore the effects of increase of mass of the central cation, since it appears that even in cases where the change in mass of the central cation is large, the effect on the M-O str. frequency is small.

D. The effect of d-orbital participation in bonding on IR frequencies

It was previously mentioned that an important factor governing the polarising power of cations was the possession of d-orbitals energetically suitable for π-bonding. This phenomenon causes considerable reduction in the sizes of cations, and a disruption in the regular monotonic change of proprties of properties with increasing at. no. down groups in the periodic table (22).

This is illustrated by the variations of the C=O str. with increasing valency for the acetylacetonates across periods in the periodic table. (Fig. 31) In group IA metals the C=O str. is seen to increase regularly with increasing at. no., but in group IIIA metals a crossover is observed, such that the C=O str. for

Sc(III) is lower than for Al(III). This same phenomenon is observed in group IVA, where the C=O str. for Ti(IV) acetylacetonate is lower than for Si(IV) acetylacetonate. It would appear that in the second and third periods, however, the effcts of π-bonding are considerably smaller than in the first transition period, since C=O str. for the acetylacetonates of the ions in these periods is, as would be expected, higher than for the second short period ions. (e.g. C=O str. for Zr(IV), Hf(IV) and Th(IV) acetylacetonates is higher than for Si(IV) acetylacetonate, while C=O str. for Ti(IV) acetylacetonate is lower than for Si(IV) acetylacetonate.)

However, the order of decrease of the M-O str. and C=C + C-CH_3 str. with increasing at. no. down these periods is regular, suggesting that π and σ-bonding have different effects on the IR spectra of these complexes. Increased M-O π-bonding involves a great decrease in the C=O str. without greatly increasing the M-O str, while increased σ-bonding causes a greater increase in M-O str., without causing so great a decrease in the C=O str.

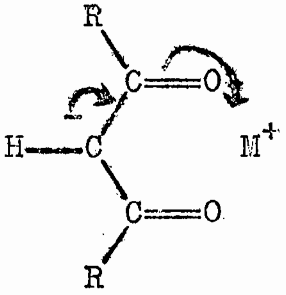
A further difference which is noticeable is that C=C str. is not raised much by π-interaction, as compared with the lowering in C=O str. which is produced, <u>e.g.</u> C=O str. in Al(III) is lowered to 1597 cm^{-1}, while in Sc(III) acetylacetonate, it is lowered to 1580 cm^{-1}. On the other hand the C=C str. is raised to 1535 cm^{-1}, while Sc(III) it is raised to only 1529 cm^{-1}. In group IVA, C=O str. in Ti(IV) is lowered to 1545 cm^{-1}, and in Si(IV) to 1575 cm^{-1}, while C=C str. is raised to only 1527 cm^{-1} in the former, but 1555 in the latter. In the second and third transition periods, however, where π-interaction is small, Zr(IV) and Hf(IV) have C=C str. raised to 1540 and 1539 cm^{-1} respectively, while C=O str. is lowered to only 1591 and 1593 cm^{-1}.

These effects may be illustrated by the following table (cm^{-1})

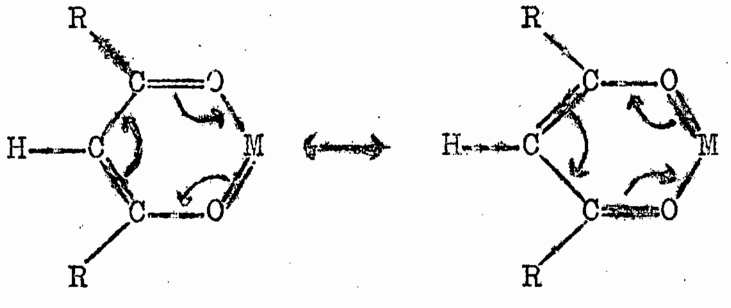
Ion	Group IIIA		Ion	Group IVA	
	C=Ostr.	C=Cstr.		C=Ostr.	C=Cstr.
Al^{+++}	1597	1540	Si^{++++}	1575	1555
Sc^{+++}	1580	1529	Ti^{++++}	1543	1527
Y^{+++}	1592	1530	Zr^{++++}	1591	1540
La^{+++}	1594	1527	Hf^{++++}	1593	1539

The anamolous behaviour of Sc(III) and Ti(IV) is attributed to π-bonding effects in ions of the first transition period.

The interpretation of this is that in predominantly π-bonding complexes, the polarisation of the ligand is of the classic type, which may be represented as



while in complexes where strong π-bonding occurs, the effect is rather one of equalisation of bond order due to a pseudo-benzenoid type resonance



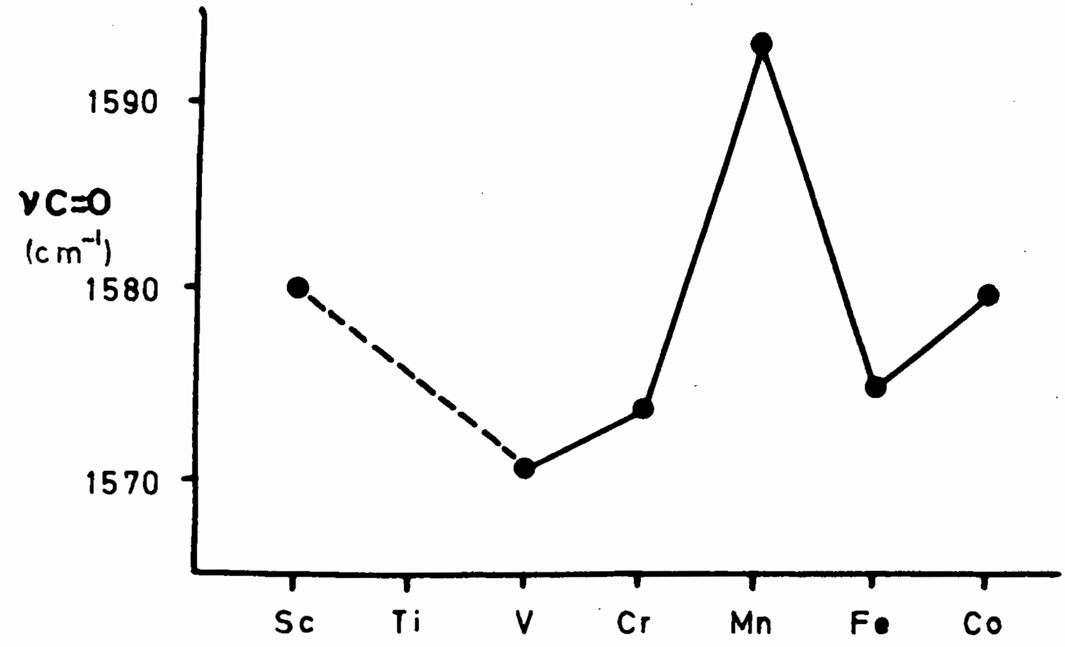
This equalisation of bond order accounts for the simultaneous lowering of both the C=C str. and C=0 str. observed with the introduction of π-bonding into the ring.

This phenomenon of low C=O str. and C=C str. is observed also in the transition metal acetylacetonates, where π-bonding is strong.

5. A. π-bonding and the carbonyl frequency in transition metal acetylacetonates.

In the divalent TM acetylacetonate series π-bonding effects do not appear to be large from the evidence of their electronic spectra. (The energy of the $\pi_3 - \pi_4^*$ transition is not much raised, as compared with non-TM beta-diketonates in which no π-bonding effects are possible, such as in the K^+ salts.) Accordingly, we do not find any marked lowering of C=O str. in beta-diketonate series of complexes of divalent TM's, compared with the acetylacetonates of divalent metals in which π-bonding effects are expected to be small (e.g. Ba, Cd, etc.)

M(Acac)$_2$, M =	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
C=O str.(cm^{-1})	1609	1569	1611	1581	1588	1598	1580	1586	1609
C=C str.	1522	1518	1520	1520	1521	1525	1536	1530	1522
M-O str.	535	590	545	558	581	593	615	564	556



Variation of $\nu C{=}O$ with at. no. in first transition period $M(Acac)_3$ complexes.

