# PHYSICAL METHODS APPLIED TO COORDINATION COMPOUNDS

by

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# CONTENTS

# ABBREVIATIONS

| | |
|---|---|
| AcacH | acetylacetone |
| Acac | acetylacetonate anion |
| Am | Primary aliphatic amine or amines in general |
| An | primary aromatic amine |
| asym. | asymmetric or antisymmetric |
| Bipy | bipyridine |
| Bu | butyl |
| Cx | cyclohexyl |
| dipy | 2,2′-dipyridyl |
| Et | ethyl |
| Im | imide |
| IR | infrared |
| L | ligand |
| m.p. | melting point |
| M | central metal atom in compound |
| Me | methyl |
| N.M.R. | nuclear magnetic resonance |
| Ph | phenyl |
| PhthH | phthalimide |
| Phth | anion of same |
| Pr | propyl |
| py | pyridine |
| R | alkyl or aryl group |
| str. | infrared stretching frequency |
| SuH | succinimide |
| Su | anion of same |
| sym. | symmetric |
| T.M.S. | tetramethylsilane |
| UV | ultraviolet |
| X | halogen |

# INTRODUCTION

The substituent constant, $\sigma$, is a measure of the sum of the inductive (or field) and mesomeric (or resonance) effects of substituents in aromatic molecules. They were determined by Hammett[1] in the following manner. Linear relationships were found to apply to the rate and the equilibrium (dissociation) constants of practically all side chain reactions of benzene derivatives *e.g.* the logarithms of the rate constants for alkaline hydrolysis of substituted ethyl benzoates and the dissociation constants of substituted benzoic acids follow an equation of the form :

$$\log k = \rho \log K + C \qquad (1)$$

where k = rate constant, K = dissociation constant, $\rho$ = slope and C = intercept.

Equation (1) can be modified:

$$\log k = \rho (\log K - \log K^{o}) + (\rho \log K^{o} + C) \qquad (2)$$

where $K^{o}$ = dissociation constant of the unsubstituted acid (benzoic acid itself). The quantity ($\rho \log K^{o} + C$) is necessarily equal to $\log k^{o}$, where $k^{o}$ is the rate constant for the saponification of ethyl benzoate itself.

Therefore from equation (2) :

$$\log k - \log k^{o} = \rho (\log K - \log K^{o}) \qquad (3)$$

This equation relates to any rate or equilibrium process, but it is convenient to relate all other reaction series to the dissociation of benzoic acids (*i.e.* K).

The substituent constant, $\sigma$, is defined as follows :

$$\sigma = \log K - \log K^{o} \qquad (4)$$

Thus equation (3) becomes :

$$\log k - \log k^{o} = \rho \sigma \qquad (5)$$

Equation (4) is more frequently written as :

$$\log k/k^{o} = \rho \sigma \qquad (6)$$

Equation (6) is the Hammett Equation.

The substituent constant, $\sigma$, is determined by the nature of the substituent and is normally independant of the nature of the reaction. Conversely the reaction constant, $\rho$, is a constant for all substituents but dependant on the nature of the reaction.

The substituent constant is thus a measure of the electron-withdrawing or electron-releasing power of a group relative to hydrogen, i.e. electron-withdrawing groups have positive and electron-releasing groups have negative substituent constants. Ortho-substituents do not have reliable substituent constants because of steric interference to the reaction imposed by the ortho-groups.

Although the majority of reaction series follow the relationship :

$$\log k/k^{o} = \rho\,\sigma$$
$$\text{or } \log K/K^{o} = \rho\,\sigma$$

sometimes certain substituents lie well off the plot of $\log k/k^{o}$ vs. $\sigma$. In these cases effective substituent constants ($\bar{\sigma}$) for that particular reaction series may be calculated by drawing the best straight line through the points for normally behaving substituents, determining the slope and calculating $\bar{\sigma}$ from :

$$\bar{\sigma} = \log \frac{k}{k^{o}} / \rho$$

For normally behaving substituents ($\sigma - \bar{\sigma}$) is small and for abnormally behaving substituents ($\sigma - \bar{\sigma}$) is large.

Since the substituent constants represent a combination of inductive and mesomeric effects, they cannot be used for aliphatic molecules. However Ingold[2] suggested that as a measure of the purely polar (inductive) effects a comparison be made of the relative rates of hydrolysis in acidic and alkaline media of aliphatic esters, $RCOOR'$ (i.e. where the mesomeric effects have been eliminated). Since the attacking species in acidic solution is $H^{+}$ and in alkaline solution $OH^{-}$ and since mesomeric effects in the aromatic sense are not possible with aliphatic compounds, Taft[3] proposed the relationship :

$$\sigma^* = \frac{1}{2.48} \log \frac{k^B/k^B_o}{k^A/k^A_o}$$

where $k^B$, $k^A$ are respective rate constants for the base and acid hydrolysis of the substituted ester and $k^B_o$, $k^A_o$ are respective rate constants for the base and acid hydrolysis of the unsubstituted ester. The factor 2.48 is introduced as an arbitary constant to scale the $\sigma^*$ values to a magnitude roughly approximating those of $\sigma$. The rate constants of substituted acetic acid esters were used to calculate the polar substituent constants, thus the reference standard is not $k^o$ for R = H but $k^o$ for R = $CH_3$ in this case.

Infrared spectroscopy has been extensively applied to free substituted aromatic, heterocyclic and aliphatic amines and correlations between the substituent constants and the N-H stretching frequencies have been found to exist. Flett[4] studied the infrared spectra of a number of substituted anilines in $CCl_4$. In each case two N-H bands were observed corresponding to the symmetrical stretching mode at approximately 3400 $cm^{-1}$ and the antisymmetrical mode at approximately 3500 $cm^{-1}$. He observed that as the substituent constant increases in a positive sense, the N-H bonds are strengthened (increase of the N-H frequency) probably as a result of pulling the hydrogen atoms closer to the nitrogen atom with development of a positive charge on it.

Similar work was carried out by Krueger and Thompson[5], also on the infrared spectra of substituted anilines. A plot of the N-H vibrational frequencies of both the symmetric and antisymmetric modes against the Jaffe[6] substituent constants of the amines, showed a slight curvature and would become more linear if the square of the frequency was plotted rather than the frequency itself. In agreement with Flett, the frequencies increased with increasing substituent constant (i.e. from negative to positive $\sigma$). The trend observed for the N-H frequencies with substituent constant is however the converse of that found for the OH stretching vibration in substituted phenols[7]. The N-H frequency trends are contrary to what would be expected because the amino hydrogen has no electrons available for increasing the N-H bond multiplicity and thus the stability and stretching frequencies of the N-H bond. As the reported spectra were determined in solvents such as $CHCl_3$ and $CCl_4$ it is conceivable that the electron-withdrawing substituents may cause a drift of electrons into the N-H from the halogen in the hydrogen bonded species N-H····Cl. Spectroscopic evidence for such hydrogen bonding has been found by Fuson et al.[8] who observed that with increase of concentration of the amines in the solvents, $CCl_4$, $CS_2$ and $CHCl_3$ caused the sharp N-H stretching band to fade out and a broader band at a lower frequency to appear.

The N-H stretching vibrations of aliphatic primary amines have been examined by Krueger and Smith[9] and correlations with Taft polar substituent constants gave trends similar to those found for aromatic amines.

Their explanation of these trends was that as the inductive electron-donation power of the alkyl group increases, the apparent electronegativity of the N atom decreases because of increased electron density consequently binding the H atoms less firmly resulting in a lowering of the bond strengths and hence stretching frequencies. This explanation also serves to explain the observations of Flett[4] and Krueger and Thompson[5] with respect to aromatic amines.

Correlations of the nuclear magnetic resonance (N.M.R.)chemical shifts of the amino protons of amilines with the substituent constants have also been reported[10,11]. Dyal[10] reported that linear correlations were found to exist in acetonitrile, carbon tetrachloride and deuterochloroform with a slope which indicated that electron-releasing substituents provide increased shielding of the amino protons giving rise to a paramagnetic or upfield shift relative to aniline itself and electron-withdrawing substituens deshield these protons giving rise to a diamagnetic or downfield shift in the expected manner.

There have therefore been many studies of substituted organic compounds and correlations have been found between substituent constants and group frequencies or chemical shifts but there have been few similar studies applied to series of coordination compounds containing organic ligands individual members of which differ only in the substituent on the ligand. Gill and Kingdom[12] have recorded the infrared spectra of a series of metal halide complexes with substituted pyridines in the region 1600 - 200 $cm^{-1}$. The study showed that there was no simple explanation for the shifts observed.

A number of complexes of divalent metal halides with aniline and substituted anilines have been previously reported in the literature[13-19]. Some spectroscopic studies have been reported[20,21], ultraviolet and far infrared spectra were recorded and the spectra were used to determine the probable coordination arrangement about the metal ions. Spectroscopic support for X-ray structural evidence[15] of tetrahedral coordination in complexes of zinc(II) halides with substituted anilines was obtained[20]. Assignments of metal to halogen vibrations were suggested and probable metal to nitrogen sensitive vibrational absorptions were also proposed. Probably the most conclusive report on the assignments of infrared absorption bands in this type of complex was that given by Jungbauer and Curran[22]. The spectra of N-deuterated aniline complexes of various metal halides were compared with those of the undeuterated complexes. The fundamental N-H modes could thus be assigned since deuteration caused these bands to shift to lower frequencies as a consequence of the replacement of the amino hydrogens with heavier deuterium atoms. Two metal to chloride absorption bands in the aniline complex of zinc(II) chloride were assigned to the bands at 295 and 284 $cm^{-1}$ corresponding, respectively, to the antisymmetric and symmetric stretching vibrations, as these bands disappear in the corresponding zinc(II) bromide or zinc(II) iodide complexes. A M-N sensitive vibration was also assigned to the band in the 450 - 370 $cm^{-1}$ region, although the frequencies were somewhat higher than expected.

There have however been many other studies on coordination compounds of this type concerning their stability constants. Pauling[23] has explained the stability of certain complexes on the basis of metal-ligand double bonding. He suggested that the transition elements can use, for multiple bonding, lower energy d-orbital electrons which are not available in the non-transition metals. Although there is at present no direct proof of metal-ligand $\pi$-bonding in amine complexes and although such $\pi$-bonding would not be anticipated on theoretical grounds, several experimental observations have been rationalised on this basis. Da Silva and Calado[24] determined the stabilisation factors ($S_f$) for a series of silver(I) aniline complexes. $S_f$ is defined by :

$$S_f = \log \frac{\beta^{ML'}/\beta^{HL'}}{\beta^{ML}/\beta^{HL}}$$

where $\beta^{ML'}$, $\beta^{ML}$ are the stability constants of the complexes of the substituted (L′) and unsubstituted (L) ligands and $\beta^{HL'}$, $\beta^{HL}$ are the respective ligand association constants. $S_f$ is related to the substituent constant, $\sigma$, thus :

$$S_f = \sigma\rho'$$

where $\sigma$ and $\rho'$ have the same significance as in the Hammett equation.

$S_f$ plotted against the substituent constant gave a linear relationship with a positive slope, which is surprising as it is the inverse of the slope of pK(-log dissociation constant) plotted against $\sigma$. The positive slope measures the susceptibility of the reaction to changes in the substituents and can only mean that the reaction studied is favoured by electron withdrawal from the metal ion and thus the stabilisation measured by $S_f$ is due to back donation of d-electrons of the metal to the antibonding orbitals of the ligand to form $\pi$-bonds. Murmann and Basolo[25] found that the stability constants of silver(I) complexes of some 3- and 4- substituted pyridines were consistent with the concept of $\pi$-bonding.

Yingst and McDaniel[26] however disagree with the theory that $\pi$-bonding contributes to the stability in certain silver(I) and copper(II) complexes. They demonstrated that the conclusion, viz. that the $S_f$ factor of da Silva measures the stabilisation additional to the $\sigma$-bond formation, hinges on the interpretation of $S_f$, by considering several systems where $\pi$-bonding may be assumed to be absent e.g.

aliphatic amine complexes of silver(I). They found the similar inverse relationship obtained for $S_f$ and base strengths as did da Silva and concluded that the inverse relationship is not support for $\pi$-bonding. They do not however attempt to explain the additional stabilisation. Furthermore, their results may merely imply that the anomalous stabilisation experienced in aniline complexes may also occur in aliphatic amine complexes and that, although formally impossible, $\pi$-bonding may be the explanation in both cases.

The reason why $\pi$-bonding is assumed to be impossible between a transition metal ion and ligands such as aliphatic and aromatic amines is that the nitrogen donor atomic orbitals are $sp^3$ hybridised and hence have not the correct symmetry for overlap with the $t_{2g}$ orbitals of the metal ion (strictly only $t_{2g}$ in the case of octahedrally coordinated metal ions), so that $\pi$-bonding based on a molecular orbital approach is not possible. Nevertheless this reasoning appears too rigid since it assumes 100% $sp^3$ hybridisation of the nitrogen donor, a situation which is unlikely to be precisely realised in practice.

Because of the anomalous stabilities of aniline complexes, it was considered that a study of the infrared spectra of a large series of substituted aniline complexes of a single metal ion, zinc(II) would help to shed some light on the mechanism of bonding in these molecules.

The preparation of aliphatic amine complexes of copper(II) succinimide were first reported by Tschugaeff[27]. The molecular formula of these complexes was found to be $[CuSu_2Am_2]$ on the basis of percentage composition and molecular weight measurements. The decomposition of these complexes in aqueous solution was also investigated and led to the following reaction pattern :

$[CuSu_2Am_2]$ (copper-red) $[CuSu_2Am(H_2O)_3]$ (blue-violet) or
$[CuAm(H_2O)_3]Su_2$ $[Cu(H_2O)_6]Su_2$ (bright blue).

A number of similar complexes have more recently been prepared[28-32]. These included the aliphatic amine complexes of Cu(II), Ni(II), Fe(III) and Mn(III) succinimide and phthalimide. Preliminary investigations concerning their analyses, molecular weights and conductances have been made. Conductance measurements indicated that the complexes were non-electrolytes and hence it was suggested that both the imide ions and the amine ligands are within the coordination sphere. It was stated that it is possible that the imide ion may be bound to the metal ion either through the nitrogen or through the oxygen of the carbonyl group, however the conclusion was reached that coordination is more likely to be through the negatively charged nitrogen (see I and II, page 63). Visible absorption measurements of the copper(II) succinimide complexes were also recorded[32]. A single absorption band in the vicinity of 630 mμ was found for all these complexes.

Infrared spectroscopic measurements were also carried out on the iron(III) phthalimide complexes[29]. These indicated that the reduction in the carbonyl stretching frequency on coordination with iron(III) and further reduction in the amine complexes was due to the corresponding increase in the negative charge on the nitrogen. Infrared spectroscopy was also applied[31] to the aliphatic amine complexes of manganese(III) succinimide. The shifts observed in the N-H stretching frequencies were attributed to the varying molecular weights of the various amines (i.e. to mass effects).

It may be assumed that changing the amine in the complexes would cause some perturbation in the electronic structure of the imide ligands and also some change in the energy levels of the metal ion concerned. Thus a series of copper(II) and nickel(II) succinimide and phthalimide complexes with various primary aliphatic amines were prepared and their infrared spectra and ultraviolet-visible absorption spectra studied. These results have been used to gain information on whether the imide is coordinated through the nitrogen or the oxygen of the carbonyl group and to the nature of the bonding in these molecules.

β-Diketones are known to form stable six-membered chelates with many metals. The acetylacetonates are particularly interesting examples of these complexes. They are derivatives of the enolic form of acetylacetone ($CH_3$-C(OH)=CH-CO-$CH_3$) and a number of metals, in which the primary valency of the metal ion is satisfied by an enolic hydroxide residue and the secondary valency by the oxygen of the carbonyl group.

Some β-diketone complexes of the divalent transition metals form isolable base adducts. Graddon and colleagues[34-38] have studied a series of nitrogenous base adducts of Zn(II), Ni(II) and Mn(II) β-diketonates. They were concerned mainly with the stereochemistry of the metal ion in the molecule. Bis(acetylacetonato)zinc(II) and bis(benzoylacetonato)zinc(II) were found[34] to form 5-coordinate (trigonal bipyramidal) and 6-coordinate (octahedral) complexes with heterocyclic bases (see III, page 79) the latter stereochemistry being relatively unstable and decomposing with time to the former. Other 5-coordinate zinc(II) complexes have also been reported[39] viz. 1 : 1 complexes of primary and secondary aliphatic amines with zinc dialkyldithiocarbamates $\left[Zn(S\text{-}CS\text{-}NR_2)_2\right]$

Nickel(II) complexes of 3-alkylacetylacetones (HL) have been studied[38] and the reaction with nitrogenous bases e.g. pyridine, was shown to give the octahedral adduct $\left[NiL_2py_2\right]$ probably with $\left[Ni_2L_4py\right]$ occurring as intermediate, the corresponding acetylacetone complex, $\left[Ni_2Acac_2py\right]$ has previously been isolated[40]. This behaviour is in contrast to that of the reaction of o-hydroxyarylcarbonyl complexes of nickel(II), which apparently add pyridine to give $\left[NiL_2py_2\right]$ in two steps with the 5-coordinate species $\left[NiL_2py\right]$ as an intermediate[35].

Both mono- and bis-pyridine adducts of bis(acetylacetonate)manganese(II) have been reported[37]. The 6-coordinate compounds were found to be unstable, differing markedly from the corresponding compounds of nickel(II), resembling rather the zinc(II) compounds.