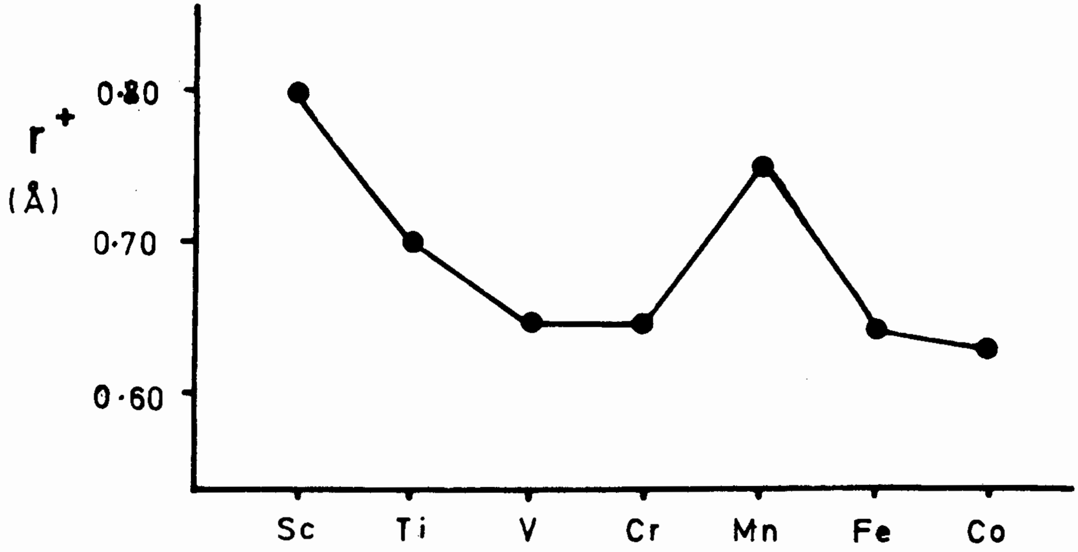


Fig. 33b. Variation of r^+ in first transition period M^{+++} ions (see ref. 19, page 73).

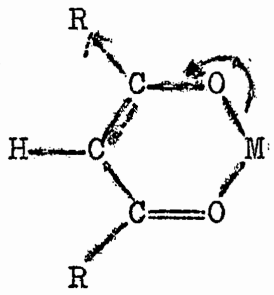
We thus find that the variations of C=O str. yield an inverse relationship with M-O str. on change of central cation. Further, C=C str. is raised above the frequencies observed for the non-TM divalent complexes.

However, in the acetylacetonate complexes of the trivalent TM ions, we find that the C=O str. for the ions which have partially filled d-orbitals (Ti(III) - Co(III)) is much lower than in the ions which do not (Sc(III) and Ga(III)), whereas C=C str. is generally lower, suggesting that π-bonding in these ions is even greater than in Sc(III) and Ga(III).

The variation of the C=O str. and the C=C str. for the trivalent tris(acetylacetonates) across the series is seen in Fig. 33. Below this is seen the variation of the ionic radii of these ions with at. no. across the series. It is noticed that the C=O str. and C=C str. do not vary much across the series, except for the high C=O str. and the low C=C str. frequencies of the Mn(III) complex. The ionic radius of the Mn(III) ion is exceptionally large, as seen in Fig.33, which is in keepingwith it having a low polarising power.

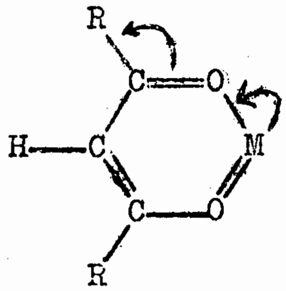
In the DBM and Bzac complexes (Fig. 23) C=O str. and C=C str. show the same trends across this series of ions, with C=O str. being exceptionally high, and C=C str. being exceptionally low for the Mn(III) complex. In TFA complexes, however, this same frequency trend is not observed. C=O str. for the Sc(III) and Ga(III) complexes is, as in the other beta-diketonate series, higher than for other ions in the series, but C=O str. for Mn(III) is not higher than for the other ions in the series. However, C=O str. for the Co(III) ion is considerably lowered as compared with the other ions in the series.

This may be interpreted in terms of the strong electron-withdrawing powers of the trifluoromethyl group. In most of the ions, π-bonding is of the $\pi \rightarrow M$ type, which is weakened by electron-withdrawing 1,3-substituents.



Therefore, π-bonding is weakened in all cases to the level of π-bonding observed in the Mn(III) complex, so that the C=O str. for all of them occurs at nearly the same frequency.

However, in the Co(III) complex, π-bonding is of the M-π* type, which is enhanced by electron withdrawing groups



This accounts for the lower frequency of the C=O str. in the Co(III) complex. We thus find similarly that the C=O str. for the Rh(III) trifluoroacetylacetonate is very low, which is in agreement with its having an electronic structure analogous to that of Co(III).

It is thus seen that the idea of weak π-bonding in Mn(III) acetylacetonate is supported by evidence from the carbonyl region of the spectrum, as is also the strong M- π^* bonding character of the Co(III) complexes. Further evidence for this is to be found in the variation of the C=C + C-R str. across the series.

As was seen earlier (Fig. 32), the frequency of this vibration increases sharply with increasing polarising power of the central cation in beta-diketonates. It is thus found that in all of the series of beta-diketonates studied, this vibration occurs at much lower frequencies in the Mn(III) complexes, and at higher frequencies for the Co(III) complexes.

This is seen in the Table below, in which the variation of the C=C + C-R str. in series of variously substituted beta-diketonates with first transition period trivalent ions is shown (cm^{-1});

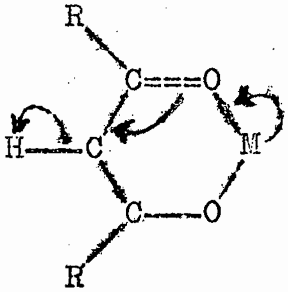
Complex	M = Sc	Ti	V	Cr	Mn	Fe	Co
$M(Acac)_3$	1276	1275	1276	1279	1256	1276	1280
$M(DBM)_3$	1318	-	1317	1319	1304	1309	1320
$M(Bzac)_3$	1294	-	1297	1299	1283	1294	1297
$M(TFA)_3$	1300	-	1299	1300	1290	1294	1302
$M(DPM)_3$	1297	-	1297	1297	1288	1294	1310
	M = Y			Mo		Ru	Rh
$M(Acac)_3$	1265			1273		1273	1272
$M(TFA)_3$	1297			1302		-	1303

Similar frequency trends may be observed for the vibration C=O + C-R str., as is seen below, although these are not so well marked due to the much lower metal sensitivity of this band.

νC=O +C-R (cm^{-1}) for beta-diketonate complexes of first transition period trivalent ions.

Complex	M = Sc	Ti	V	Cr	Mn	Fe	Co	Y	Rh	Ru	Mo
$M(Acac)_3$	929	930	932	933	925	929	936	935	935	940	932
$M(Bzac)_3$	961	-	959	961	956	960	965	-	-	-	-
$M(DBM)_3$	941	-	941	945	939	940	950	-	-	-	-
$M(TFA)_3$	954	-	947	950	948	949	954	943	947	-	947
$M(DPM)_3$	965	-	965	965	960	962	969	-	-	-	-

We find in the variation of the C-H bend of the ring proton across these series evidence for electronic shifts of the type



in that the C–H bend for the Cr(III), and particularly the Co(III) complexes is extremely low, while in the other ions it is high.

C–H in-plane bend (cm^{-1}) in series of differently substituted beta-diketonate complexes.

Complex	M = Sc	Ti	V	Cr	Mn	Fe	Co	Rh	Ru	Y
$M(Acac)_3$	802	801	803	791	802	802	782	792	782	-
$M(Bzac)_3$	806	-	804	792	804	806	790	-	-	-
$M(DBM)_3$	817	-	814	811	813	813	807	-	-	-
$M(TFA)_3$	805	-	803	799	802	802	793	795	-	807
$M(DPM)_3$	799	-	796	792	793	795	785	-	-	-

There is thus ample evidence from ligand vibrations that π–bonding in the Mn(III) complexes is weak, and strong in those of the Co(III), Rh(III) and Ru(III) complexes, with π-bonding of intermediate strength being found in the Cr(III) complexes. This is therefore in agreement with evidence from the UV and NMR spectra of these complexes, and also with the degree of π–bonding suggested by the variation of the M–O str. across these series.

B. Ionic radii, and the CF interpretation of the stability of TM complexes

In both the trivalent $M(Acac)_3$ and divalent $[M(Acac)_2]_n$ series of acetylacetonates with transition metals, we have seen that C=O str. and C=C str. vary as would be expected from the concomitant variation of r^+ across the series (i.e. C=O str. exhibits an inverse relationship with both C=C str. and r^+ on change of cation across the series). In the divalent series, M-O str. also varies as would be expected from the accompanying variation of r^+. (i.e. The order of stability indicated by M-O str. is the Irving-Williams stability order.)

When correlating stabilities of complexes with the ionic radii of their central cations it should be remembered that decreasing ionic radius, as determined from M-L bond lengths in the crystal lattice, is the result and not the cause of increasing M-L bond strength. In the divalent β-diketonates evidence from the UV and IR suggests that π-bonding is weak.

It may therefore be expected that the variation in M–O bond strength (and hence r^+) will be a function of the σ–bonding alone, and hence of $-\delta H$ (as was discussed previously, in the absence of strong π–bonding effects, $-\delta H$ is a measure of the M–L σ–bonding strength of the complex). We therefore find an agreement between stability orders for complexes of divalent ions predicted both by the variation of r^+ and $-\delta H$ across the series, in that r^+ must be a function of $-\delta H$.

However, in the trivalent acetylacetonates it is seen that the variation of r^+ in no way reflects the variation of M–O str. across the series (Figs 3,33) which follows instead the order suggested by CFT. However, the variation of C=O str. follows the order predicted by the concomitant variation of r^+. This suggests that the effects governing the frequency of M–O str. and C=O str. in the trivalent series are fundamentally different.

The variation of the r^+ values across the trivalent series which we have used, is derived from the variation of M-O bond distances in more ionic complexes such as oxides. In these it is probable that $-\delta H$ is very small so that in the variation of M-O bond strength across the series π-bonding effects will overshadow variations in $-\delta H$. The poor π-bonding ability of the Mn (111) ion therefore accounts for the relatively large radius reported for this ion in these environments.

In trivalent acetylacetonates however, where π-bonding does not affect the M-O bond order to such a great extent as do CF effects, we find that Mn-O bond distances (68) are similar to those of other first transition period trivalent ions and that the variation of M-O bond distances is consistent with CFT.

However, even in the Acac complexes, where π-bonding effects are not as large as CF effects, the poor π-bonding ability of the Mn(III) ion is evidenced by an M-O str. (570cm^{-1}) which is lower than the theoretical value (590 cm^{-1}) calculated using eq. 4 and 10Dq estimated from f and g values.

Non-TM acetylacetonate M-O bond distances yield a good linear relationship with ionic radii derived from M-O distances in the metal oxides (Pauling crystal radii), but in transition metal acetylacetonates, the M-O bond distances are shorter than estimated graphically using their ionic radii and the linear relationship between M-O bond length and r^+ for non-TM acetylacetonates. This shortening of M-O bond lengths is taken (68) to indicate an increased covalency in TM acetylacetonates compared with the oxides used in the establishment of Pauling's radii. Since the M-O bond distance in Zn(II) acetylacetonate is also shortened, the increased covalency cannot only be an effect of increased $-\delta H$ in passing from the oxide to the acetylacetonate system , but must also be partially due to π-bonding effects ($-\delta H$ for Zn(II) = 0.)

Further, the relative order of stabilities indicated by ionic radii and by the actual M-O bond lengths for TM acetylacetonates are not the same, suggesting that change from one system to another alters the relative importance of σ- and π- bonding (e.g. Mn-O in Mn_2O_3 is longer than in other first transition period oxides, but in $Mn(Acac)_3$ it is of a similar length to M-O in other tris(acetylacetonates).)

It is therefore seen that, since r^+ for a series of ions in one particular system is a result of their bond ~~bond~~ stabilisation in that system, these M-L bond lengths cannot be reliably used to predict bond stabilities in other systems, where the relative importance of different stabilising factors such as $-\delta H$, or π-bonding may not be the same. However, the LFT approach may be used, since it takes into account both the effects of stabilisation by CF effects ($-\delta H$), and also π-bonding. This is amply illustrated by the failure of the ionic radius model to predict correctly the order of stability of trivalent transition metal acetylacetonates as indicated by their M-O str. frequencies, which the LF model was able to do.

6. The trivalent rare-earth acetylacetonates.

It is not at present possible to demonstrate CF effects in rare-earth compounds, since there are insufficient available data for the calculation of energies of lattice formation from a common valence state of the free metal ions. Because of the small interaction of the f-orbitals with the ligands, these are, however, likely to be small. For example, a CF stabilisation of 1·5 kcal/mole has been estimated for $Nd(BrO_3)_3 \cdot 9H_2O$ (10).

More important than CF effects, however, in determining the chemical and physical properties of these ions, is the lanthanide contraction, which is the regular decrease in ionic radius from La(III) to Lu(III). Properties such as stability constants, for example, increase regularly with concomitant decreases in ionic radius.

In Figs. 34 and 35 the variation of the M-O str., C=O str., C=C str. and C=C + $C-CH_3$ str. with increasing at. no. across the lanthanide series is shown. The