It would be expected that since these metal β-diketonates form adducts with bases such as pyridine, they would equally well form similar complexes with aliphatic and aromatic amines. Ammine adducts of the zinc(II) analogue have actually been prepared[34,35]. The synthesis of a series of various aliphatic and aromatic amine adducts of bis(acetylacetonato)nickel(II) was therefore investigated in this work. Nickel was chosen because of the fact that of the metal ions previously investigated, it formed the most stable 6-coordinate pyridine adduct. A series of aliphatic amine adducts of bis(acetylacetonato)zinc(II) was also prepared and the stereochemical configuration of the zinc ion investigated by means of microanalysis, infrared and nuclear magnetic resonance spectroscopy. It has been found[41] that, in a series of metal β-diketonates, the nature of the substituents in the β-diketone ligand has a direct bearing on the carbonyl and metal to oxygen vibrational frequencies. It was hoped here to show that the changing electronic effects in a series of variously substituted amine adducts of bis(acetylacetonato)nickel(II) and -zinc(II) would produce a correlation with the characteristic group frequencies of the chelate ring.

There have been many reports[42-44] on pyridine adducts of uranyl acetylacetonate. These complexes consist of two molecules of acetylacetone which are co-planar with the uranuim atom. In addition to the two bound "oxo" groups, one molecule of pyridine is bound directly to the uranium(VI) ion to form a 7-coordinate complex of formula $\left[UO_2Acac_2py\right]$. The most significant feature of the infrared spectra of these complexes is the intense band in the region of 900 $cm^{-1}$ which can be correlated with the U=O stretching vibration of the uranyl group.

It was considered that primary aromatic amines would form 1 : 1 adducts with the uranyl acetylacetonate (V, page 105) analogous to the pyridine complexes. A series of amine complexes were prepared and their infrared and nuclear magnetic resonance spectra recorded in the hope of studying the electronic effects induced by the various substituted amines.

# EXPERIMENTAL

## Method of Preparation

### (1) Amine complexes of zinc(II) halides, $\left[ZnX_2An_2\right]$

The coordination compounds were prepared by adding the appropriate primary aromatic amine (2.2 moles) to zinc(II) chloride or zinc(II) bromide (1 mole) in absolute ethanol. The product precipitated immediately or after shaking. The resulting white precipitate was filtered off, purified by recrystallisation from ethanol and dried *in vacuo* at room temperature for 24 hours. This general method was applied to all the amine complexes with substituent constants in the range -0.6 to +0.39, but the high positive substituent constant of the other amine ligands resulted in the complexes being too unstable to precipitate from ethanol. Therefore in these cases, instead of an ethanolic reaction medium, diethylether was used. Purity was checked by analysis for halogen using Volhard's procedure[45] : 0.05 g compound was weighed accurately into a 150 ml conical flask. To the flask was added 10 ml distilled water, 3 ml approximately 5 N nitric acid, 5.00 ml 0.1000 N silver nitrate solution and 1 ml ferric alum indicator. In the case of the chlorides, 2 ml nitrobenzene was also added. The excess silver nitrate was titrated with 0.1000 N ammonium thiocyanate until the first appearance of a permanent reddish-brown colouration. The percentage halide in the sample was calculated and compared with the theoretical percentage calculated on the basis that the complexes are tetrahedral and monomeric. A few of the complexes which had been prepared by others in this laboratory gave analyses of carbon and hydrogen which were in good agreement with those calculated from the empirical formulae.

Melting points were determined on a Kofler hot stage. Details concerning these complexes appear in Table 1.

## (2) Amine complexes of metal imides.

### (a) $[CuSu_2Am_2]$

$$CuCl_2 + 2\ SuH + 4\ Am \qquad [CuSu_2Am_2] + 2\ Am{\cdot}HCl.$$

The complexes were prepared according to the method of Tschugaeff[27], by addition of the primary aliphatic amine (4 moles) to an ethanolic solution of copper(II) chloride (1 mole) and succinimide (2 moles). On addition of the amine, the green solution immediately turned blue and the pink complex precipitated out on standing for a short period. This was filtered off and washed with ethanol and ether. Prolonged sucking caused the complexes to decompose because of their instability to water vapour. Therefore they were quickly transferred to a vacuum drying pistol and dried at room temperature and 0.1 mm Hg pressure for 12 hours.

### (b) $[CuPhth_2Am_2]$

The procedure was identical to that used for the succinimide complexes using phthalimide in place of succinimide. The complexes were pale pink.

### (c) $[NiSu_2Am_2]$

A similar procedure was followed to that described in (a) but

TABLE 1

ANALYTICAL DATA FOR ZINC COMPLEXES, $[ZnX_2(R\text{-}C_6H_4\text{-}NH_2)_2]$

| | X = Cl | | | X = Br | | |
|---|---|---|---|---|---|---|
| R | m.p. (°C) | %Cl calc. | %Cl found | m.p. | %Br calc. | %Br found |
| 4-$NMe_2$ | | | | 190-192 | 32.12 | 31.91 |
| 4-OH | 221-223 | 20.00 | 19.70 | 210-212 | 36.04 | 35.75 |
| 4-OMe | 219-221 | 18.53 | 18.36 | 184-186 | 33.89 | 33.75 |
| 4-OEt | 207-209 | 17.27 | 17.20 | 205-207 | 31.99 | 31.90 |
| 3:4-diMe | 189-190 | 18.73 | 18.68 | 197-198 | 34.18 | 34.11 |
| 4-Me | 235-236 | 20.23 | 20.11 | 183-185 | 36.36 | 36.02 |
| 4-Et | 186-187 | 18.73 | 18.70 | 195-196 | 34.18 | 33.00 |
| 3-Me | 194-195 | 20.23 | 20.21 | 182-183 | 36.36 | 36.19 |
| 4-NHCOMe | 218-221 | 16.24 | 15.93 | | | |
| H | 228-230 | 21.98 | 21.89 | 192-194 | 38.84 | 38.66 |
| 4-Ph | 238-239 | 14.94 | 14.59 | | | |
| 4-F | 228-229 | 19.78 | 19.46 | 204-206 | 35.72 | 35.57 |
| 3-OMe | 192.193 | 18.53 | 18.51 | 179-181 | 33.89 | 33.71 |
| 3-OEt | 215-216 | 17.27 | 17.13 | 193-194 | 31.99 | 31.91 |
| 4-Cl | 203-205 | 18.12 | 17.89 | 185-186 | 33.27 | 33.20 |
| 4-Br | 158-160 | 14.76 | 14.51 | 184-185 | 28.08 | 28.01 |
| 3-Cl,4-Me | 225-226 | 16.90 | 16.84 | 198-200 | 31.44 | 31.09 |
| 4-COOH | 198-199 | 17.27 | 16.93 | | | |
| 4-I | 202-203 | 12.35 | 12.21 | 196-197 | 24.10 | 23.87 |
| 3-F | 214-215 | 19.78 | 19.60 | 194-196 | 35.72 | 35.61 |
| 3-I | 234-235 | 12.35 | 12.31 | 205-207 | 24.10 | 24.01 |
| 3-Cl | 203-205 | 18.12 | 17.95 | 185-186 | 33.27 | 32.87 |
| 3-Br | 204-206 | 14.76 | 14.56 | 194-196 | 28.08 | 27.82 |
| 4-COPh | 169-171 | 13.36 | 13.11 | 165-167 | 25.79 | 25.74 |
| 4-COMe | 176-177 | 17.44 | 17.09 | | | |
| 4-COOEt | 209-210 | 15.20 | 14.91 | | | |
| 4-CN | 202-203 | 19.03 | 18.88 | 195-197 | 34.63 | 34.46 |
| 3-$NO_2$ | 185-186 | 17.19 | 16.90 | | | |

nickel(II) chloride was used instead of copper(II) chloride. The complexes were pale yellow.

(d) $\left[NiPhth_2Am_2\right]$

The procedure was similar to that used for the nickel(II) succinimide complexes, but phthalimide was used instead of succinimide. The complexes were pale orange-yellow.

Melting points were determined on a Kofler hot stage for the copper(II) series; the nickel(II) series all had m.p.'s >360°C. Details concerning these complexes appear in Tables 2, 3 and 4.

### (3) Amine adducts of metal β-diketonates.

(a) $\left[NiAcac_2Am_2\right]$

The metal chelate amine adducts were prepared from the diaquo adduct of bis(acetylacetonato)nickel(II) which was prepared as follows :

$$Ni(NO_3)_2 + 2\ AcacH + 2\ H_2O \qquad \left[NiAcac_2(H_2O)_2\right] + 2\ HNO_3$$

To an aqueous solution of nickel(II) nitrate (1 mole) and acetylacetone (2 moles), 25% sodium hydroxide solution was added to raise the pH of the solution. The resulting green precipitate was filtered off, washed with water and methanol and dried *in vacuo* at 50°C.

The amine adducts were prepared by recrystallising the above complex from the appropriate amine. The pale blue amine complexes were filtered off, washed with ether and dried *in vacuo* at room temperature for a few hours. All the liquid amine adducts were prepared by this method. The solid aromatic amines were first dissolved in methanol.

## TABLE 2

ANALYTICAL DATA FOR COPPER(II) COMPLEXES, $[CuIm_2(R-NH_2)_2]$

Im = Su

| R | m.p. (°C) | % calc. | | % found | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| t-Bu | 161-162° | 47.34 | 7.45 | 46.50 | 7.37 |
| Cx | 177-178° | 52.44 | 7.48 | 52.36 | 7.74 |
| iso-Pr | 153-154° | 44.51 | 6.94 | 43.91 | 7.00 |
| n-Bu | 165-166° | 47.34 | 7.45 | 47.18 | 7.50 |
| iso-Bu | 171-172° | 47.34 | 7.45 | 47.37 | 7.51 |
| n-Pr | 168-169° | 44.51 | 6.94 | 44.27 | 6.95 |
| Me | 168-169° | 37.32 | 5.64 | 37.32 | 5.55 |
| $CH_2CH_2Ph$ | 167-168° | 57.42 | 6.02 | 57.49 | 6.13 |
| $CH_2Ph$ | 179-180° | 55.73 | 5.53 | 55.09 | 5.42 |
| H | 190-192° | 32.71 | 4.80 | 32.44 | 4.77 |
| $CH_2CH_2OH$ | 158-159° | 37.74 | 5.81 | 37.80 | 5.74 |

## TABLE 3

ANALYTICAL DATA FOR COPPER(II) COMPLEXES, $[CuIm_2(R-NH_2)_2]$

Im = Phth

| R | m.p. (°C) | % calc. | | % found | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| t-Bu | - | 57.19 | 5.99 | 57.16 | 6.08 |
| Cx | 164-165° | 60.47 | 6.16 | 60.24 | 6.11 |
| iso-Pr | 171-172° | 55.51 | 5.51 | 55.64 | 5.45 |
| n-Bu | 163-164° | 57.18 | 5.99 | 57.33 | 5.97 |
| iso-Bu | 156-158° | 57.18 | 5.99 | 57.09 | 6.04 |
| n-Pr | 175-176° | 55.51 | 5.51 | 55.46 | 5.36 |
| Me | 174-175° | 51.48 | 4.32 | 51.64 | 4.41 |
| $CH_2CH_2Ph$ | 170-171° | 64.04 | 5.04 | 64.02 | 5.09 |
| $CH_2Ph$ | 165-167° | 62.98 | 4.58 | 63.00 | 4.67 |
| H | - | 49.04 | 3.60 | 48.93 | 3.59 |

## TABLE 4

ANALYTICAL DATA FOR NICKEL(II) COMPLEXES, $[NiIm_2(R\text{-}NH_2)_2]$

| | Im = Su | | | | Im = Phth | | | |
|---|---|---|---|---|---|---|---|---|
| R | % calc. | | % found | | % calc. | | % found | |
| | C | H | C | H | C | H | C | H |
| Cx | 53.00 | 7.56 | 53.20 | 7.44 | 61.00 | 6.22 | 60.86 | 6.45 |
| iso-Pr | | | | | 56.08 | 5.56 | 56.20 | 5.31 |
| n-Bu | 47.91 | 7.54 | 47.75 | 7.45 | 57.74 | 6.06 | 57.75 | 5.87 |
| iso-Bu | 47.91 | 7.54 | 47.11 | 7.39 | 57.74 | 6.06 | 57.69 | 5.94 |
| n-Pr | 45.07 | 7.02 | 45.01 | 6.87 | 56.08 | 5.56 | 55.79 | 5.46 |
| Et | | | | | 54.21 | 5.00 | 53.98 | 4.90 |
| Me | 37.89 | 5.72 | 36.73 | 5.81 | | | | |
| $CH_2CH_2Ph$ | 57.97 | 6.08 | 57.93 | 6.15 | 64.56 | 5.08 | 64.33 | 4.91 |
| $CH_2Ph$ | 56.32 | 5.59 | 56.16 | 5.55 | 63.52 | 4.62 | 63.31 | 4.54 |

## TABLE 5

ANALYTICAL DATA FOR NICKEL(II) COMPLEXES $[NiAcac_2(R\text{-}NH_2)_2]$

| R | % calculated | | % found | |
|---|---|---|---|---|
| | C | H | C | H |
| Cx | 57.78 | 8.82 | 58.01 | 8.90 |
| iso-Pr | 50.95 | 8.55 | 50.73 | 8.54 |
| n-Bu | 53.35 | 8.95 | 53.33 | 9.04 |
| iso-Bu | 53.35 | 8.95 | 53.15 | 9.10 |
| n-Pr | 50.95 | 8.55 | 51.12 | 8.65 |
| Et | 48.16 | 8.08 | 48.08 | 7.98 |
| Me | 44.89 | 7.53 | 45.13 | 7.70 |
| $CH_2CH_2Ph$ | 62.29 | 7.24 | 62.57 | 7.28 |
| $CH_2Ph$ | 60.91 | 6.81 | 60.17 | 6.79 |
| H | 40.99 | 6.88 | 41.60 | 6.86 |
| $CH_2CH_2OH$ | 44.11 | 7.40 | 45.18 | 7.20 |
| Ph | 59.35 | 6.34 | 59.22 | 6.24 |

An alternative method of preparation for the aliphatic amine adducts :

$$\mathrm{NiCl_2} + 2\ \mathrm{AcacH} + 2\ \mathrm{Am} \qquad [\mathrm{NiAcac_2Am_2}] + 2\ \mathrm{HCl}$$

To a solution of nickel(II) chloride (1 mole) and acetylacetone (2 moles) in methanol, the aliphatic amine (2.2 moles) was added. The amine complexes precipitated out almost immediately. These were removed by filtration, washed with methanol and ether and dried *in vacuo* at room temperature. The ammine adduct was prepared by bubbling ammonia gas through the solution.

### (b) $[\mathrm{ZnAcac_2Am_{1\ or\ 2}}]$

The amine adducts of bis(acetylacetonato)zinc(II) were prepared by recrystallisation of the aquo adduct of bis(acetylacetonato)zinc(II) from the amine. The white crystalline precipitate was filtered off, washed with ether and dried *in vacuo* at room temperature for a short period.

The aquo adduct of bis(acetylacetonato)zinc(II) was prepared by adding 25% sodium hydroxide solution to an aqueous solution of zinc(II) sulphate (1 mole) and acetylacetone (2 moles). The white precipitate was filtered at the pump, washed with water, recrystallised from ethanol and dried *in vacuo* at room temperature for 12 hours.

The ammine adduct was prepared by adding an ethanolic solution of ammonia to an ethanolic solution of the aquo adduct.

Melting points for both the nickel(II) and zinc(II) series could not be determined because the complexes decomposed slowly on heating with evolution of the amine, giving rise to a wide melting range. Details concerning these complexes appear in Tables 5 - 8.

(4) Amine complexes with uranyl acetylacetonate.

These complexes were prepared by the addition of the primary aromatic amine (1 mole) to a solution of uranyl nitrate (1 mole) and acetylacetone (3 moles) in methanol. The yellow complexes crystallised out of the orange-yellow solution on standing. These were filtered off and washed with methanol. Purification was achieved by recrystallisation from methanol. The complexes were dried *in vacuo* at room temperature for 12 hours.

Not all the amines formed isolable complexes and only 10 in all could be obtained in sufficient quantity for spectroscopic determinations.

Melting points were determined on a Kofler hot stage. Details concerning these complexes appear in Table 9.

The acetylacetone adduct of uranyl acetylacetonate was prepared by recrystallising uranyl acetylacetonate from acetylacetone. The orange complex crystallised out of the solution on standing, was washed with methanol and dried *in vacuo* for 12 hours. (Analysis, found : C, 31.74; H, 3.85%. Calculated for $C_{15}H_{22}O_8U$; C, 31.59; H, 3.89%.)