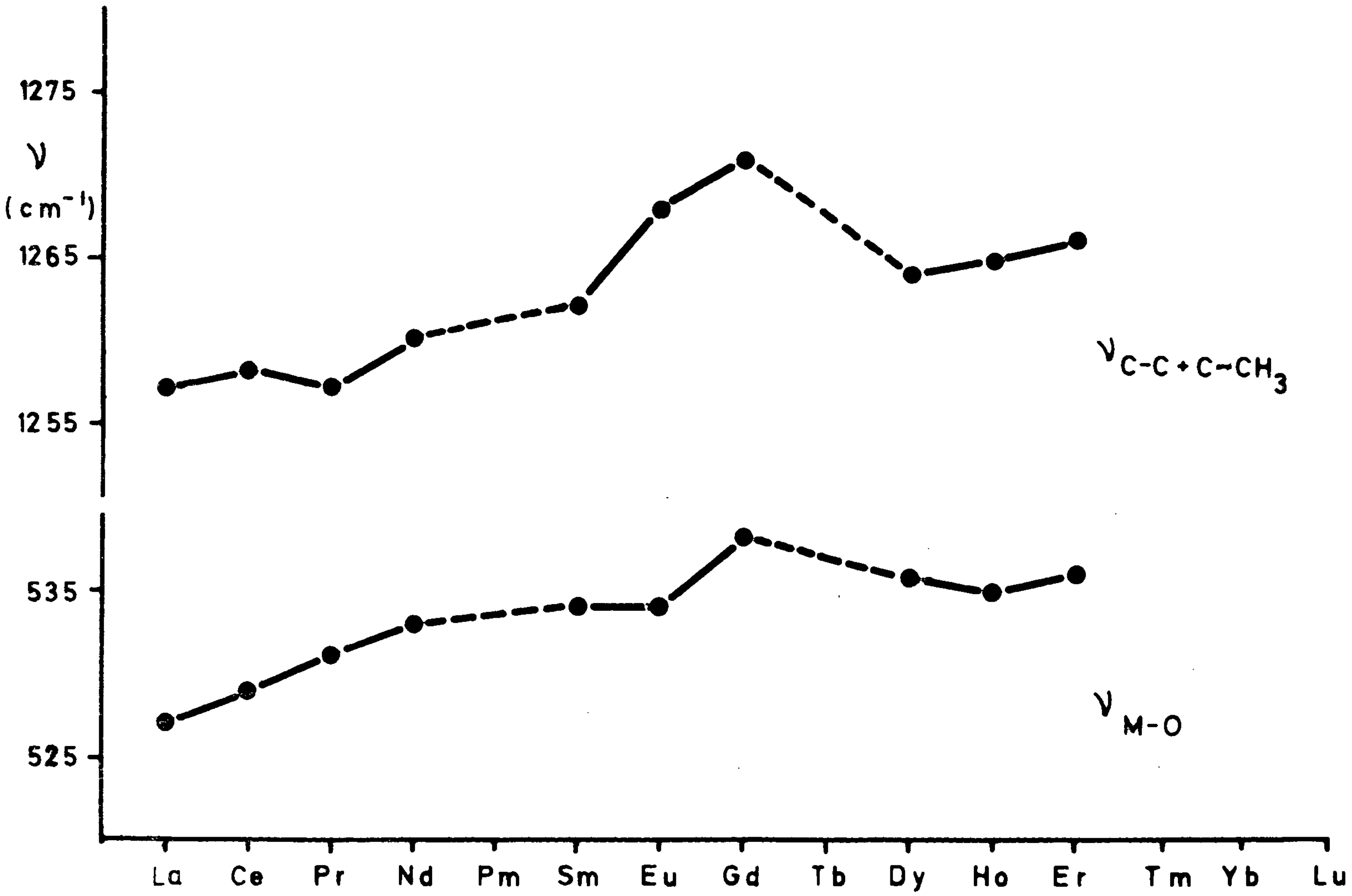


Fig. 34. νM-O and νC=C+C-CH_3 vs. at. no. for rare earth [$M(Acac)_3(H_2O)_2$] complexes.

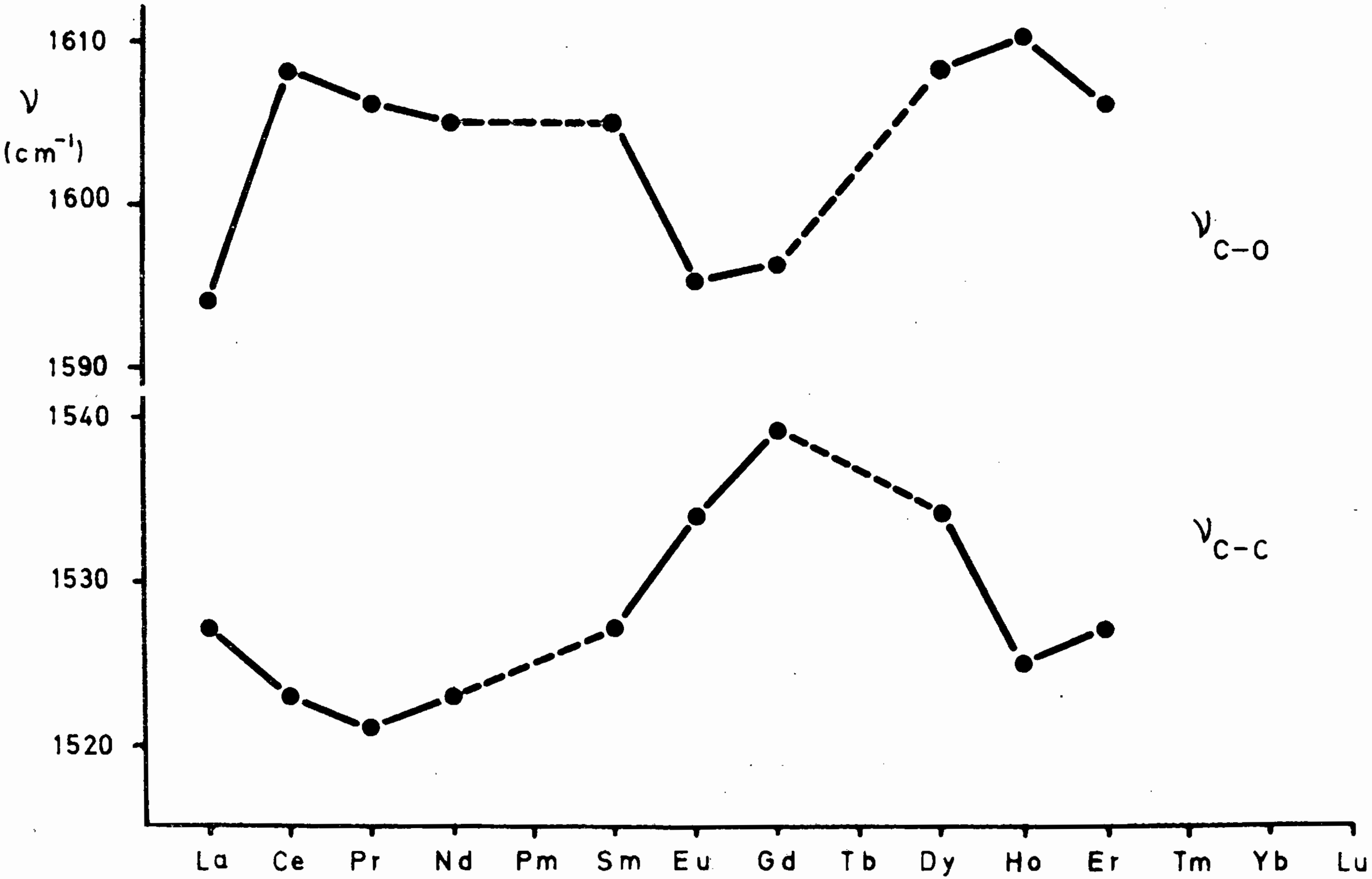
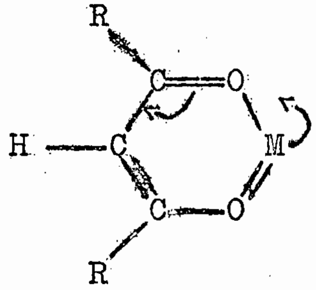


Fig. 35. Variation of νC=O and νC=C with at. no. for rare earth $[M(Acac)_3(H_2O)_2]$ complexes.

variations in these vibrations are consistent with electron shifts of the type below



However, it is observed that although the M-O str. increases from La(III) across the series to Er(III) (the last three members of the series, Tm(Acac)$_3$, Yb(Acac)$_3$ and Lu(Acac)$_3$ were not prepared), the increase is not regular, there being a rise to the f^7 configuration complex, and a slight decrease after it (see Fig. 34). This is in agreement with the fact that the f^7 configuration, which is the "half-filled shell" configuration, has been quoted (62) as being of exceptional stability, in that all variations from the trivalent oxidation state in lanthanide compounds appear to be directed towards attainment of this, or else the d^0 or

f^{14} configurations. (e.g. Eu (f^7s^2) forms a stable divalent oxidation state, since this then has the stable f^7 configuration, Ce (f^2s^2) forms a stable tetravalent state with the f^0 configuration, etc.)

However, a flaw in the argument of the stability of the f^7 configuration per se has been pointed out (22) in that oxidation states higher or lower than the trivalent state also occur which produce f^6 (valency 2) or f^1 (valency 4) configurations, as though even approach to the f^0 and f^7 configurations results in extra stability. (Because f^7 configurations are extra stable because they have half-filled shell configurations, there is no apparent reason why the f^6 configuration should be more stable than the f^5 configuration.)

If we turn, however, to the variation of the M-O str. with at. no., it is seen that an extra stability is associated with the f^6 configuration, as is also evidenced by the low C=O str. frequency for the acetylacetonate of the d^6 configuration ion. The origin of this stabilisation probably lies in the exchange energies which are associated with electrons of parallel spin (19). The exchange energy is given by (19) the expression

$$E = NK$$

where E is the exchange energy, K is a constant, and n is the number of distinct pairs of electrons having parallel spins. In configurations in which the number of f-electrons is less than, or equal to 7, the number of pairs of electrons having parallel spins is given by $(n - 1)!$ (where n = the number of f-electrons), while with more than 7 f-electrons, the number of pairs having parallel spins is given by

$$N = (n - 8)! + 21$$

so that the exchange energy of the various configurations are given by NK where N for the M^{3+} lanthanides is as below

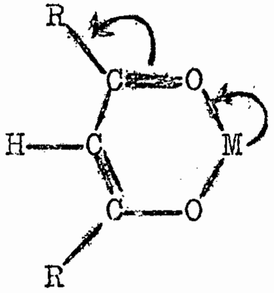
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
n =	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
N =	0	0	1	3	6	10	15	21	21	22	24	27	31	36	42

It is therefore seen that a node results at the f^7 configuration, which possibly accounts for the node observed in the variation of the M-O str. with at. no. at the f^7 configuration in the trivalent rare-earth tris(acetylacetonates). Similarly, the stability of the f^6 configuration is accounted for by this idea.

The generally high C=O str. and low M-O str. frequencies observed for rare-earth acetylacetonates are consistent with the small π and σ interactions expected for these complexes, as evidenced also by the close resemblance of their UV spectra to those of the free ions.

7. The effect of change of 1,3-substituent on the beta-diketonate IR spectrum

As was discussed in section 3.C., the band at 455 cm^{-1}, and the corresponding bands in other beta-diketonates (band 4, assigned to **M-O** + C-R str.) appears to be the most reliable for the purposes of examining the effects of change of 1,3- substituent on the beta-diketonate spectrum, for the reason that the M-O str. is coupled to the C-R str., which both should exhibit parallel shifts on change of 1,3- substituent, as indicby the electron shifts



while the M–O str. itself was inconvenient for use in studying the effect of change of 1,3- substituent, because of the coupling of this band to ring def. vibrations which also occur in the same region as the M–O str. frequency.

In the Table below we see M–O + C–CH_3 str., the M–O str., and stability constant data for the complexes NiL_2 and CuL_2, where L = DBM, Bzac, Acac, TFA and HFA. (cm^{-1}). M–O_4 str. is the M–O + C–R str.

Complex	log K_1K_2[a]	M–O str.	M–O_4 str.	C=O str.
$Cu(DBM)_2$	24.94	658	465	1549
$Cu(Bzac)_2$	23.01	629	459	1562
$Cu(Acac)_2$	23.66	615	455	1580
$Cu(TFA)_2$	17.20	534	445	1616
$Cu(HFA)_2$	–	520	415	1655
$Ni(DBM)_2$	20.72	–	458[a]	1544[a]
$Ni(Bzac)_2$	18.00	–	455[a]	1554[a]
$Ni(Acac)_2$	17.08	593	437	1598
$Ni(TFA)_2$	14.02	497	431	1637
$Ni(HFA)_2$	–	–	397[a]	1644[a]

[a] ref. 55.

It is seen that the variation of both the M–O str. and M–O + C–R str. (which we shall refer to in future as the M–O_4str.) indicates the same order of increase of stability for these complexes on change of 1,3-substituent as is indicated by stability constant data for these complexes (viz. HFA < TFA < Acac < Bzac < DBM). The reason for this variation is most likely to be found in the electron shifts indicated on page 272 for beta-diketonate complexes on change of 1,3- substituent.

Recently Swain and Lupton (69) have shown that a substituent effect (σ) may be expressed in the form

$$\sigma = fF + rR$$

where F and R are field and resonance parameters, and f and r are coeeficients which determine the relative weightings of the field and resonance effects appropriate to the system being examined.

The weighting factors appropriate to the beta-diketonate system are not known, but it is seen in the Table below that for the complexes of the K^+ and Al^{+++}

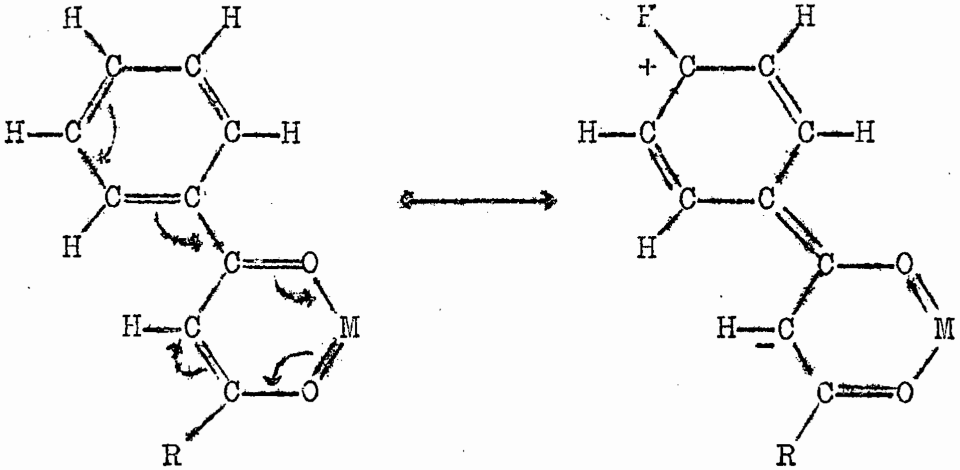
ions the order of increase of the M-O_4str. is approximately the same as the order of decrease of both F and R for the different substituents.

Table 16

Field and resonance contributions of 1,3 substituents of beta-diketonates of Al(III) and K(I) compared with M-O_4str. (cm^{-1}) for these complexes.

Substituents				M-O_4str.	
R_1	R_2	$F_{R1} + F_{R2}$	$R_{R1} + R_{R2}$	Al^{+++}	K^+
CH_3	CH_3	-0.10	-0.28	493	412
CH_3	Ph	0.09	-0.23	472	404
Ph	Ph	0.28	-0.18	455	355
CH_3	CF_3	0.58	0.05	464	387
CF_3	CF_3	1.26	0.38	424	364

However, if we examine the order of decrease of the M-O_4str. in complexes of these ligands with TM's, the complexes of the phenyl-substituted ligands appear to be stabilised relative to those of acetylacetone, rather than destabilised, as in non-TM complexes. We may interpret this as the weighting of the F and R components of σ being altered to favour the resonance (R) component, since the d-orbitals present the possibility of the additional canonical structures below, which are not possible with non-TM's where no d-orbitals are energetically available for π -bonding



We thus find that in TM beta-diketonates, the order of increase of the $M-O_4$ str. is HFA < TFA < Acac < Bzac < DBM, compared to the order DBM < HFA < TFA < Bzac < Acac. in non-TM's.

We may rationalise this data in terms of the weightings of F and R as follows. We suppose that in non-TM beta-diketonates, the resonance contribution to stabilisation (r) is always less than 25%, with the field contribution (f) being more than 75%. In TM complexes, however, a high degree of resonance is possible in phenyl-substituted forms, so that f and r should have values of about 25% and 75% respectively in the Bzac complexes, and 0% and 100% in the DBM complexes respectively. Using these f and r values, σ for these various types of complex shows an inverse relationship with the concomitant $M-O_4$ str. frequencies.

Table 17

Field and resonance contributions, σ and the $M-O_4$ str. (cm^{-1}) in a non-TM (Al^{+++}) compared with a TM (Cu^{++}).

Complex	f (%)	r (%)	σ	$M-O_4$ str.
$Al(Acac)_3$	100	0	−0·10	493
$Al(Bzac)_3$	100	0	0·09	472
$Al(DBM)_3$	100	0	0·28	455
$Al(TFA)_3$	100	0	0·58	464
$Al(HFA)_3$	100	0	1·26	424
$Cu(DBM)_2$	0	100	−0·18	465
$Cu(Bzac^2)_2$	25	75	−0·15	459
$Cu(Acac)_2$	75	25	−0·10	455
$Cu(TFA)_2$	75	25	0·45	445
$Cu(HFA)_2$	75	25	1·04	415