TABLE 6

ANALYTICAL DATA FOR NICKEL(II) COMPLEXES $[Niacac_2(R\text{-}C_6H_4\text{-}NH_2)_2]$

| R | % calculated C | % calculated H | % found C | % found H |
|---|---|---|---|---|
| 4-OMe | 57.05 | 6.38 | 56.80 | 6.35 |
| 4-OEt | 58.55 | 6.80 | 58.37 | 6.73 |
| 3:4-diMe | 62.29 | 7.24 | 62.04 | 7.28 |
| 4-Me | 60.91 | 6.81 | 60.01 | 6.81 |
| 3-Me | 60.91 | 6.81 | 61.01 | 6.89 |
| H | 59.35 | 6.34 | 59.22 | 6.24 |
| 4-F | 54.91 | 5.45 | 55.00 | 5.49 |
| 3-OMe | 57.05 | 6.38 | 57.10 | 6.44 |
| 3-OEt | 62.29 | 7.24 | 62.51 | 7.29 |
| 4-Cl | 51.40 | 5.10 | 51.19 | 5.09 |
| 3-Cl,4-Me | 53.17 | 5.58 | 53.26 | 5.62 |
| 3-F | 54.91 | 5.45 | 55.01 | 5.47 |
| 3-Br | 43.82 | 4.35 | 44.01 | 4.37 |

TABLE 7

ANALYTICAL DATA FOR ZINC(II) COMPLEXES, $[Znacac_2(R\text{-}NH_2)_2]$

| R | %calculated C | %calculated H | % found C | % found H |
|---|---|---|---|---|
| Cx | 56.95 | 8.69 | 56.95 | 8.90 |
| n-Bu | 52.49 | 8.81 | 52.60 | 8.83 |
| iso-Bu | 52.49 | 8.81 | 52.27 | 8.94 |
| n-Pr | 50.07 | 8.40 | 49.96 | 8.34 |
| Et | 47.26 | 7.93 | 46.71 | 7.72 |
| $CH_2CH_2Ph$ | 61.47 | 7.14 | 61.60 | 7.20 |
| $CH_2Ph$ | 60.06 | 6.72 | 60.04 | 6.63 |
| $CH_2CH_2OH$ | 43.27 | 7.26 | 43.50 | 7.14 |
| Ph | 58.47 | 6.25 | 57.66 | 6.39 |

TABLE 8

ANALYTICAL DATA FOR ZINC(II) COMPLEXES, $\left[ZnAcac_2(R\text{-}NH_2)_2\right]$

| R | % calculated |  | % found |  |
|---|---|---|---|---|
|  | C | H | C | H |
| t-Bu | 49.64 | 6.84 | 49.46 | 7.01 |
| iso-Pr | 47.00 | 6.52 | 47.09 | 6.52 |
| Me | 44.53 | 6.44 | 44.44 | 6.16 |
| H | 42.48 | 6.06 | 42.02 | 6.11 |

TABLE 9

ANALYTICAL DATA FOR URANYL COMPLEXES, $\left[UO_2Acac_2AcacH(R\text{-}C_6H_4\text{-}NH_2)\right]$ (I) OR $\left[UO_2Acac_2((4\text{-}R\text{-}C_6H_4\text{-}NH)\text{-}3\text{-}penten\text{-}2\text{-}one)\right]$ (II)

| R | m.p. (°C) | % calc. (I) |  | % calc. (II) |  | % found |  |
|---|---|---|---|---|---|---|---|
|  |  | C | H | C | H | C | H |
| 3:4-diMe | 157-158 | 39.94 | 4.81 | 41.01 | 4.64 | 40.27 | 4.66 |
| 4-Me | 165-167 | 39.00 | 4.61 | 40.06 | 4.43 | 39.58 | 4.07 |
| 3-Me | 168-169 | 39.00 | 4.61 | 40.06 | 4.43 | 38.70 | 4.44 |
| H | 178-179 | 38.01 | 4.41 | 39.07 | 4.22 | 39.35 | 4.21 |
| 4-F | 168-169 | 37.01 | 4.14 | 38.01 | 3.95 | 38.06 | 3.98 |
| 3-OMe | 177-178 | 38.10 | 4.51 | 39.11 | 4.33 | 38.38 | 4.46 |
| 3-OEt | 137-138 | 39.04 | 4.70 | 40.06 | 4.53 | 39.24 | 4.65 |
| 3-Cl | 166-167 | 36.14 | 4.04 | 37.09 | 3.85 | 36.34 | 3.79 |
| 3-Br | 160-161 | 33.97 | 3.80 | 34.81 | 3.62 | 34.12 | 3.56 |
| 3-Cl,4-Me | 176-177 | 37.11 | 4.25 | 38.07 | 4.07 | 37.55 | 4.06 |

## Infrared spectroscopy

The infrared spectra were obtained in the range 4000 - 200 cm$^{-1}$ on a Beckman IR-12 spectrophotometer, calibrated against polystyrene and carbon dioxide. The samples were determined as nujol mulls between CsBr plates. Because it was necessary to detect small frequency shifts for some absorption bands, the frequencies were obtained by horizontal and vertical scale expansion which was possible directly on this particular spectrophotometer. The frequencies were read directly from the frequency drum and not from the chart paper. Thus eliminating any error due to backlash of the gears or arising from lack of precision in the calibration of the chart paper. Using this method reproducibility and accuracy of 1 cm$^{-1}$ were obtained in the range 2000 - 200 cm$^{-1}$ and of 2 cm$^{-1}$ in the range of 4000 - 2000 cm$^{-1}$.

## Ultraviolet and visible absorption spectroscopy

The ultraviolet-visible absorption spectra were obtained as solution spectra in the range 1200 - 200 mμ, at a concentration of $10^{-3}$ M on a Beckman DK-2A spectrophotometer, with a precision of 2 mμ. Preliminary spectra were obtained on a Beckman DB spectrophotometer. However, because greater precision was required in determining the wavelengths of the absorption maxima, the values quoted are those taken on the former instrument.

## Nuclear magnetic resonance spectrometry

The spectra were obtained as approximately 100 mg/ml $CDCl_3$

solutions using a Varian A-60 spectrometer. Tetramethylsilane (T.M.S.) was used as internal standard. Chemical shifts were measured in p.p.m. downfield from the reference signal (i.e. the T.M.S. signal has a value of 0 p.p.m. and all the other downfield signals have a negative chemical shift). $D_2O$ exchange was carried out by the addition of a few drops of $D_2O$ to the solution.

## Conductivity determinations

The conductance measurements were determined on a Metrohm Model E 382 Conductometer at 25°C in methanol and nitrobenzene with a final concentration of 0.001 M. The conductivity cell had a cell constant of 0.69 $cm^{-1}$.

The molar conductances were calculated as follows :

The resistance (R) of a conductor is directly proportional to its length (L) and inversely proportional to its area of cross-section (a).

$$R = \rho\ L/a \qquad (1)$$

$\rho$, the constant of proportionality is called the specific resistance. Specific conductance ($\bar{K}$) is the reciprocal.

$$\bar{K} = 1/\rho \qquad (2)$$

$$= L/aR \qquad (3)$$

The cell constant $k = L/a$ (4)

so that $\bar{K} = k/R$ (5a)

$$= k\bar{C} \qquad (5b)$$

where $\bar{C}$ = conductance in $ohm^{-1}\ cm^2$

Molar conductance (Y) is given by :

$$Y = 1000\,\bar{K}/c \qquad (6)$$

where c = concentration in g equiv./litre.

To determine the molar conductance for a solution of concentration, c g equiv./litre, the resistance, R is measured and hence $\bar{K}$ determined from equation (5a) where the cell constant (k) is equal to 0.69 $cm^{-1}$. Hence the molar conductance can be calculated from equation (6).

## Magnetic moment measurements.

Magnetic susceptibilities were determined on a Newport-Stanton single temperature magnetic balance, consisting of an analytical balance, an electromagnet and an associated power supply.

The magnetic moments were calculated as follows :

If a cylindrical specimen is suspended in a magnetic field with the lower end in the region of maximum field and the upper end in a region of effectively zero field, it can be shown that the gram susceptibility of the specimen is given by :

$$\chi = (Kv + Bw)/W \qquad (1)$$

where K is the volume susceptibility of air = $0.029 \times 10^{-6}$ (in cgs units); v is the volume of the specimen; w is the force exerted on the specimen by the field; W is the weight of the specimen; B is the constant involving the dimensions of the specimen and the field strength and is determined by calibration with mercury tetrathiocyanatocobalt(III) for which the gram susceptibility is accurately known, viz. $16.44 \times 10^{-6}$ (in cgs units). v is obtained from (weight of tube filled with water -

weight of empty tube)/density of water at $t^{\circ}C$. W is obtained from (weight of tube filled with the specimen - weight of empty tube) in grams. w is obtained from (weight of tube with specimen, magnet "on" - weight of tube with specimen, magnet "off" - diamagnetic force of tube) in milligrams.

$\chi$ can now be calculated from equation (1).

The molar magnetic susceptibility ($\chi$ m) is equal to the product of the gram susceptibility and the molecular weight of the complex.

Allowance must be made for the diamagnetism of the ligands, which can be calculated[86]. The correction is applied to determine the susceptibility of the metal ion $\chi_A$ by :

$$\chi_A = \chi_M - \chi_L$$

where $\chi_L$ is the total susceptibility of the ligands.

The magnetic moments ($\mu$) can be calculated from :

$$\mu = 2.84(\chi_A T)^{\frac{1}{2}} \tag{2}$$

where T is the absolute temperature.

The number of unpaired electrons of the metal ion can now be calculated from the "spin only" formula :

$$\mu = \left[n(n = 2)\right]^{\frac{1}{2}}$$

where n is the number of unpaired electrons.

# DISCUSSION

## (1) Primary aromatic amine complexes of zinc(II) halides.

In a preliminary communication[47] which provided the basis of the present work the infrared spectra of a series of complexes of zinc halides with substituted anilines were briefly reported on. This work suffered from some limitations: a spectrophotometer with limited range and precision was employed, sampling was by means of KBr pellets and a limited number of substituted amines was available for study. Nevertheless some interesting results emerged from which some deductions concerning the bonding in these molecules could be made. It was considered of interest to extend the range of ligands studied and to take advantage of the more favourable instrumental conditions currently available to us, the redetermined spectra covering the range 4000 - 200 $cm^{-1}$ which includes the important metal-ligand stretching region.

It was considered that a study of the infrared spectra of a large series of substituted aniline complexes of a single metal ion, would shed light on the influence of aromatic ring substituents on the metal to nitrogen and nitrogen to hydrogen bond strengths and possibly assist in the determination of the mechanism of bonding in the molecule. For these reasons a series of complexes $\left[ZnCl_2An_2\right]$ and $\left[ZnBr_2An_2\right]$ containing, respectively 27 and 22 differently substituted anilines, was prepared.

Zinc(II) was chosen as the coordinated metal ion because the tetrahedral configuration of the amine complexes is well authenticated. Zinc(II) halides complexed with 4-methyl-pyridine have been shown[48] by

X-ray crystallography to have a tetrahedral orientation about the metal atom. Bis(p-toluidine)zinc(II) chloride has been shown by diffraction methods to be tetrahedral[16]. Information on the stereochemistry of the zinc complexes cannot be obtained from their ultraviolet spectra, but it has been reported[21] that the far-infrared spectra of zinc(II) halide complexes of certain substituted anilines are very closely similar to the spectra of the corresponding cobalt(II) complexes, which have been shown to have tetrahedral coordination about the metal ion[49].

The infrared spectra yielded two strong and sharp absorption maxima in the region 3290 - 3215 $cm^{-1}$, the higher and lower frequency bands being unambiguously assigned to the antisymmetric and symmetric N-H stretching frequencies respectively. For 18 of the 28 amines employed, the N-H frequencies of the free ligands have been reported[5]. The N-H stretching frequencies of the complexes occur at an average frequency of 200 $cm^{-1}$ (for the antisymmetric vibration) and 165 $cm^{-1}$ (for the symmetric vibration) lower than those in the parent amines. This shift is of similar magnitude to that observed for coordinated ammonia in complex ammines[50-52] and for other amine complexes[53]. This weakening of the N-H bonds can be explained on the basis of the electron drainage from the nitrogen atom due to its coordination to the metal ion.

Two strong bands were observed in the region 1625 - 1560 $cm^{-1}$. For free primary aromatic amines, some confusion exists in the literature as to their assignment; This is the result of overlap of the reported ranges of 1620 - 1560 $cm^{-1}$ for N-H bonding (scissoring) vibration and 1625 - 1575 $cm^{-1}$ for the first of the four infrared active aromatic ring stretching modes. However on coordination with a metal the first of these bands i.e. the one of higher frequency, remains virtually unaffected e.g. for p-chloroaniline the reported value is 1604 cm$^{-1}$ and the value found after coordination is 1603 cm$^{-1}$; thus this band can be assigned to the first aromatic ring vibration, as one would not expect it to be affected by coordination. The frequency of the second band is lowered on coordination and can be assigned to the N-H bending vibration. This has been confirmed[22] by N-deuteration of aniline complexes of different metal halides. In addition, since the complexed amines have a 4-covalent nitrogen atom, the frequency might be expected to lie closer to the value associated with quaternary ammonium salts. For such ions this frequency is often encountered[54,55] near 1580 cm$^{-1}$, in good agreement with the observed values between 1585 and 1570 cm$^{-1}$.

The far infrared region is of particular interest as it includes low frequency metal to ligand vibrations which should be of greater importance, because trends in the metal to ligand vibrational frequencies are more directly related to the strength of metal-ligand bonds than are the trends of the N-H vibrations of the coordinated anilines.

Bands at 294 and 230 cm$^{-1}$ have been assigned[20] to M-X (X = halogen) stretching modes in bis(aniline)zinc(II) chloride and bromide respectively. All the spectra studied exhibited maxima corresponding to these frequency regions.

The assignment of Zn-N vibrations in bis(aniline)zinc(II) chloride has tentatively been made[20] for bands found at 402 and 362 cm$^{-1}$. However a further study[22] by N-deuteration methods has shown that only the absorption in the 400 cm$^{-1}$ region is likely to be associated with the M-N stretching vibration and the absorption in the 365 $cm^{-1}$ region is associated, at least partly, with an $NH_2$ deformation. In practically all the spectra studied, a single peak was observed to occur in the region 440 to 400 $cm^{-1}$ and this has been assigned to the M-N stretching mode. The M-N frequencies of a few substituted aniline complexes of zinc(II) have been reported[21]. These correspond well with the observed values. A typical infrared spectrum of these complexes appears in Fig. 9.

In a series of complexes of variously substituted primary aromatic amines with a common metal ion, it would be anticipated that, since $\pi$-bonding is not formally possible on a molecular orbital basis, the M-N bond would be destabilised by electron-withdrawing substituents, The N-H bond could behave similarly or inversely. Correlations between the vibrational group frequencies of the zinc complexes $[ZnX_2An_2]$ and the Hammett substituent constant, $\sigma$, were therefore made in order to ascertain what type of metal to donor atom bonding occurs and to explain the electron shifts within the molecule.

The variations of the group frequencies with substituent constant are given in Tables 10 and 11 and graphically portrayed in Figs. 1 - 8.

It is clear that there is no uniform trend over the whole range of $\sigma$ values, but a noted factor is that the general trends are similar whichever group frequency is used. Furthermore similar trends are obtained for the alternative sampling methods of KBr pellets and nujol mulls so that the frequency shifts are clearly not the result of pressure effects or metathetical halogen-exchange reactions occuring in the pellets. Of particular interest is the fact that both the N-H and M-N frequencies show a similar dependence on the nature of the substituent. It would therefore appear that simultaneous stabilisation of the M-N and N-H bonds occurs, but that this is likely to be at the expense of the C-N bond multiplicity. However, because completely unambiguous assignment of the C-N stretching frequencies is not possible this supposition cannot be proved. The trend of the correlation between the Hammett substituent constant and the C-N stretching frequency should be opposite to those observed for the N-H and M-N frequencies.

For the purpose of this discussion Fig. 1 is divided into the three sections indicated. In area A increased electron-releasing character of the substituent raises both the M-N and N-H frequencies. The trends are those expected on the basis of pure M-L $\sigma$-bonding viz. stabilisation of the M-N bond by increased electron release of the substituents. This is not necessarily expected for the N-H bond too, however obviously the electron drift must be partly transferred to the N-H bond as well.

In area B, there is a marked transition to higher frequencies caused by substituents which are mildly electron-withdrawing. This trend implies stabilisation of the M-N bond and N-H bond by electron-withdrawing substituents and is the converse of what would be expected on a purely $\sigma$-bonding hypothesis. Substituent aided $\pi$-bonding would make such stabilisation understandable, but it is difficult to rationalise $\pi$-bonding in these complexes on a theoretical basis. Nevertheless there is an increasing body of experimental evidence[56-59] which suggests that anomaous stabilities are often observed in metal-amine complexes with electron-withdrawing substituents. Probably the most convincing evidence[24] for this phenomenon is provided by the "stabilisation factor" ($S_f$) which has been determined for a series of silver(I) aniline complexes. The stabilisation factors plotted against the substituent constants ($\sigma$) exhibit a linear relationship the slope of which indicates stabilisation by electron withdrawing groups (see Introduction, page 8). The complexes described here contain $d^{10}$ zinc(II) ions and may therefore be expected to exhibit similarities (with respect to the nature of the bonding) with the $d^{10}$ silver(I) complexes studied by da Silva and Calado[24].

However the stabilisation is shortlived since substituents with relatively large positive $\sigma$ values lower the frequencies in the expected manner i.e. as in area C. The destabilisation of the M-N bond by strongly electron-withdrawing substituents is clearly reflected by certain preparative aspects of these complexes e.g. $[ZnCl_2(\text{m-nitroaniline})_2]$ was found to be too unstable to precipitate from ethanol, presumably a result of the reduced donor capacity of the nitrogen.

It should be noted that the overall effect is that electron-releasing substituents raise the N-H frequency and electron-withdrawing substituents have the reverse effect. This is expected but nevertheless noteworthy in view of the reverse trend exhibited by the free amines[60].

The electronegativity of the halogen would be expected to influence the electronic effects in the amine complexes of zinc(II) chloride and bromide. In general it was found that the zinc chloride complexes exhibited N-H frequencies which were higher than those of the zinc bromide analogues by an average of 5 $cm^{-1}$ i.e. an unexpected increase of frequency with increasing halogen electronegativity. A similar relationship has previously been demonstrated[57] for a series of amine complexes of platinum(II) and palladium(II) halides. It was suggested that dative $\pi$-bonding from the metal to the halogen increases so rapidly along the series Cl<Br<I that the total electron drift from metal to halogen also increases in that order i.e. against the normal trends of electronegativity. An alternative explanation may be proposed. As the electronegativity of the halogen increases so the electron drift from the substituent is enhanced aiding release of electrons to the N-H bond.