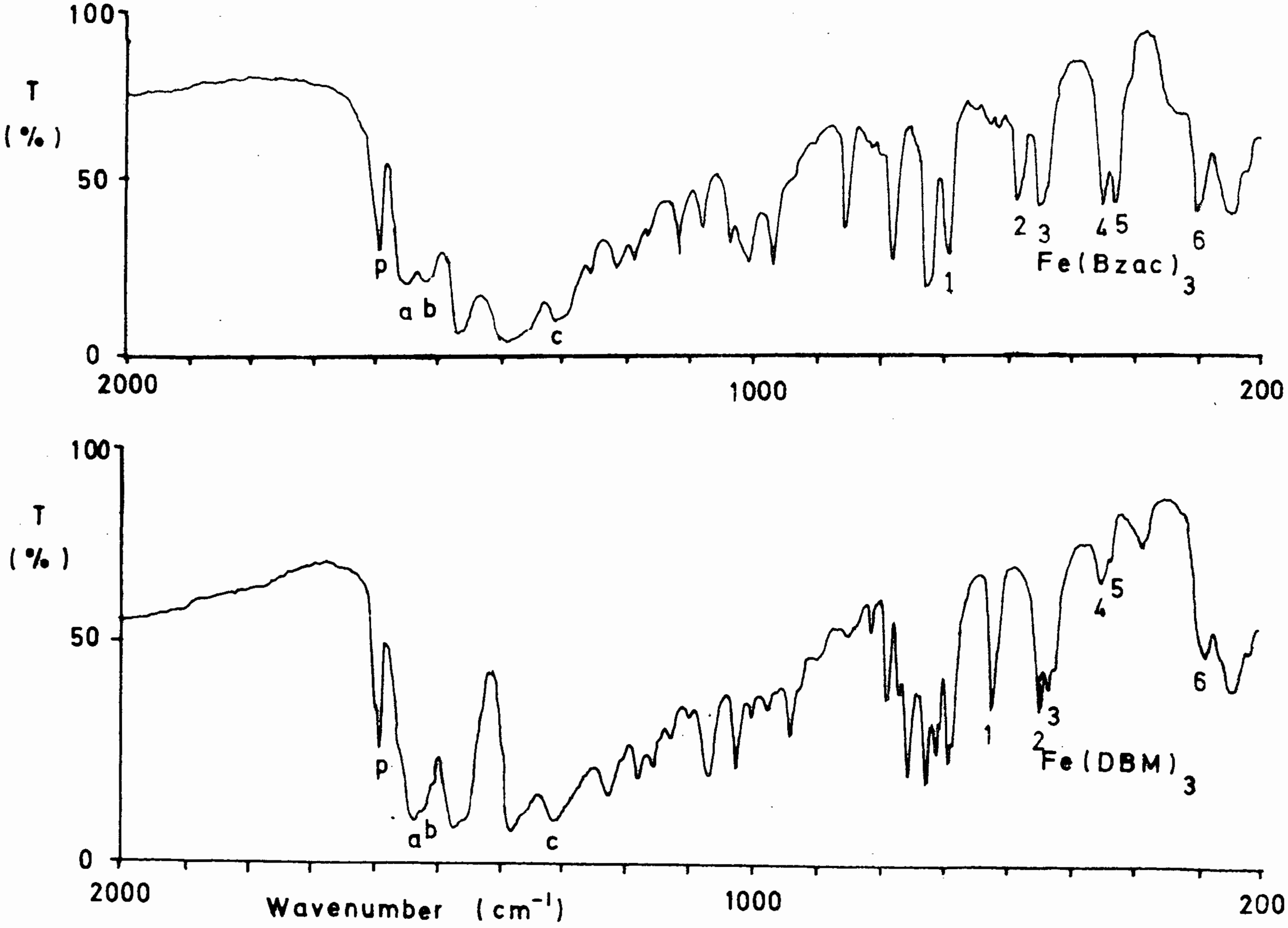


Fig. 36. Spectra of Fe(Bzac)$_3$ and Fe(DBM)$_3$ an the region 200 - 2000 cm^{-1}.

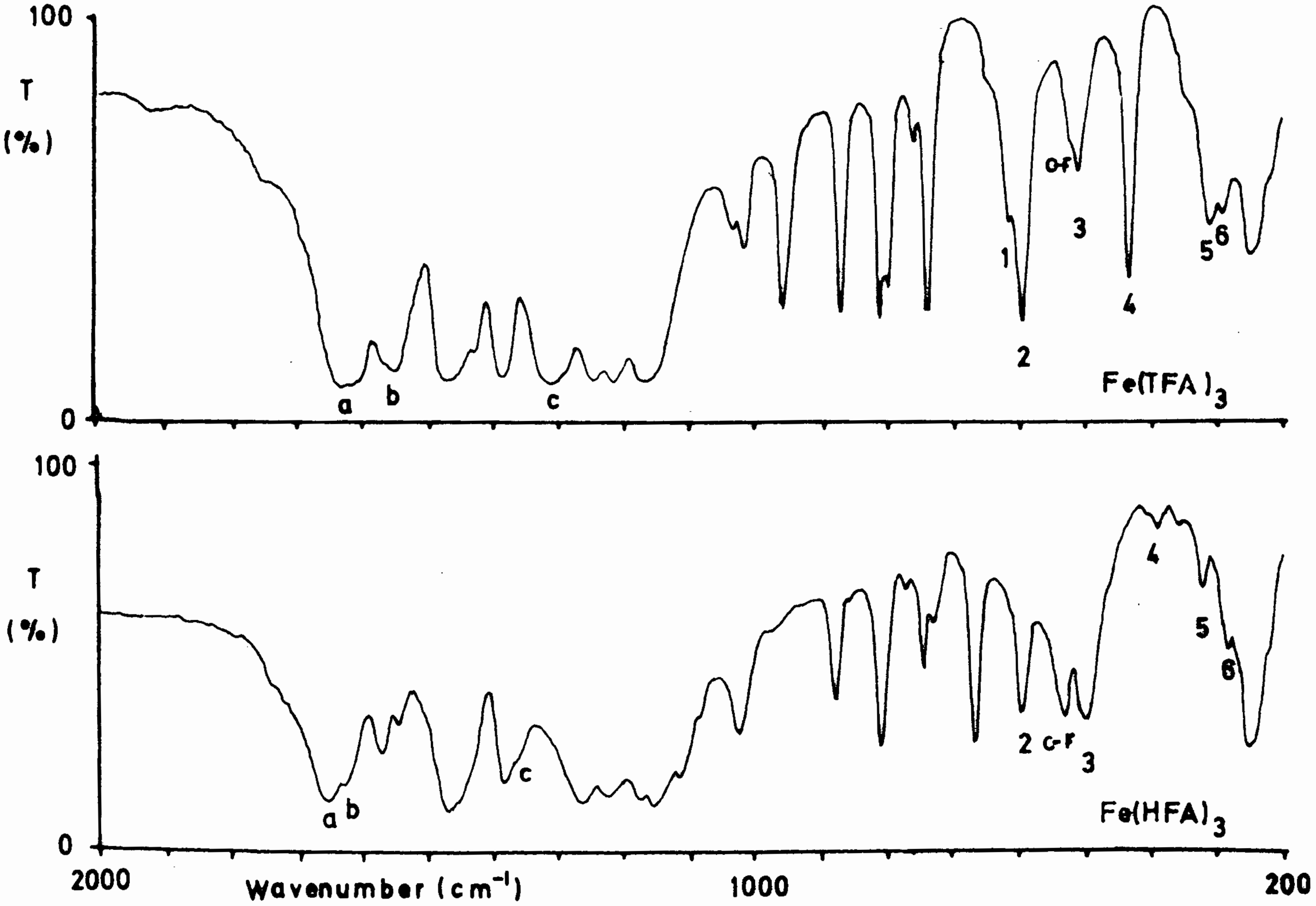


Fig. 37. Spectra of Fe(TFA)$_3$ and Fe(HFA)$_3$ in the region 200 - 2000 cm^{-1}.