The M-X stretching frequencies assigned[20] to a strong band near 300 cm$^{-1}$ in the zinc(II) chloride complexes studied were found to lack uniformity and there was no simple explanation for the shifts observed.

TABLE 10

Infrared frequencies (cm$^{-1}$) of zinc(II) complexes, $[ZnCl_2(R-C_6H_4-NH_2)_2]$

| σ | R | $NH_2$ stretching |  | $NH_2$ | metal-nitrogen |
|---|---|---|---|---|---|
|  |  | asym. | sym. | bending | stretching |
| -0.36 | 4-OH | 3275 | 3231 | 1584 | 440 |
| -0.27 | 4-OMe | 3272 | 3230 | 1586 | 430 |
| -0.25 | 4-OEt | 3272 | 3229 | 1585 | 438 |
| -0.24 | 3:4-diMe | 3274 | 3229 | 1583 | 417 |
| -0.17 | 4-Me | 3274 | 3233 | 1585 | 425 |
| -0.15 | 4-Et | 3271 | 3228 | 1584 | 447 |
| -0.07 | 3-Me | 3273 | 3227 | 1583 | 423 |
| -0.015 | 4-NHCOMe | 3270 | 3223 | - | 407 |
| 0 | H | 3269 | 3224 | 1580 | 402 |
| +0.01 | 4-Ph | 3273 | 3217 | 1580 | 413 |
| +0.06 | 4-F | 3278 | 3232 | 1586 | 427 |
| +0.115 | 3-OMe | 3286 | 3237 | 1587 | 465 |
| +0.15 | 3-OEt | 3284 | 3235 | 1586 | 464 |
| +0.23 | 4-Cl | 3289 | 3242 | 1584 | 422 |
| +0.23 | 4-Br | 3275 | 3231 | 1583 | 428 |
| +0.235 | 3-Cl, 4-Me | 3274 | 3228 | 1583 | 426 |
| +0.265 | 4-COOH | 3272 | 3227 | 1582 | 421 |
| +0.28 | 4-I | 3272 | 3227 | 1581 | 425 |
| +0.34 | 3-F | 3271 | 3225 | 1581 | - |
| +0.35 | 3-I | 3271 | 3227 | 1580 | 416 |
| +0.37 | 3-Cl | 3273 | 3228 | 1584 | 410 |
| +0.39 | 3-Br | 3272 | 3227 | 1581 | 412 |
| +0.46 | 4-COPh | (3277<br>(3257 | 3226 | 1578 | 411 |
| +0.52 | 4-COMe | 3270 | 3225 | - | - |
| +0.52 | 4-COOEt | 3271 | 3224 | 1580 | 402 |
| +0.63 | 4-CN | 3268 | 3219 | 1578 | 369 |
| +0.68 | 3-$NO_2$ | 3268 | 3215 | 1580 | 372 |

TABLE 11

Infrared frequencies (cm$^{-1}$) of zinc(II) complexes, $[ZnBr_2(R-C_6H_4-NH_2)_2]$

| σ | R | $NH_2$ stretching |  | $NH_2$ | metal-nitrogen |
|---|---|---|---|---|---|
|  |  | asym. | sym. | bending | stretching |
| -0.60 | 4-$NMe_2$ | 3275 | 3238 | 1585 | - |
| -0.36 | 4-OH | 3270 | 3229 | 1579 | 440 |
| -0.27 | 4-OMe | 3270 | 3227 | 1581 | 430 |
| -0.25 | 4-OEt | 3269 | 3226 | 1578 | 443 |
| -0.24 | 3:4-diMe | 3278 | 3230 | 1577 | 415 |
| -0.17 | 4-Me | 3287 | 3237 | 1579 | 412 |
| -0.15 | 4-Et | 3267 | 3225 | 1578 | 442 |
| -0.07 | 3-Me | 3270 | 3222 | 1576 | 419 |
| 0 | H | 3265 | 3221 | 1574 | 401 |
| +0.06 | 4-F | 3272 | 3227 | 1580 | 426 |
| +0.115 | 3-OMe | 3283 | 3231 | 1581 | 461 |
| +0.15 | 3-OEt | 3281 | 3231 | 1581 | 463 |
| +0.23 | 4-Cl | 3272 | 3221 | 1575 | 427 |
| +0.23 | 4-Br | 3274 | 3225 | 1576 | 423 |
| +0.235 | 3-Cl,4-Me | 3270 | 3224 | 1577 | 422 |
| +0.28 | 4-I | 3289 | 3220 | 1573 | 421 |
| +0.34 | 3-F | 3266 | 3218 | 1573 | - |
| +0.35 | 3-I | 3268 | 3223 | 1574 | 408 |
| +0.37 | 3-Cl | 3266 | 3218 | 1573 | 411 |
| +0.39 | 3-Br | 3268 | 3223 | 1573 | 405 |
| +0.46 | 4-COPh | 3268 | 3215 | 1572 | 411 |
| +0.63 | 4-CN | 3261 | 3212 | 1571 | 362 |

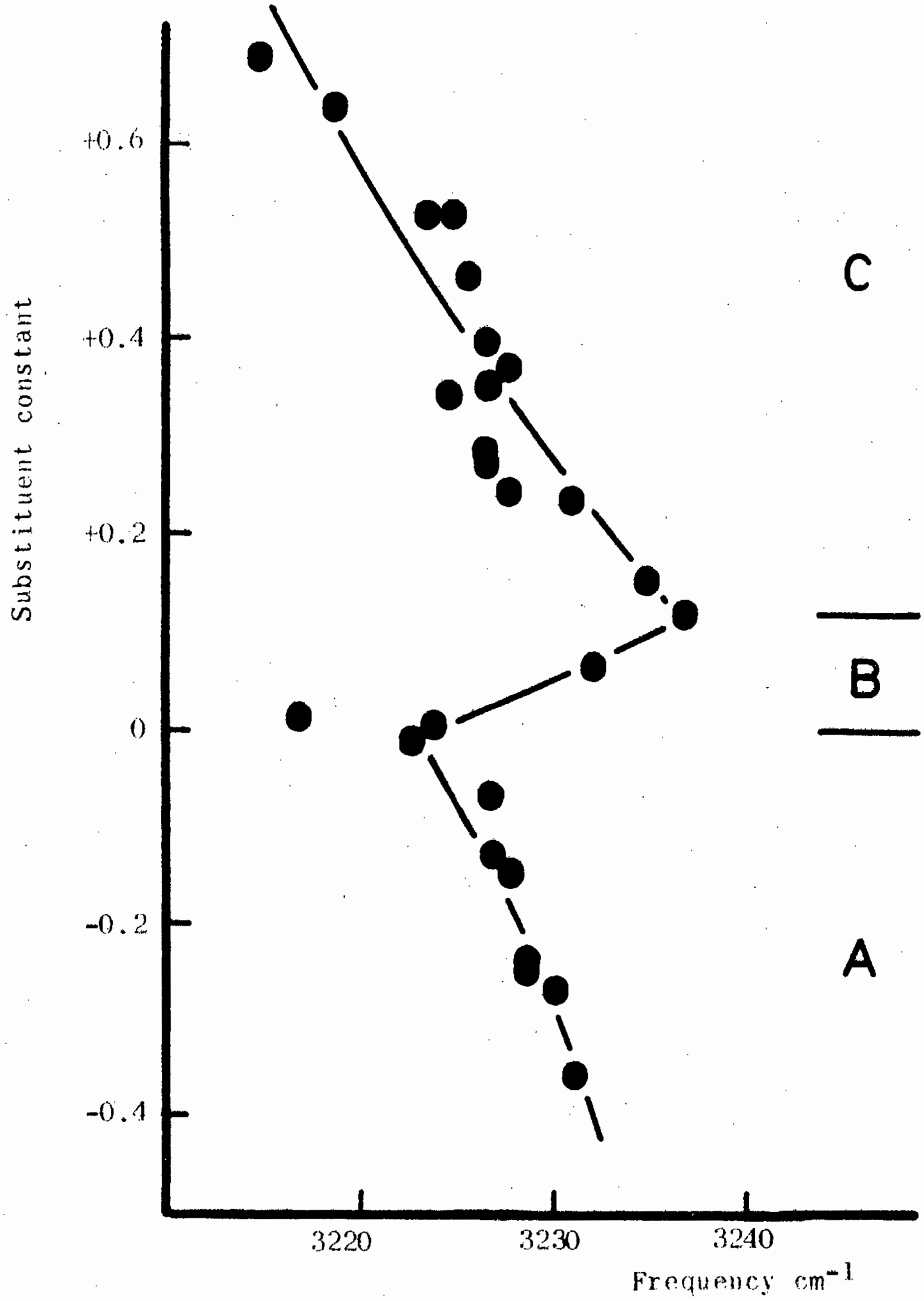


Fig. 1. Plot of N-H symmetric stretching frequency against substituent constant for $[ZnCl_2An_2]$.

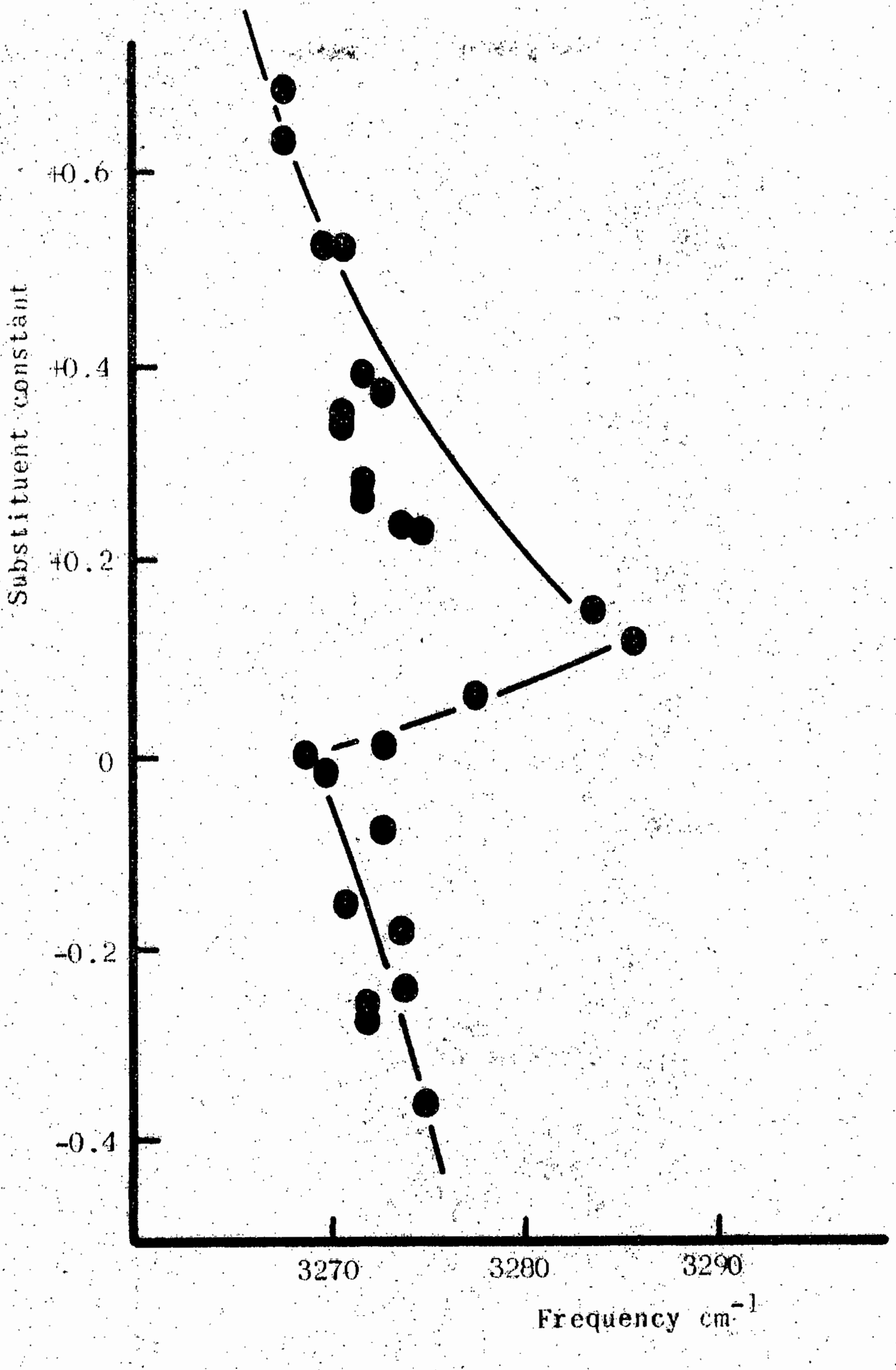


Fig. 2. Plot of N-H asymmetric stretching frequency against substituent constant for $[ZnCl_2An_2]$.

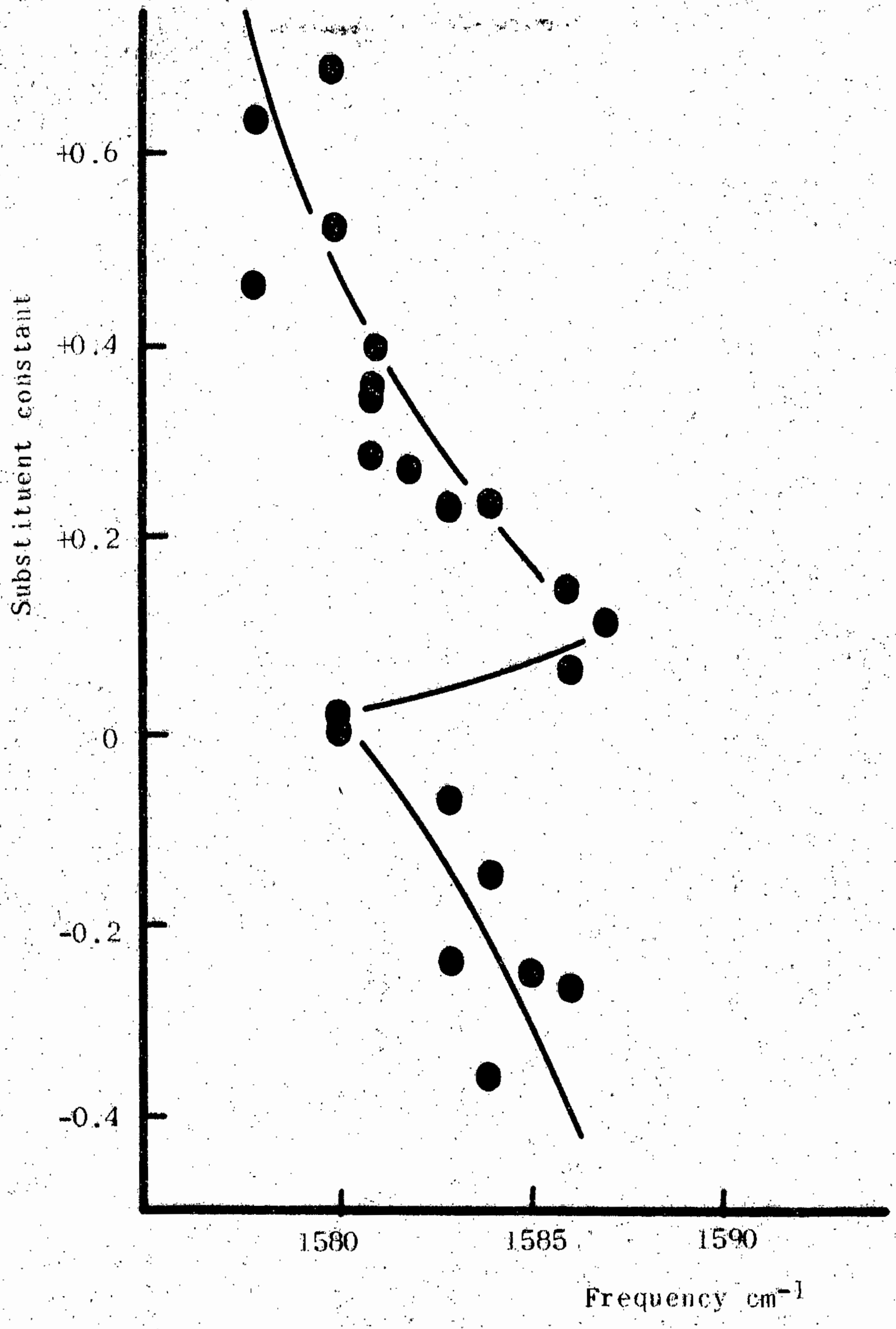


Fig. 3. Plot of N-H bending frequency against substituent constant for $[ZnCl_2An_2]$.

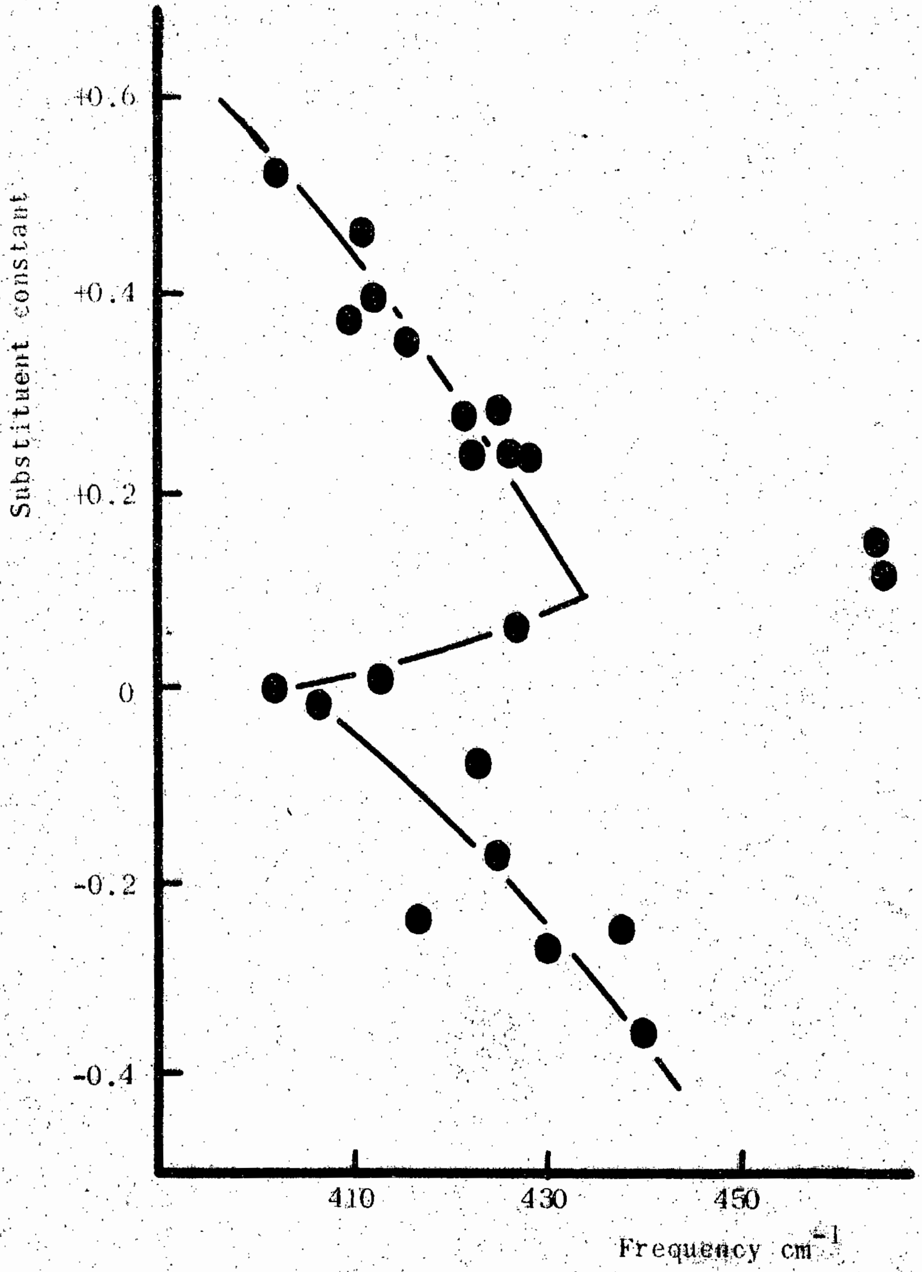


Fig. 4. Plot of M-N stretching frequency against substituent constant for $[ZnCl_2An_2]$.

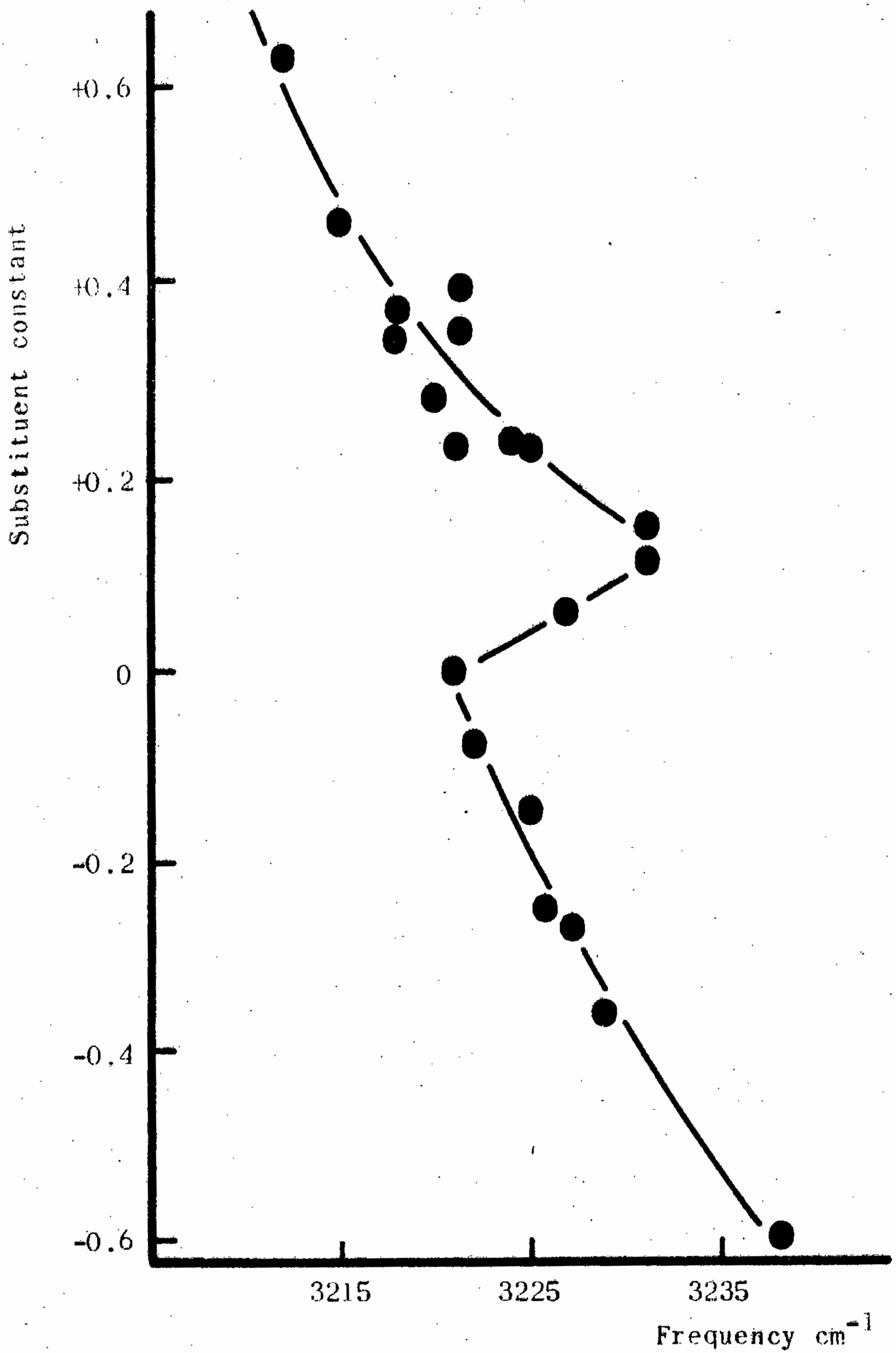


Fig. 5. Plot of N-H symmetric stretching frequency against substituent constant for $[ZnBr_2An_2]$.

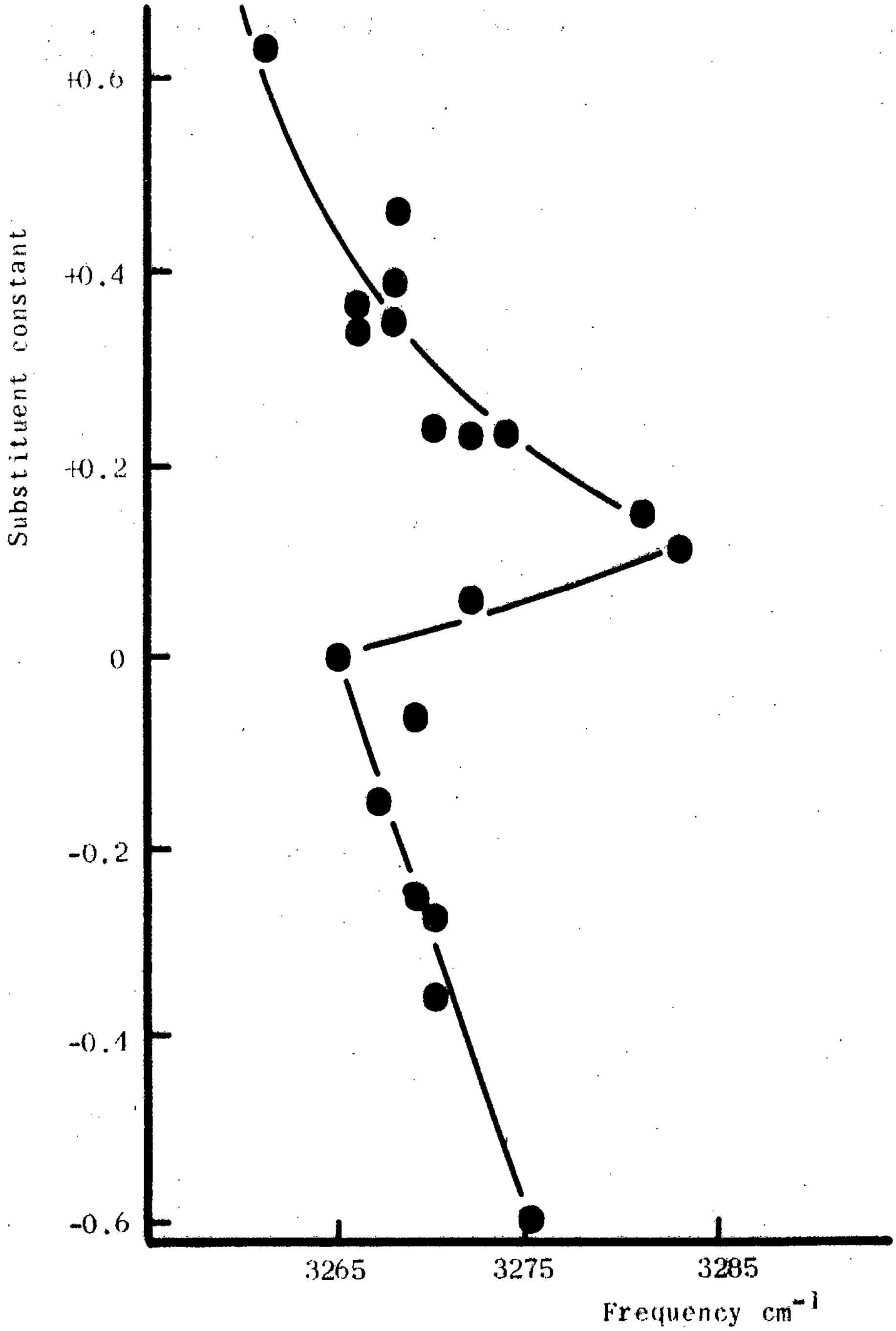


Fig. 6. Plot of N-H asymmetric stretching frequency against substituent constant for $[ZnBr_2An_2]$.

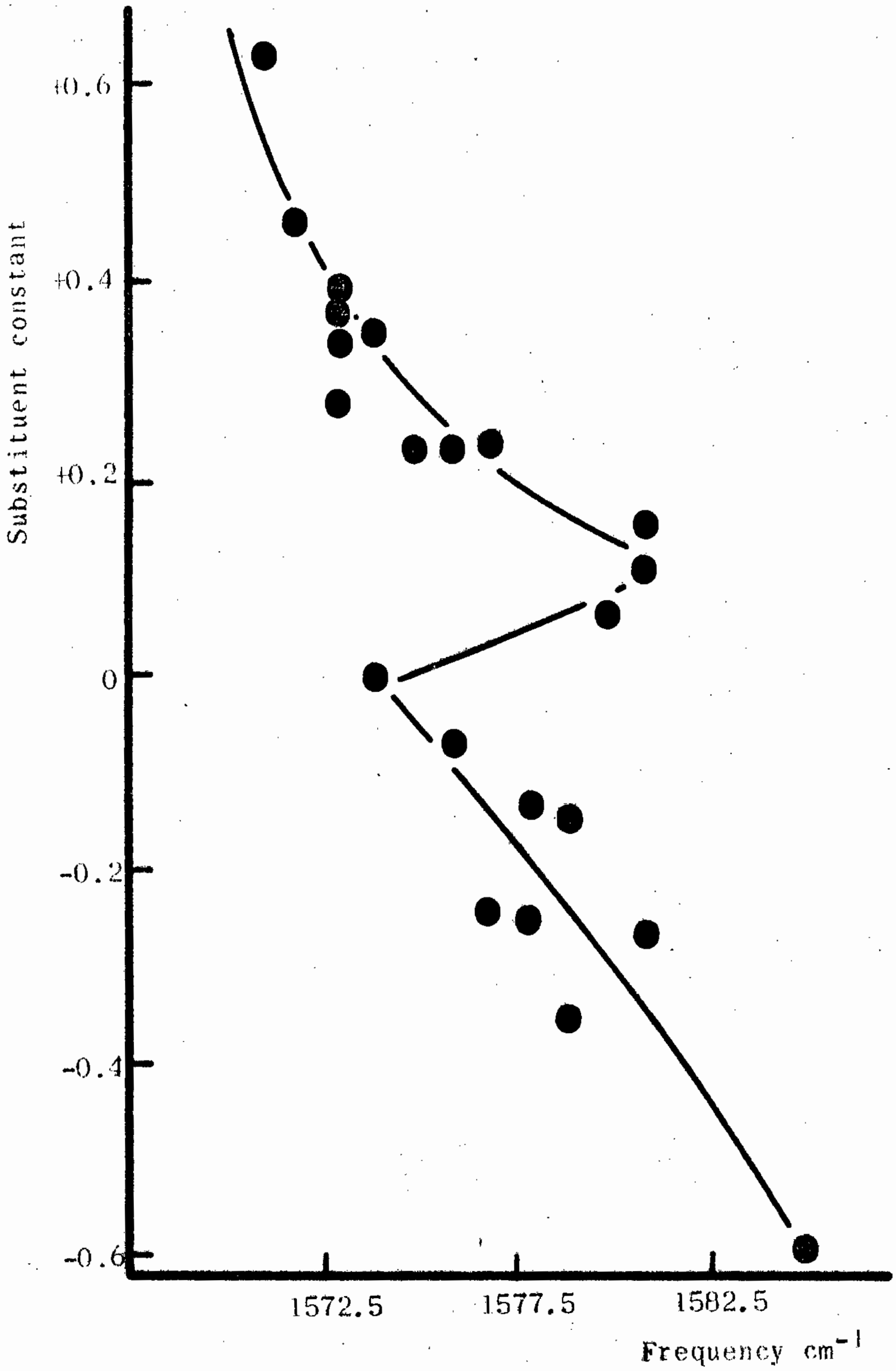


Fig. 7. Plot of N-H bending frequency against substituent constant for $[ZnBr_2An_2]$.