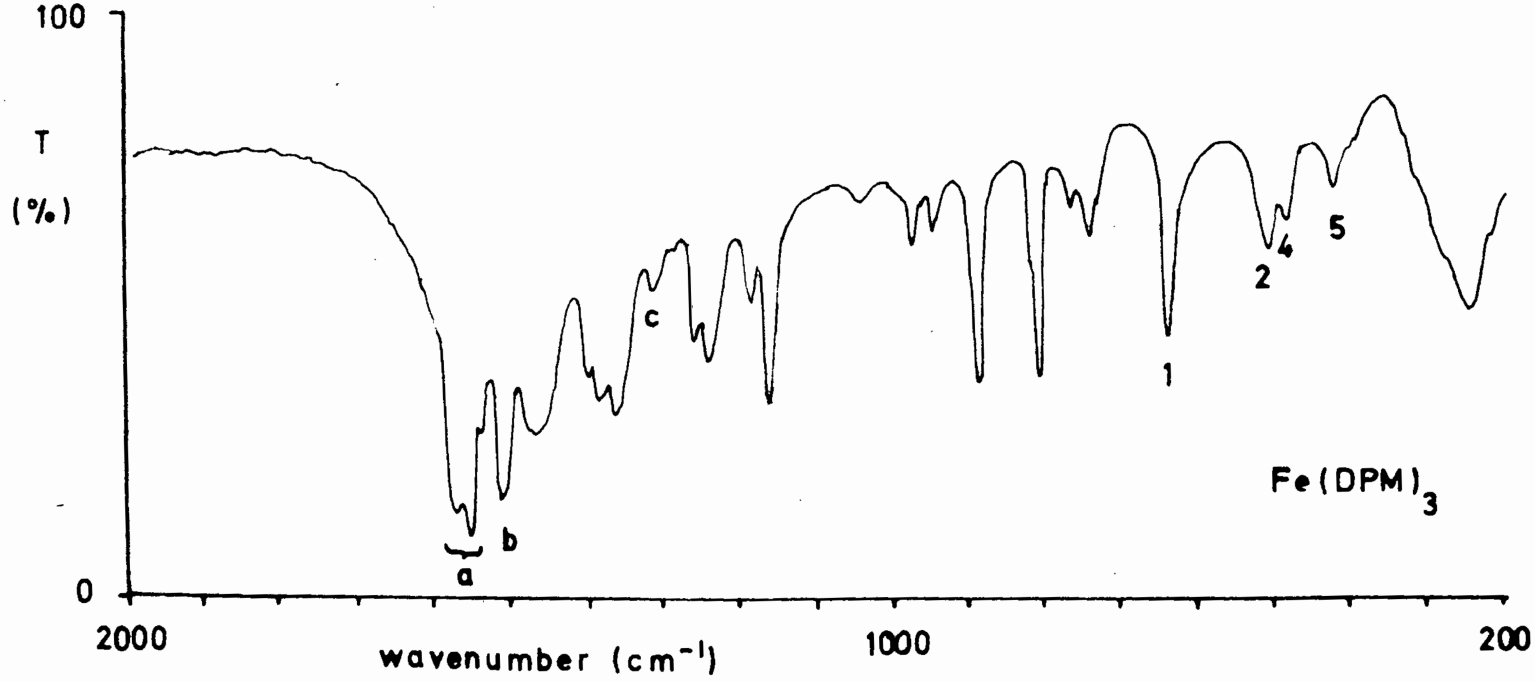


Fig. 38. Spectrum of Fe(DPM)$_3$ in the region 200 - 2000 cm^{-1}.

It is possible to adjust the f and r coefficients for the TFA and HFA complexes of Al(III) and K(I) so as to lower σ to a lower value than in the DBM complexes of these two ions. This would then fit the observation that the M–O_4str. is higher in the TFA complexes of AL(III) and K(I) than in the DBM complexes. However, it would involve raising the resonance contributions to σ in the TFA and HFA complexes to 75% and 100% respectively, which seems extremely unlikely. (There is no reason why trifluoromethyl groups should be able to enhance resonance in non-TM complexes, as compared with resonance in phenyl substituted forms.) It is more probable that the magnitude of F for the phenyl group has been underestimated.)

The effect on the M–O_4str. of change of 1,3-substituent is illustrated in Fig. 39, where the effect of change of metal type from TM to non-TM is also seen. There is a marked change-over from upward to downward slope in the series Acac, Bzac, DBM on change of central cation from TM to non-TM. The greater the upward slope, the greater is the stabilisation of the complex

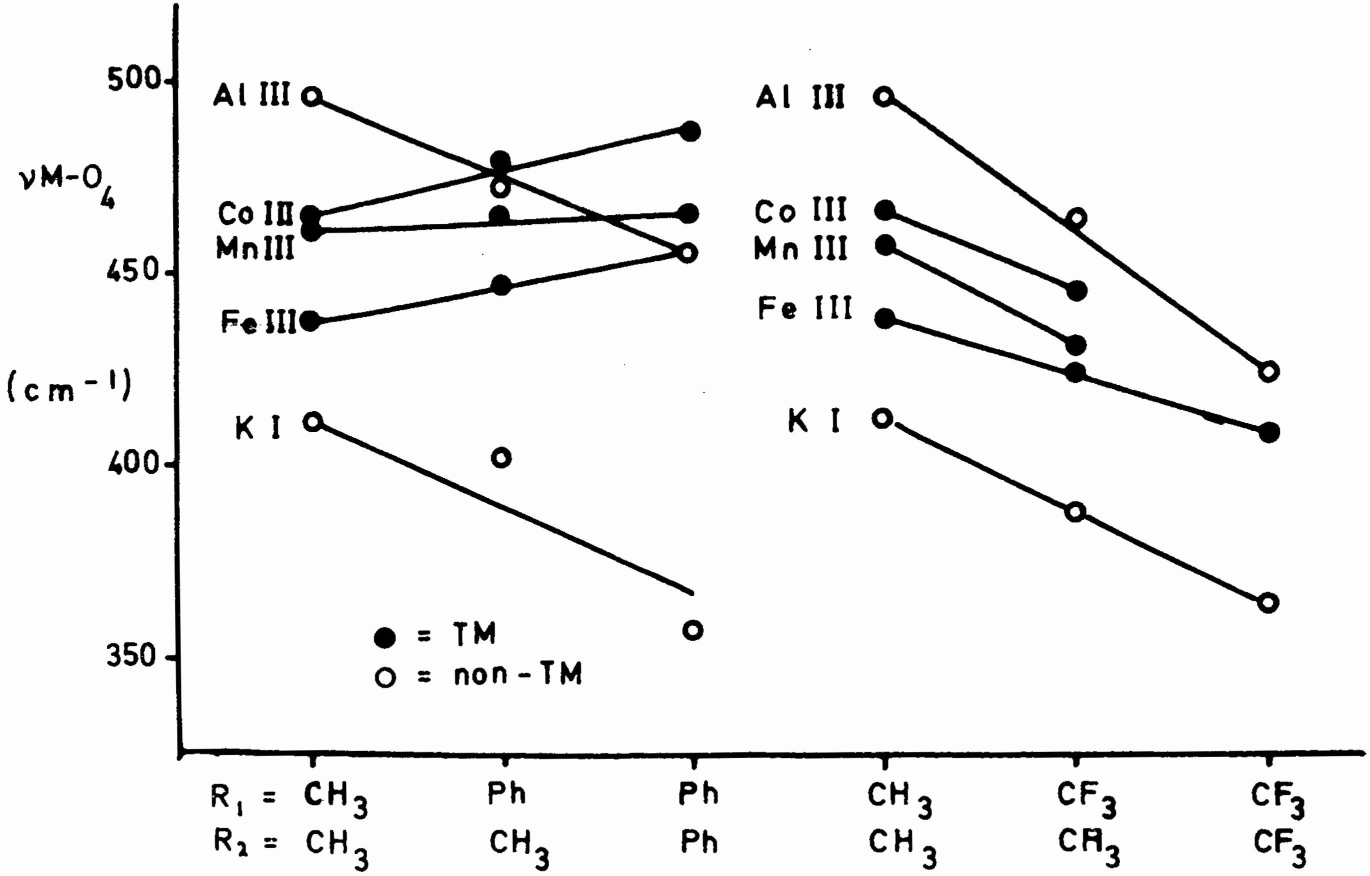


Fig. 39. Effect of successive substitution of (a) phenyl (b) trifluoromethyl groups for methyl groups on $\nu M\text{-}O_4$ in the β-diketonate IR spectrum.