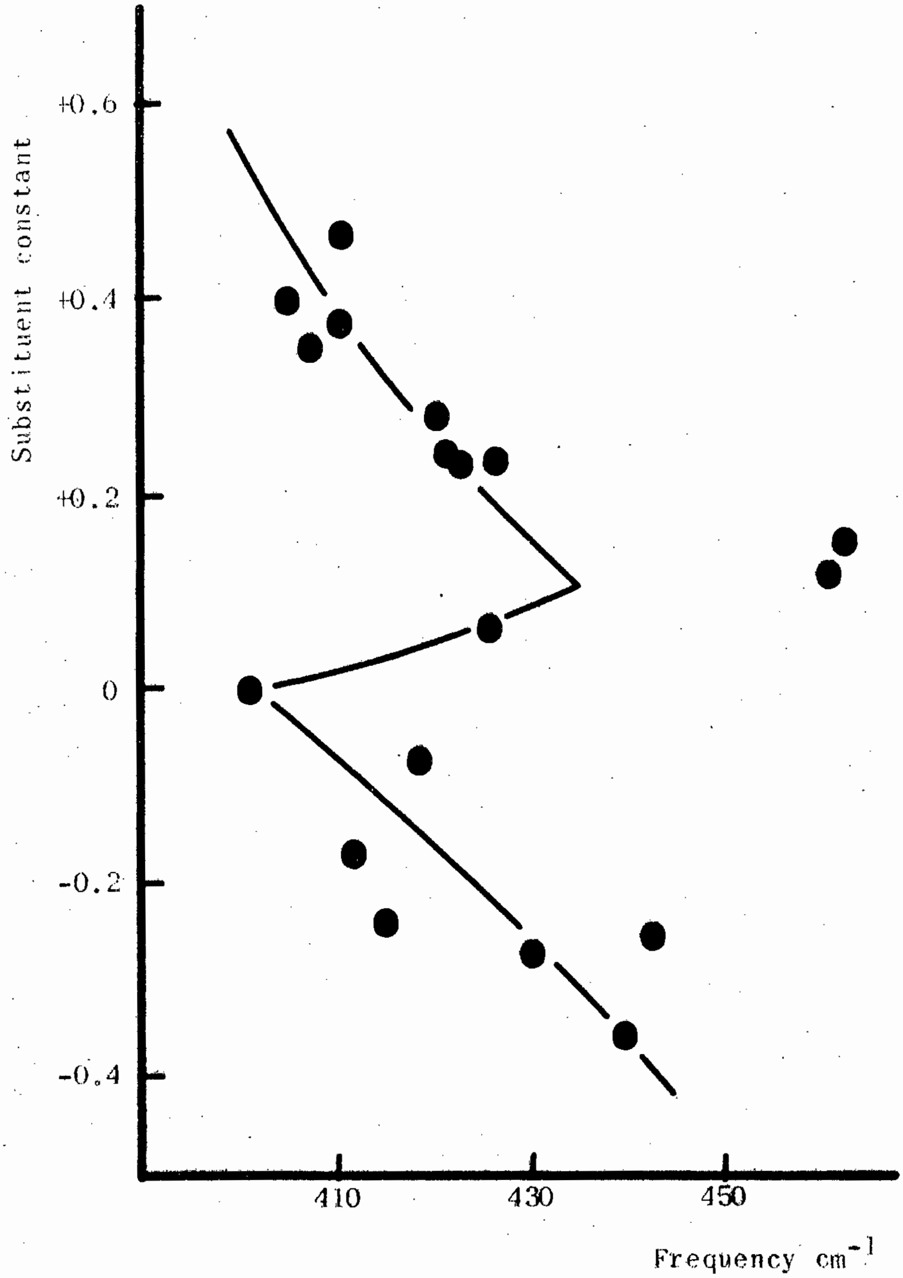
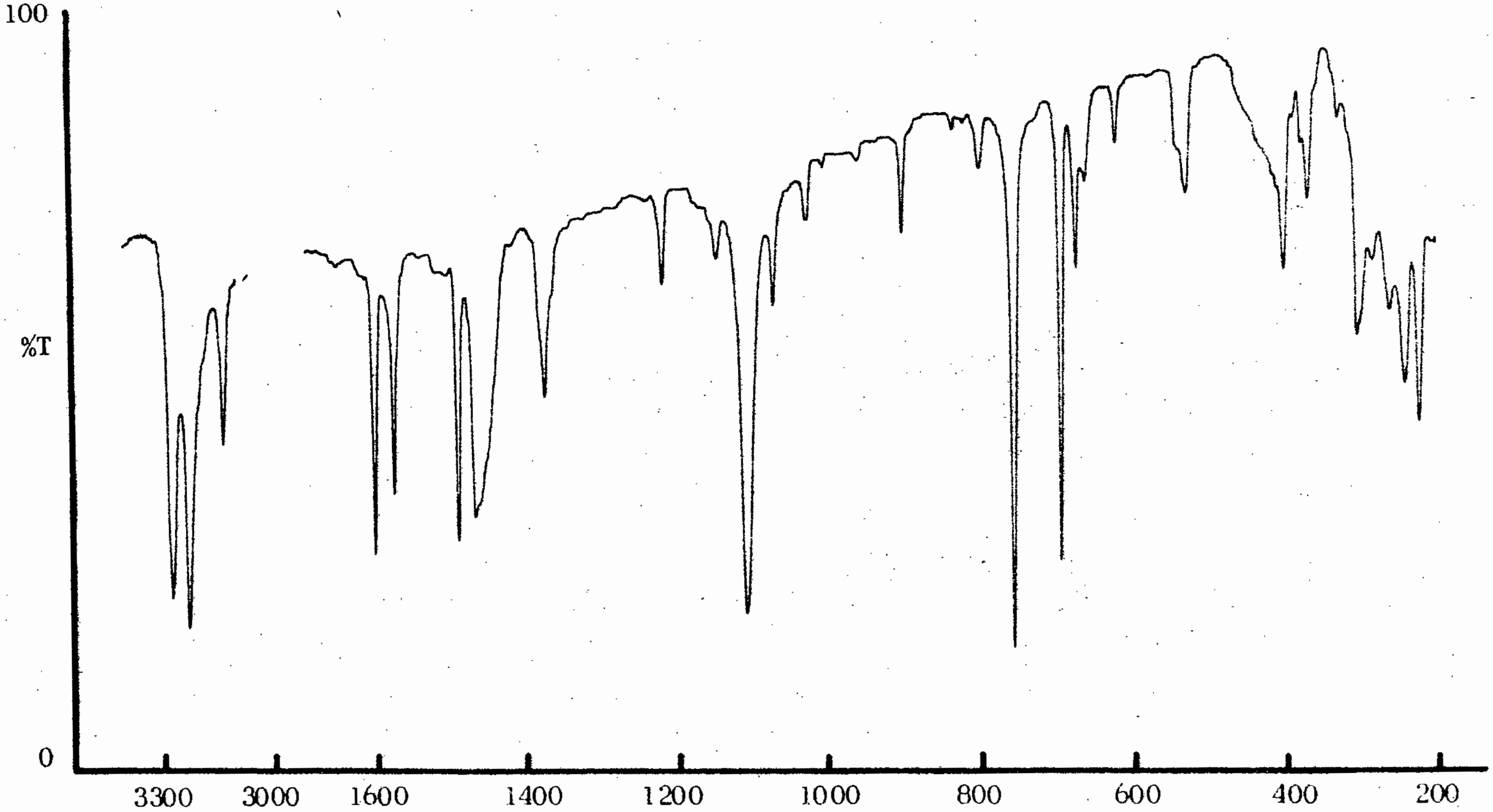


Fig. 8. Plot of M-N stretching frequency against substituent constant for $[ZnBr_2An_2]$.

Fig. 9. Infrared spectrum of $[ZnCl_2(aniline)_2]$.



Frequency $cm^{-1}$

### (2) Amine complexes of copper(II) and nickel(II) succinimide and phthalimide.

The cyclic imides, succinimide and phthalimide are weak acids with $pK_a$ (acid dissociation) values of 10.52 and 14.13 respectively[61]. Phthalimide is therefore the stronger acid but both imides are capable of forming salts with alkali and other metals because of the joint activation of the imide hydrogen by both carbonyl groups. The metal imides are in turn capable of forming coordination compounds with donor ligands such as nitrogenous bases. A large series of copper(II) and nickel(II) succinimide and phthalimide complexes with various aliphatic amines was prepared in this work and their infrared and ultraviolet-visible absorption spectra recorded.

The characteristic coordination environment of copper(II) is either an octahedron distorted by stretching along one axis or the limitimg case of such distortion viz. square-planar. Previous reports[28,32] indicate that copper(II) imide complexes in the solid state are square-planar and monomeric on the basis of percentage composition, molecular weight determinations and non-electrolytic character. The molecular formula of these complexes is thus $[CuSu_2Am_2]$ or $[CuPhth_2Am_2]$. However there is an exception in the case of the ethylamine complex. In support of a previous[27] composition determination, it was found that the complex contains an extra two molecules of water. The infrared spectrum of this compound gave an intense band at 3440 $cm^{-1}$, which indicates that the water is coordinated along with the other ligands, as the normal O-H stretching vibration region for water (i.e. true hydrates) is

3650 - 3590 $cm^{-1}$, therefore the value 3440 $cm^{-1}$ would seem to indicate the formation of a $H_2O$-M bond, which in turn would lower the frequency of the O-H vibration. In this case the structure is clearly that of a (probably) distorted octahedron.

The colour of the copper(II) complexes is pink while the majority of complexes of copper(II) are blue or green. The exceptions are generally caused by strong ultraviolet bands tailing off into the blue end of the visible spectrum and thus causing the substances to appear reddish. Actual ultraviolet solution spectra did not show this as the copper(II) imide complexes give blue solutions in both water and chloroform and their spectra are therefore not relevant to the species existing in the solid state.

The magnetic moments of members of the copper(II) series were found to have $\mu$ eff approx. = 1.73 B.M.. This is expected for square planar structure, but does not allow distinction from the alternative of octahedral coordination as both structures give paramagnetic complexes corresponding the single unpaired electron present. The conductivities of these complexes in nitrobenzene indicate that they are essentially non-electrolytes because all the molar conductivity values were found to be less than 1 mho. This is in support of a previous report[28].

The possibility of geometric isomerism exists but it has been reported[62] that the solid cis.-square-planar unidentate complexes of copper(II) are rarely found. Therefore it is assumed that all the complexes are trans-.

The nickel(II) analogues have also been reported[30] to be square-planar and monomeric on the basis of composition, molecular weights and non-electrolytic character. This receives support from the measured magnetic moment of these complexes which are found to have $\mu_{eff}$ approx. = 0.1 B.M.. Square-planar nickel(II) requires the complex to be diamagnetic by virtue of the $dsp^2$ hybridisation involved. The complexes were all yellow to pale-orange in colour, which is also characteristic of square planar nickel(II)[63].

All the complexes show sharp absorption bands in their infrared in the range 3300 - 3100 $cm^{-1}$, which can be unambiguously assigned to the N-H stretching vibrations of the coordinated amines. In free aliphatic amines these bands occur in the region of 3450 $cm^{-1}$; this lowering of the free amine N-H stretching frequency is expected on coordination, as mentioned in the previous section.

The carbonyl stretching frequencies of the imide are of particular interest. In succinimide itself two bands occur which have been assigned[65] to the carbonyl stretching vibration occurring at 1777 $cm^{-1}$ (medium intensity) and 1697 $cm^{-1}$ (strong). In phthalimide these two bands occur at 1779 $cm^{-1}$ (medium) and 1755 $cm^{-1}$ (strong). In the complexes these carbonyl vibrations are all lowered by approximately 70 $cm^{-1}$ e.g. in $[CuSu_2(\text{methylamine})_2]$ the bands occur at 1709 and 1620 $cm^{-1}$.

The origin of these bands in free imides has been attributed to the individual carbonyl groups[64] or to the symmetric and asymmetric vibrational coupling of the two carbonyl groups[65]. The latter is favoured because two bands are also found in symmetric cyclic imides e.g. succinimide itself, where both carbonyl groups are in similar environments.

Typical infrared spectra of these complexes appear in Figs. 13 and 14.

It is possible that the imide ion may be coordinated to the metal ion either through the nitrogen (see I and II, page 63) or through the carbonyl oxygen. On the basis of the Lewis concept it has been suggested[29] that it is more likely that the nitrogen (which is negatively charged) will have a higher probability of being coordinated than the oxygen. Nevertheless, the possibility of bonding through the carbonyl oxygen of the imide cannot be excluded since this could occur via the enol form. Coordination via the oxygen would, however, give rise to a big difference in the fundamental carbonyl stretching frequencies of the two carbonyl groups and hence reduce their possibility of coupling. The origin of the two bands would then be centred largely on the vibrations of the (now uncoupled) carbonyl groups. Under these conditions coordination via one oxygen would be expected to have a greater effect on that carbonyl and hence on its stretching frequency than on the other. In practice it is found that both carbonyl stretching frequencies are lowered to a similar extent on coordination, supporting the view that coordination is through the nitrogen.

The lowering of both carbonyl frequencies on coordination with the imide nitrogen is expected since, on formation of the complex, a proton is lost from the imide yielding a negatively charged nitrogen species and any change in the imide nitrogen which is directly linked to the carbonyl group will alter the molecular environment and accordingly the frequency of the latter.

An analogous situation occurs in the complexes of platinum(II)[66,67] and gold(I)[68] with β-diketones. The keto-tautomer of the β-diketone molecule is similar in structure to that of the imide, in that there are two symmetric carbonyl groups flanking a central carbon atom in the case of the β-diketones and a nitrogen atom in the case of the imides. The crystal structure[69] of $\mathrm{K[Ptacac_2Cl]}$ shows the coordination spere around platinum to consist of the chloride ion, a bidentate acetylacetonate ion and a unidentate acetylacetonate ion bonded through the 3-carbon. The latter is stabilised in the keto-form and is basically similar to the nitrogen-bonded imide ion. The carbonyl stretching frequencies of the keto-tautomer of the free acetylacetone molecule occur at 1728 and 1710 $cm^{-1}$, whilst in the carbon-bonded platinum(II) acetylacetonate complex these frequencies occur at 1695 and 1653 $cm^{-1}$. Similarly in trifluoroacetylacetone the corresponding frequencies are found at 1775 and 1745 $cm^{-1}$ and in the carbon-bonded complex at 1721 $cm^{-1}$. The extent of the lowering of the carbonyl stretching frequencies on coordination of the carbon-bonded β-diketone is analogous to the succinimide and phthalimide complexes.

As seen in Tables 12 - 15 the various amines have a measurable although small effect on the carbonyl stretching frequencies, in spite of the fact that they are far removed from the carbonyl groups. Polar substituent constants ($\sigma^*$) for groups (R) directly adjoining the reaction centre (e.g. R-COOR′ and R-$NH_2$) have been calculated[3]. Using Taft's substituent constants as an index of the electron-releasing character of the substituents, it is found that both the carbonyl stretching frequencies move to higher frequencies as the electron-releasing power of the amine increases. The effect on the frequencies of the one carbonyl band is similar to that of the other. This suggests that both carbonyl groups are in a symmetrical environment with respect to the donor atom favouring the assumption that the nitrogen of the imide is coordinated and not the carbonyl oxygen.

The above observations and deductions apply to both the copper(II) and nickel(II) succinimide complexes. The lower frequency carbonyl band of the phthalimide complexes is overlaid by phenyl absorption bands, therefore only the higher frequency band can be assigned without ambiguity.

Unfortunately the N-H stretching vibrational bands lack uniformity in that the number of bands varies through a particular set (either 2 or 3 bands are observed as seen in Tables 12 - 15). No correlation was found between these frequencies and the substituent constants of the amines, doubtless a result of the frequencies being subject to both mass and electronic effects.

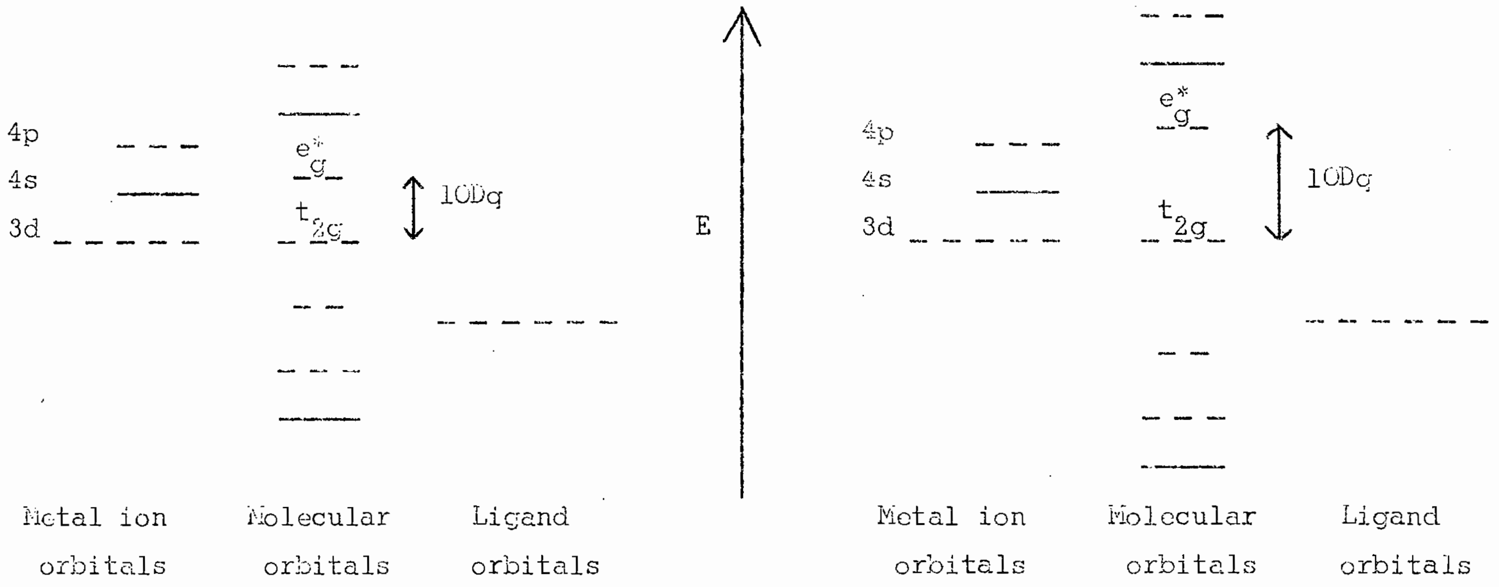
The far infrared region was found to be too complex to enable an interpretation of the spectra to be made because of the mixture of two types of metal to nitrogen bonds (i.e. to the N of the amine and the N of the imide).

The ultraviolet-visible absorption spectra of soluble members of the copper(II) succinimide series were recorded as aqueous solutions.

The insolubility of the copper(II) phthalimide and nickel(II) complexes limited the investigation. The copper(II) succinimide complexes were especially suitable for study because the majority of them are soluble in water producing blue solutions. In addition the absorption band is easily identified and is of known origin, arising from the transition $^2E_g \leftarrow {}^2T_{2g}$. Tschugaeff[27] has made a study of the species present in aqueous solution and has shown $[CuSu_2Am(H_2O)_3]$ (A) to be formed initially. This decays on standing or dilution to $[Cu(H_2O)_6]Su_2$ (B). A is formed by elimination of amine, detectable by its odour when the complex is dissolved in water. Because of the reaction A $\longrightarrow$ B the solutions used were made as concentrated as possible and in addition the spectra were determined immediately after dissolving the complex in order to ensure the identity of the species present in each case. Two absorption maxima were observed; the absorption at 250 m$\mu$ ($\varepsilon$ approx = 1500) being due to the carbonyl $\pi \longrightarrow \pi^*$ transition of the imide and the absorption in the range 660 - 600 m$\mu$ ($\varepsilon$ approx. = 100) being due to the $^2E_g \leftarrow {}^2T_{2g}$ transition of the copper(II) ion. It was found that the wavelength of the absorption maximum of the latter transition increases with increasing electron-releasing character of the amine substituents (Table 12).

Increased electron release by the substituents on the amine may be expected to have three effects on the energy of the system.

(1) The metal d-orbitals will suffer a greater repulsion which will increase the value of 10Dq and hence the seperation between the $e_g$ and $t_{2g}$ levels and will necessarily result in a reduction of $\lambda$ max, see Fig A.


Mild electron release:

Strong electron release:

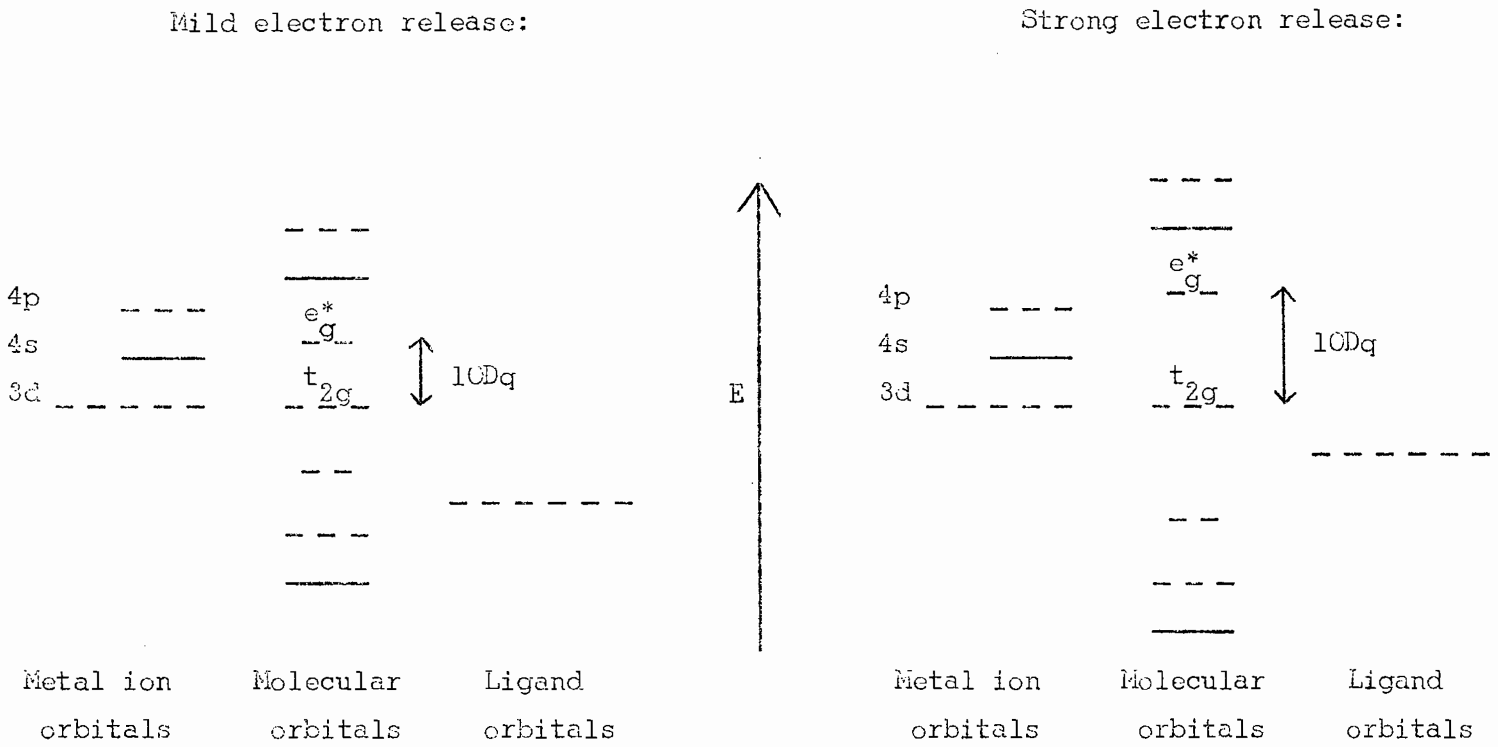
(For simplicity the ligand orbitals are assumed to be degenerate.)

Fig. A. The molecular orbital energy level diagram for an octahedral complex.

(2) The positive charge on the metal ion will be partially neutralised leading to a decrease in the metal ion to imide ligand attraction. Effectively this implies that the difference in energy levels between the metal 3d level and the ligand level is reduced hence seperation between the $e_g$ and $t_{2g}$ levels is increased, because the limiting case of this, where both the atomic orbitals have similar energy levels, is required by the molecular orbital theory to have the greatest seperation of molecular orbitals. The end result is that the value of 10Dq is raised and hence $\lambda$ max. is lowered , see Fig. B.

(3) In the above two cases it has been assumed that only $\sigma$ -bonding occurs between the metal ion and the imide ligands. However it is possible for the metal ion to form $\pi$-bonds with the imide nitrogen. If we assume that the M-N bond and the two C-N bonds of the imide are formed using the $sp_xp_y$ trigonal hybrid orbitals ($sp^2$ hybridisation) of the nitrogen, then the nonbonding electrons of the nitrogen would occupy the $2p_z$ orbital. The transition metal ions have 3d ($t_{2g}$) orbitals with the correct orientation to overlap with the $2p_z$ orbital of the nitrogen resulting in $\pi$-bond formation. An analogous phenomenon occurs in the compound $N(SiH_3)_3$ [70]. $\pi$-Bonding is not possible between the metal ion and the N of the amine (see Introduction, page 9).

It would be expected that increased electron release by the substituents on the amine would encourage $\pi$-bonding between the metal ion and the imide, leading to a decrease in the value of 10Dq and hence an increase in $\lambda$max. in the following manner, see Fig. C.

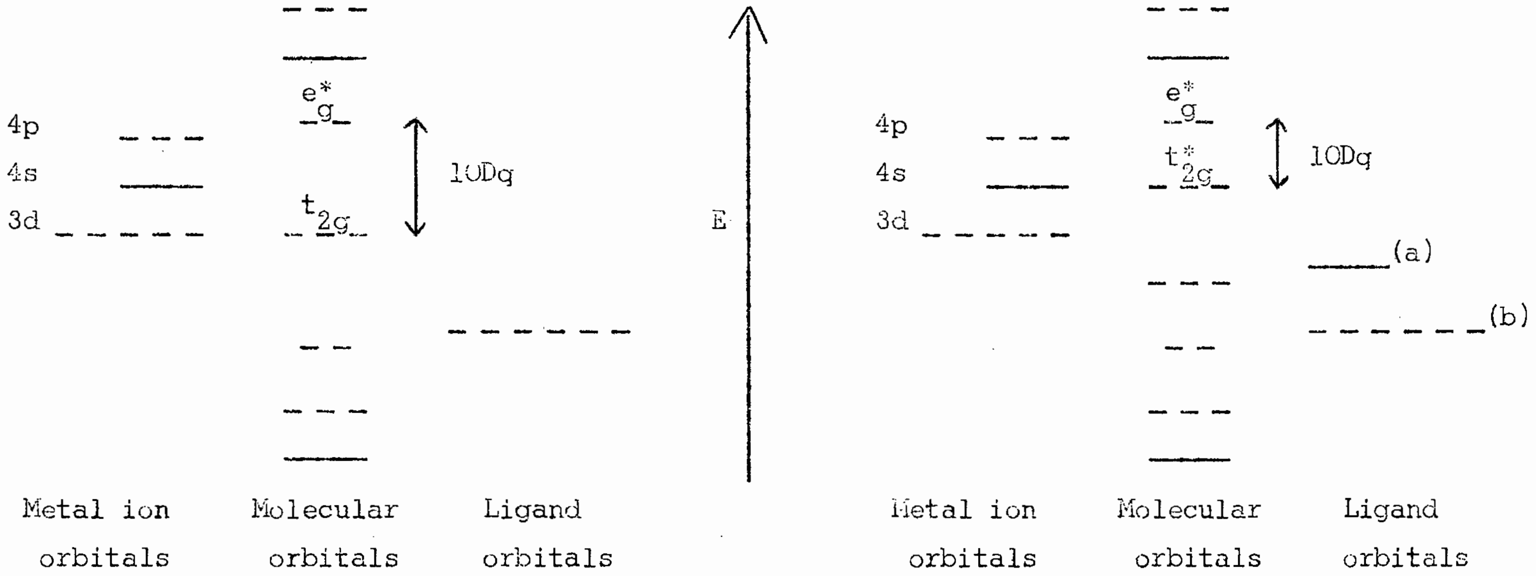


(Note difference in ligand orbital energy levels.)

Fig. B. The molecular orbital energy level diagram for an octahedral complex.

Mild electron release; no pi-bonding:

Strong electron release; pi-bonding involving occupied ligand orbitals:



(a) = ligand pi-bonding orbitals; (b) = ligand $\sigma$-bonding orbitals.

Fig. C. The molecular orbital energy level diagram for an octohedral complex.

The fact that λmax. increases with increased electron release of the amine substituent, indicates that the latter process, i.e. (3) is much more significant, although all these processes may well occur simultaneously.

The electronic absorption spectra of the copper(II) succinimide and copper(II) phthalimide series were also recorded in chloroform solution. The formation of blue solutions in this solvent indicated a structural change to a species of unknown structure; nevertheless the trends observed in the λmax. values were found to be similar to those in aqueous medium (Tables 12 and 13).

The absorption spectra of the nickel(II) series were also determined in chloroform solution. Four absorption maxima were observed in the region of 250 mμ (ε approx. = 1500), 380 mμ (ε approx. = 21), 630 mμ ( εapprox. = 9) and 1050 mμ (ε approx. = 3), corresonding to the spectra of typical octahedral nickel(II) complexes[71]. The first transition being due to the $\pi \longrightarrow \pi^*$ of the imide carbonyl and the latter three respectively to the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ transitions of the nickel(II) ion. Clearly the species existing in chloroform solution is octahedral, in the members of the nickel(II) series, but it is difficult to rationalise the donor role of chloroform. It was first thought that the chloroform was slightly "wet" and that the water molecules were in fact acting as donors converting the square-planar complexes to octahedral entities. However even in dried chloroform the yellow nickel(II) complexes dissolved to give green solutions, typical of octahedral nickel(II) complexes[71]. The copper(II) series would thus also be expected to be of octahedral structure in chloroform solution; this is in fact supported by the fact that the absorption maxima and trends observed in this solvent are similar to those in aqueous solution, where an octahedral species of known structure occurs.

Two of the three "d - d" transitions of the nickel(II) complexes also showed a dependance on the amine present and similar trends to those shown by their copper(II) analogues were observed (Table 14) viz. the wavelength of maximum absorption increases with increased electron releasing character of the amine substituents. The third transition in the region of 1050 mμ was found to be very broad and of such low intensity that a precise determination of λ max. was not possible. Clearly the same explanations of the shifts are relevant as in the copper(II) succinimide complexes since the wavelengths of the absorption maxima of the nickel(II) complexes are similarly related to the magnitude of 10Dq.

The visible absorption spectra of copper(II) succinimide complexes in aqueous medium have been previously recorded[32]. λmax. was found to be approximately constant at 630 mμ. This we supposed to be due to the fact that (according to Tschugaeff[27]) if the solutions are left to stand for a short period a final product $[Cu(H_2O)_6]Su_2$ is obtained irrespective of the nature of the coordinated amine. This supposition could not be tested however, because after a short time the solutions became cloudy and their absorption spectra were thus unobtainable. On the other hand the complexes underwent no apparent change in chloroform solution and are recoverable simply by evaporation of the solvent.

We now reconsider the infrared evidence that the carbonyl stretching frequencies of the imide increases with increased electron-releasing character of the amine substituents. $\pi$-bonding has been shown to be possible between the imide nitrogen and the metal ion. This is supported by the ultraviolet-visible evidence. It would be expected that this $\pi$-bonding would also have an effect on the carbonyl stretching frequencies. Effectively $\pi$-bonding implies the back donation of metal d-electrons to the ligand orbitals. This back donation from the metal ion to the imide ligand will be assisted by strongly electron releasing amine substituents. It is likely that this electronic effect would be transmitted to the rest of the imide molecule, increasing the electron density in the imide system and hence the carbonyl stretching frequencies. This is observed (Tables 12 - 15). The correlations between the carbonyl stretching frequencies and the Taft polar substituent constants are graphically portrayed in Figs. 10 - 12.

This effect is supported by the carbonyl stretching frequencies of potassium phthalimide, which are exceptionally low (1700 and 1640 $cm^{-1}$). In this case there is no $\pi$-bonding possible between the potassium ion and the imide, consequently the drainage of electrons from the imide ring to the imide nitrogen is at a maximum and hence the carbonyl frequencies are exceptionally low.

In the plots involving the substituents cyclohexyl (Cx) and $\beta$-hydroxyethyl ($CH_2CH_2OH$) the respective $\sigma^*$ values -0.22 and +0.54 have been used. However, Taft[3] did not include these substituents in his determinations of $\sigma^*$, hence the $\sigma$'s for these substituents are not known. The above values were used because the carbonyl stretching frequencies and the $\lambda$ max. values of the imide complexes together with the M-O stretching frequencies and the N.M.R. chemical shifts for the complexes $[\text{MAcac}_2(\text{RNH}_2)_2]$, where M = Ni, Zn (see Sections 3 and 4) suggest that the substituent constant for Cx lies between that for iso-Pr (-0.19) and t-Bu (-0.30) while that for $-CH_2CH_2OH$ lies between that for H (+0.49) and Ph (+0.60). The values of -0.22 for Cx and +0.54 for $-CH_2CH_2OH$ have been used as those providing the best fit with all the infrared, ultraviolet and N.M.R. spectral data available in this work.

TABLE 12

Infrared frequencies ($cm^{-1}$) and visible absorption maxima (mμ) of copper complexes, $[CuSu_2(R\text{-}NH_2)_2]$.

| σ | R | NH stretching | | | C=O stretch | | $^2E_g \leftarrow {}^2T_{2g}$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | (1) | (2) | in water | in chloroform |
| -0.30 | t-Bu | 3286 | 3253 | 3174 | 1717 | 1628 | 660 | 657 |
| | Cx | 3276 | 3250 | 3167 | 1714 | 1625 | - | 617 |
| -0.19 | iso-Pr | 3254 | | 3166 | 1713 | 1624 | 653 | 615 |
| -0.13 | n-Bu | 3261 | | 3165 | 1711 | 1624 | - | 608 |
| -0.125 | iso-Bu | 3289 | 3252 | 3168 | 1712 | 1622 | 645 | 610 |
| -0.115 | n-Pr | 3263 | | 3169 | 1711 | 1621 | 648 | 610 |
| 0 | Me | 3264 | | 3173 | 1709 | 1620 | 630 | 595 |
| +0.08 | $CH_2CH_2Ph$ | 3259 | | 3166 | 1710 | 1619 | - | 600 |
| +0.215 | $CH_2Ph$ | 3266 | | 3162 | 1709 | 1618 | - | - |
| +0.49 | H | 3309 | 3239 | 3161 | 1706 | 1615 | - | - |
| | $CH_2CH_2OH$ | 3256 | | 3161 | 1697 | 1601 | 615 | - |

(- indicates complexes not soluble in the solvent)

TABLE 13

Infrared frequencies (cm$^{-1}$) and visible absorption maxima (mμ) of copper complexes, $[CuPhth_2(R\text{-}NH_2)_2]$.

| σ | R | N-H stretching | | | C=O str. | $^2E_g \leftarrow {}^2T_{2g}$ in $CHCl_3$ |
|---|---|---|---|---|---|---|
| -0.30 | t-Bu | 3290 | 3252 | 3172 | 1729 | 655 |
| | Cx | 3287 | 3248 | 3168 | 1727 | 615 |
| -0.19 | iso-Pr | 3281 | 3247 | 3165 | 1727 | 610 |
| -0.13 | n-Bu | 3263 | | 3161 | 1721 | 604 |
| -0125 | iso-Bu | 3298 | 3258 | 3176 | 1725 | 607 |
| -0.115 | n-Pr | 3274 | 3254 | 3169 | 1723 | 600 |
| -0 | Me | 3278 | 3259 | 3172 | 1721 | 590 |
| +0.08 | $CH_2CH_2Ph$ | 3272 | 3251 | 3166 | 1719 | 592 |
| +0.215 | $CH_2Ph$ | 3260 | | 3158 | 1718 | - |
| +0.49 | H | 3324 | 3178 | 3063 | 1710 | - |

(- indicates complexes not soluble in chloroform)

TABLE 14

Infrared frequencies ($cm^{-1}$) and ultraviolet-visible absorption maxima ($m\mu$) in chloroform of nickel(II) complexes, $[NiBu_2(R\text{-}NH_2)_2]$

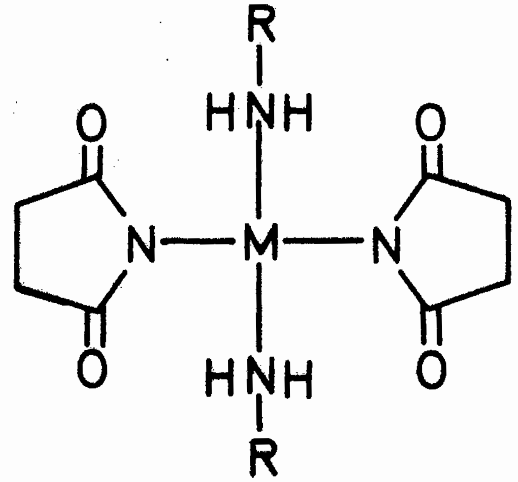
| σ | R | N-H stretching | | | C=O str. (1) | (2) | $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ | $^3A_{2g} \rightarrow {}^3T_{2g}(P)$ |
|---|---|---|---|---|---|---|---|---|
| | Cx | 3260 | | 3165 | 1716 | 1629 | 644 | 393 |
| -0.13 | n-Bu | 3243 | | 3163 | 1712 | 1626 | - | - |
| -0.125 | iso-Bu | 3273 | 3241 | 3162 | 1713 | 1622 | 636 | 387 |
| -0.115 | n-Pr | 3247 | | 3164 | 1712 | 1626 | 633 | 387 |
| 0 | Me | 3259 | 3252 | 3172 | 1710 | 1624 | 627 | 381 |
| +0.08 | $CH_2CH_2Ph$ | 3247 | | 3163 | 1710 | 1624 | 629 | 382 |
| +0.215 | $CH_2Ph$ | 3242 | | 3157 | 1709 | 1622 | 625 | 378 |