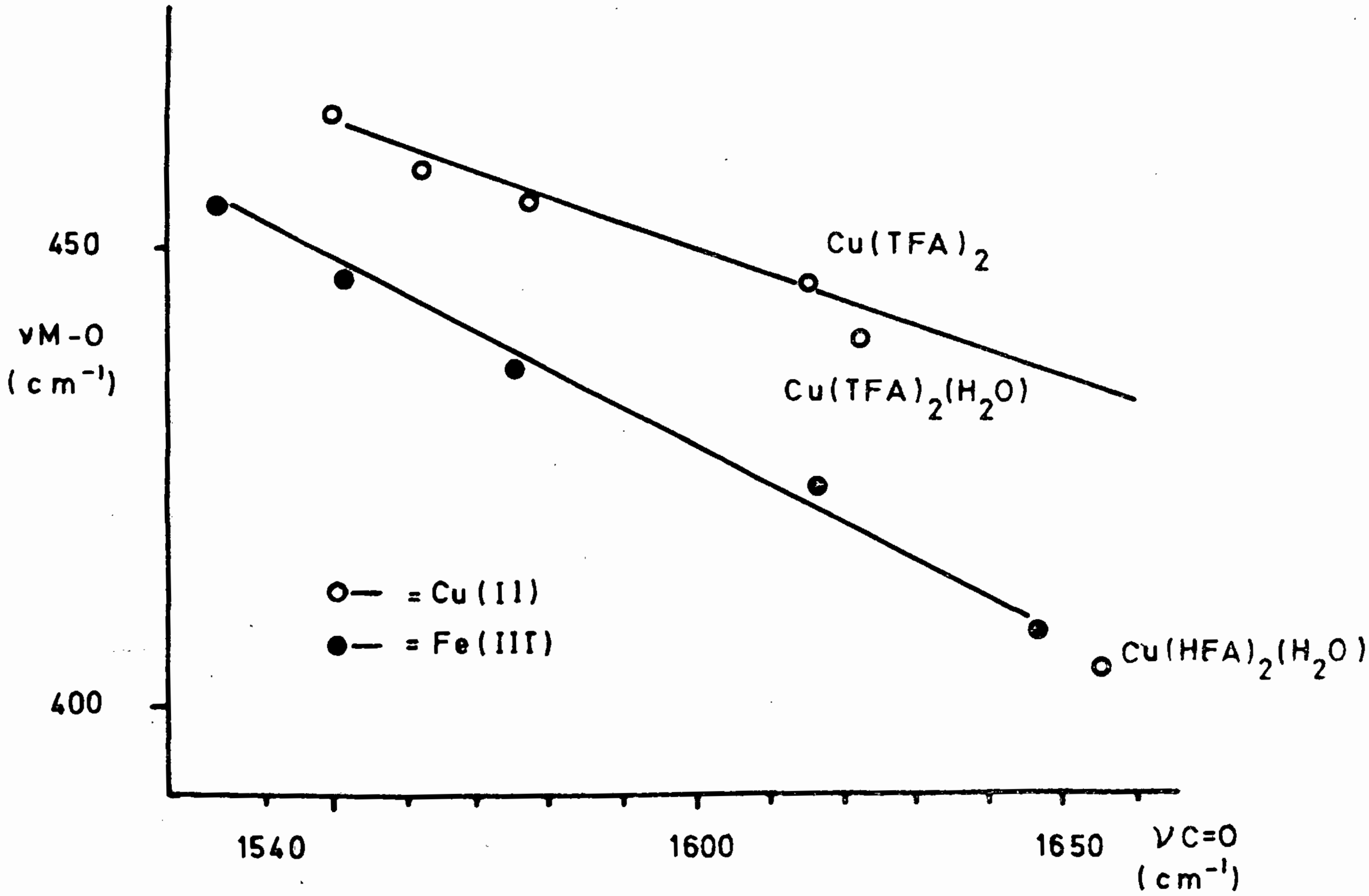


Fig. 40. Variation of νM-O with νC=O in Fe(III) and Cu(II) β-diketonates on change of 1,3-substituent.

resulting from phenyl substitution.

It is noticed that the upward slope in the series Acac $<$ Bzac $<$ DBM is steepest in the Co(III) ion, indicating the greatest π-interaction between this ion and the beta-diketonate ring, which is in agreement with previous observations on the extent of π-bonding in the beta-diketonate complexes of this ion. Further, it is noticed that the upward slope Acac $<$ Bzac $<$ DBM is least steep in the Mn(III) complexes, which agrees further with our observations on the poor π-bonding ability of this ion.

Similarly, in the series Acac $>$ TFA $>$ HFA, it is noticed that the destabilisation of the complex is least with the TM ions. Moreover, in Mn(III), the downward trend indicated (the HFA complex of Mn(III) was unfortunately not prepared) appear to be as steep as those observed in non-TM's, supporting once more the idea of weak π-bonding in this ion.

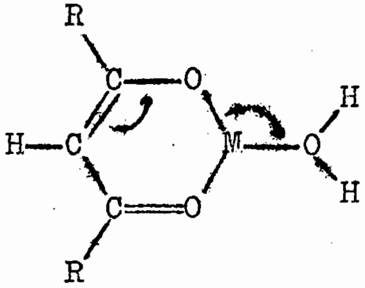
It is noticed that reasonably good linear relationships are observed between M-O_4 str. and C=O str. on change of 1,3- substituent. (Fig. 27). This linearity is however, broken by a change in structure along the series. Thus we observe that, whereas the relationship of M-O_4str. with C=O str. is linear for the complexes Fe(DBM)$_3$, Fe(Bzac)$_3$, Fe(Acac)$_3$, Fe(TFA)$_3$ and Fe(HFA)$_3$, with the analogous Cu(II) series Cu(DBM)$_2$, Cu(Bzac)$_2$, Cu(Acac)$_2$, Cu(TFA)$_2$ and Cu(HFA)$_2$(H_2O), the M-O_4str. for the latter complex is much lower than would be expected from interpolation of the best straight line through the points for the other complexes.

Further, we see that the point for the complex Cu(TFA)$_2$(H_2O), is lowered relative to M-O_4 str. for the anhydrous complex. However, the lowering is not as large as would be expected by comparison with the extremely low M-O_4str. observed for Cu(HFA)$_2$(H_2O). This may be explained in terms of the relative polarisability of the oxygen atom in the HFA complex, and in other complexes.

In most beta-diketonate anions, the polarisability of the oxygen atoms coordinated to the metal is greater than the polarisability of the oxygen atom of the water molecules, so that the water molecules are less firmly bound. However, the polarisability of the oxygen atom of the water molecule is greater than those on the HFA$^-$ anion, as is evidenced by the fact that hexafluoroacetylacetona complexes (107) may be hydrolysed by water, as is found in the Mn(III) complex, which may be hydrolysed by water from the atmosphere

$$Mn(HFA)_3 + 12H_2O \longrightarrow Mn(H_2O)_6^{+++} + 3(HFA.2H_2O)^*$$

This suggests that the electron shift below



which is not very large in $Cu(TFA)_2(H_2O)$, is of paramount importance in $Cu(HFA)_2(H_2O)$, accounting for the extremeky low $M\text{-}O_4$str. By comparison, we see that the water in $Cu(TFA)_2(H_2O)$ is lost on standing at room temperature, while $Cu(HFA)_2(H_2O)$ may be sublimed <u>in</u>

vacuo without loss of coordinated water.

CONCLUSIONS

We have come to the conclusion that the variation of M-L frequencies in the IR spectra of TM complexes may be rationalised in terms of the CFT. Where variations from CFT predictions are observed, these may be attributed to two main effects;

(1) π-bonding. Strong π-bonding encountered in low-spin ions, as in $Co(Acac)_3$ and $Rh(Acac)_3$, or $[Mn(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$, causes M-L str. frequencies higher than predicted by the CFT, while very weak π-bonding, as encountered in Mn(III) beta-diketonates, may cause lower M-L str. frequencies than expected from CFT.

(2). Differences in structure across a series of TM complexes, as was seen in the square-planar or tetragonally distorted complexes of Mn(III) and Cu(II).

Further, it was found that the effects on change of 1,3- substituent could be rationalised in terms of the electron-withdrawing powers of the 1,3- substituent. The phenyl group was found to vary in its effect on the stability of the complex, having a destabilising effect on the complexes of metals in which π-bonding was not possible, but having a stabilising effect on the complexes of metals in which π-bonding was strong.

It was further found possible to rationalise the variation of M-L frequencies of non-TM complexes in terms of their ionic radii, and the charge on the central cation. The variation of the M-L frequencies in the tris(acetylacetonates) of rare-earth trivalent ions were rationalised in terms of the concomitant variations of the exchange energy across the series.

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