(- indicates insoluble in chloroform)

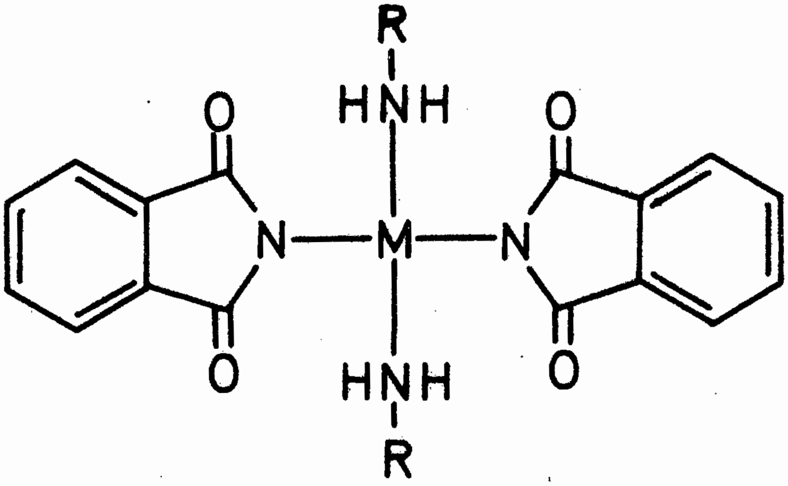
TABLE 15

Infrared frequencies of nickel(II) complexes, $[NiPhth_2(R\text{-}NH_2)_2]$

| σ | R | N-H stretching | | | C=O stretching |
|---|---|---|---|---|---|
| | Cx | 3265 | | 3170 | 1728 |
| -0.19 | iso-Pr | 3267 | 3244 | 3165 | 1728 |
| -0.13 | n-Bu | 3242 | | 3160 | 1724 |
| -0.125 | iso-Bu | 3278 | 3240 | 3165 | 1726 |
| -0.115 | n-Pr | 3244 | | 3158 | 1724 |
| -0.100 | Et | 3246 | | 3159 | 1724 |
| 0 | Me | 3277 | 3243 | 3164 | 1725 |
| -0.08 | $CH_2CH_2Ph$ | 3244 | | 3162 | 1723 |
| -0.215 | $CH_2Ph$ | 3240 | | 3151 | 1722 |



(I)



(II)

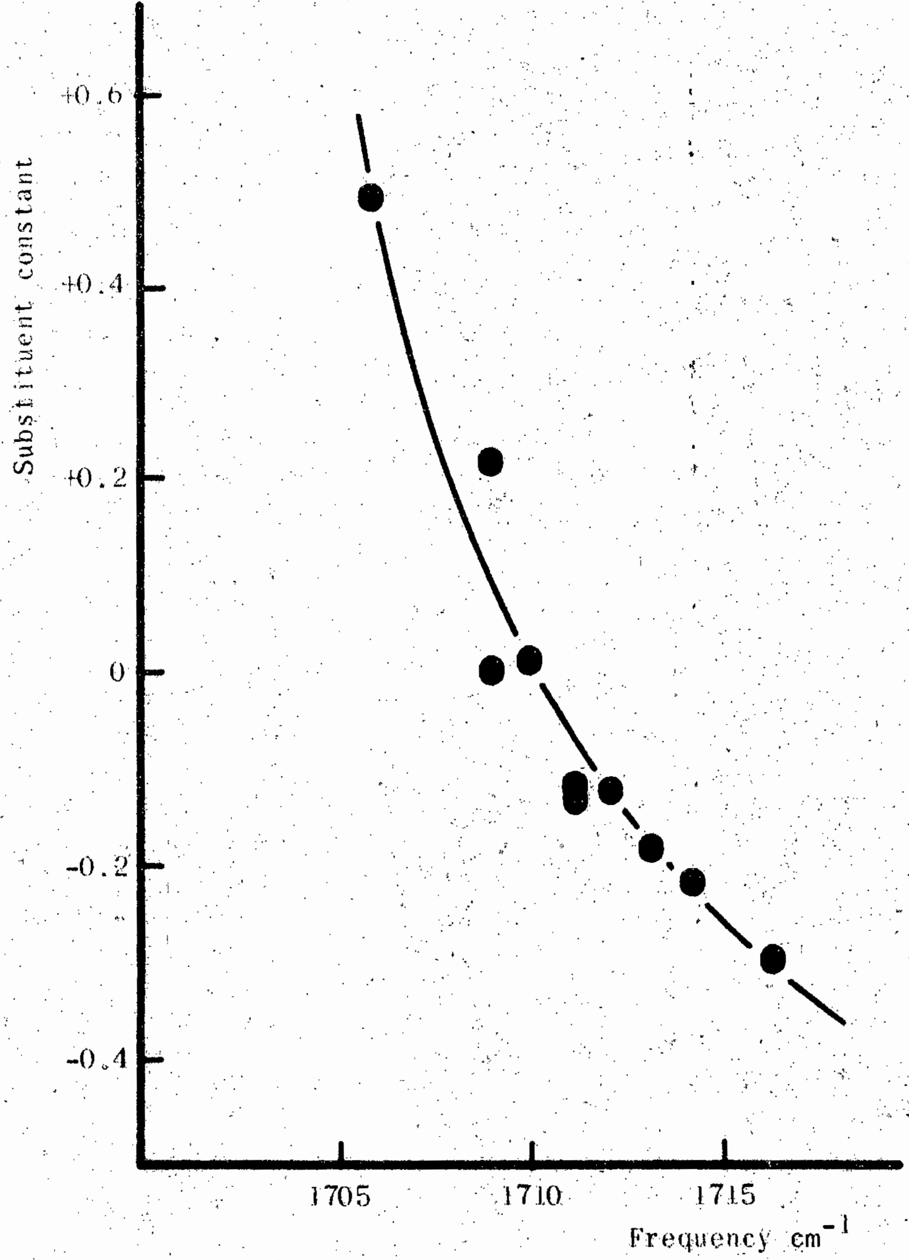


Fig. 10. Plot of C=O stretching frequency against substituent constant for $[CuSu_2Am_2]$.

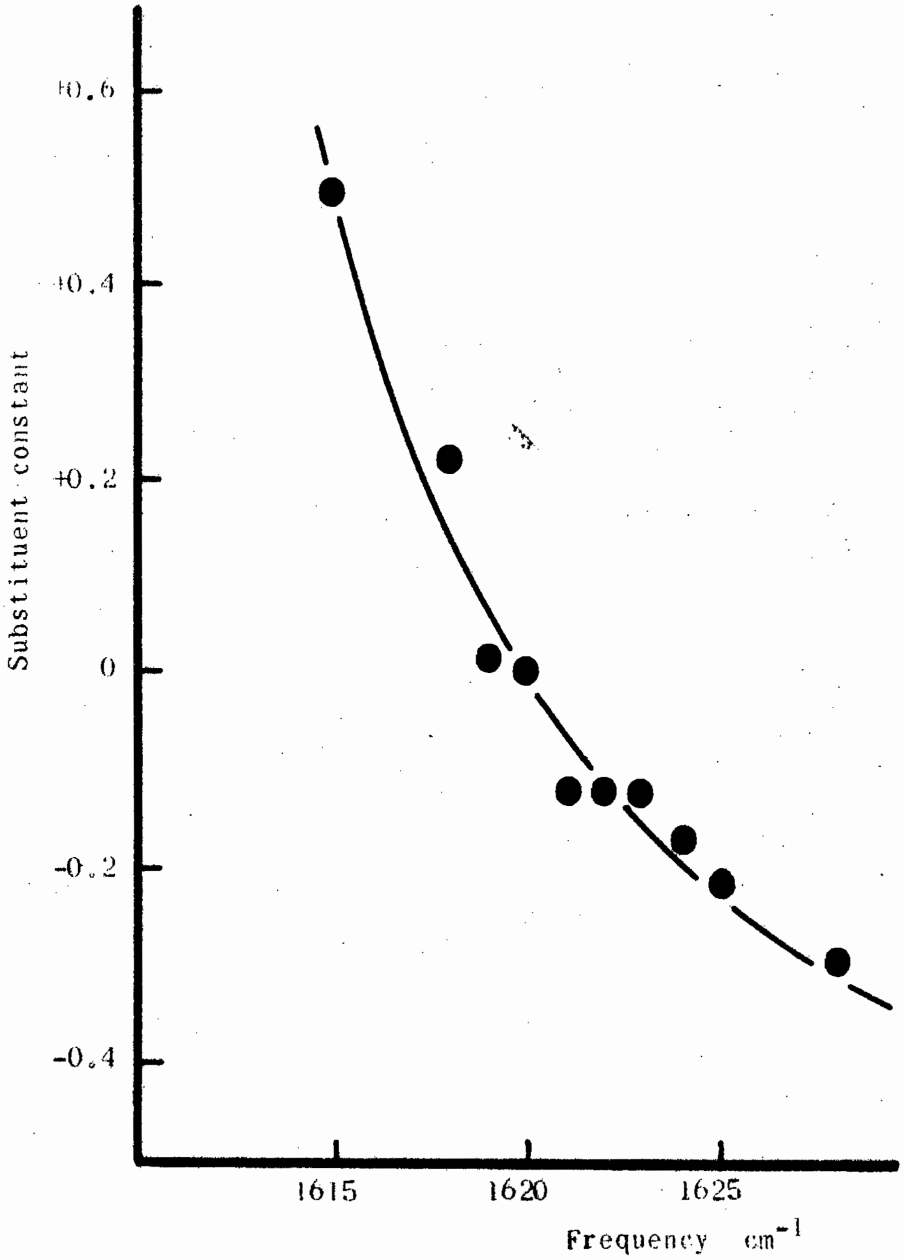


Fig. 11. Plot of C-O stretching frequency against substituent constant for [$CuSu_2Am_2$].

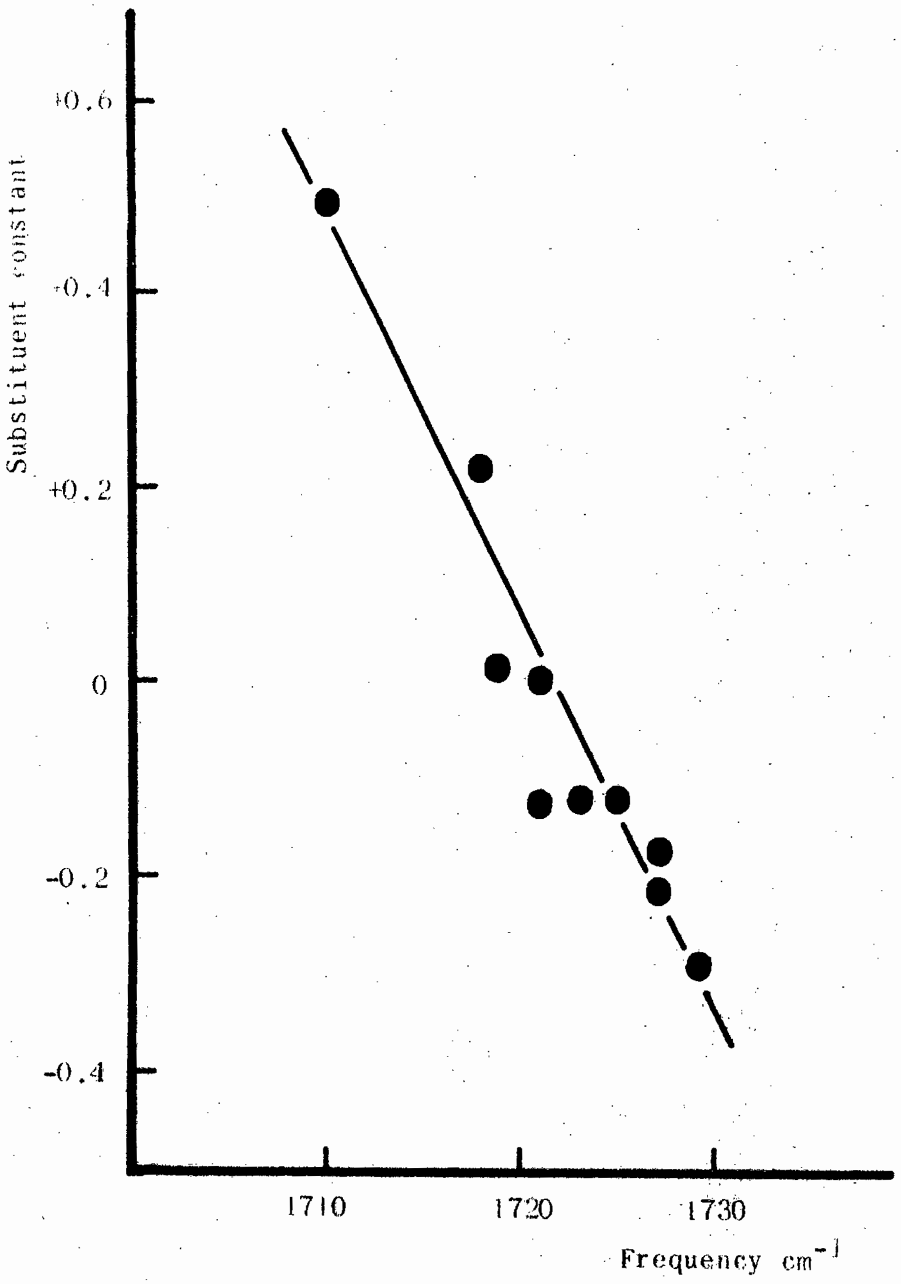
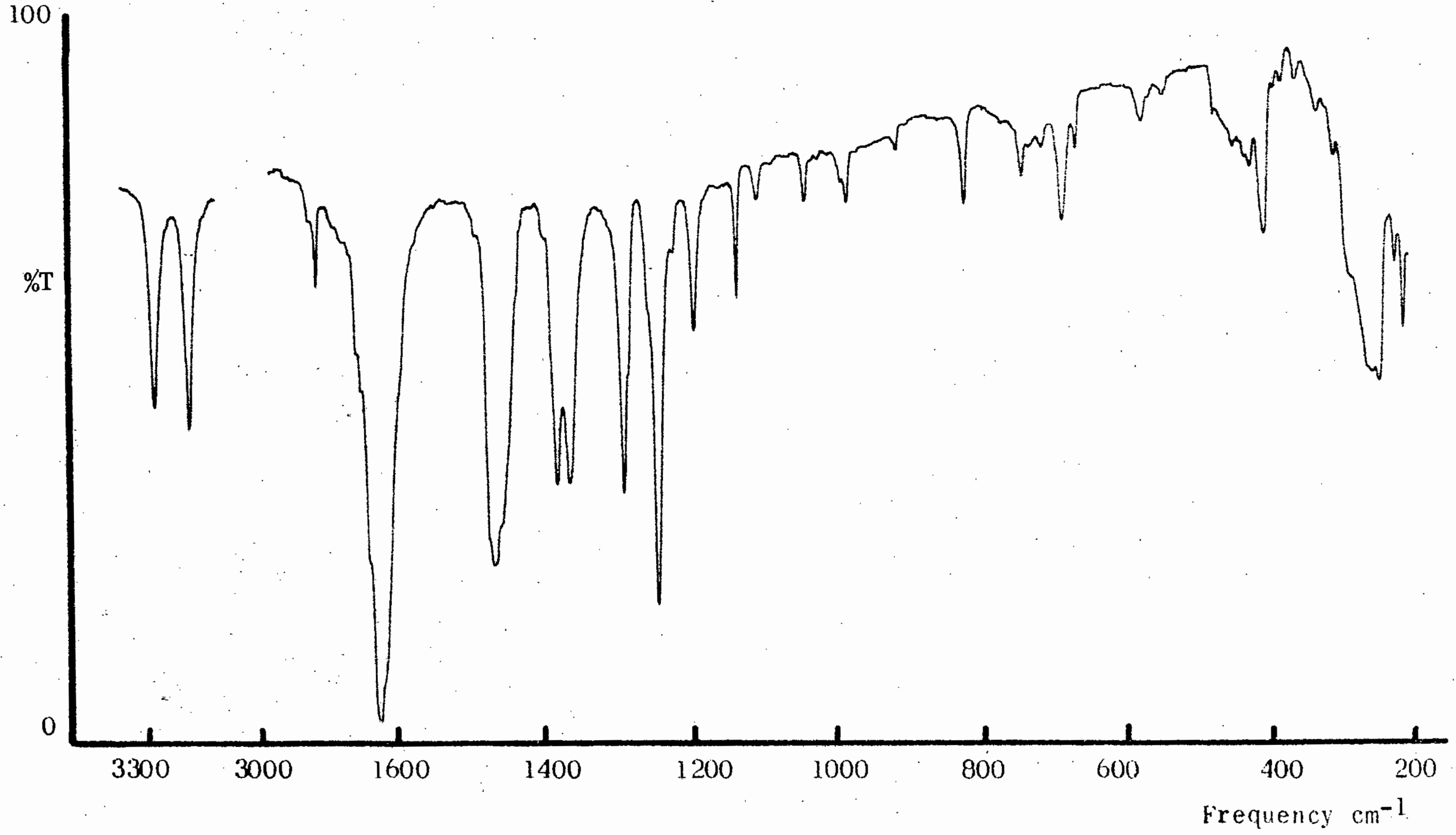


Fig. 12. Plot of C=O stretching frequency against substituent constant for $[CuPhth_2Am_2]$.

Fig. 13. Infrared spectrum of $[CuSu_2(n\text{-butylamine})_2]$.



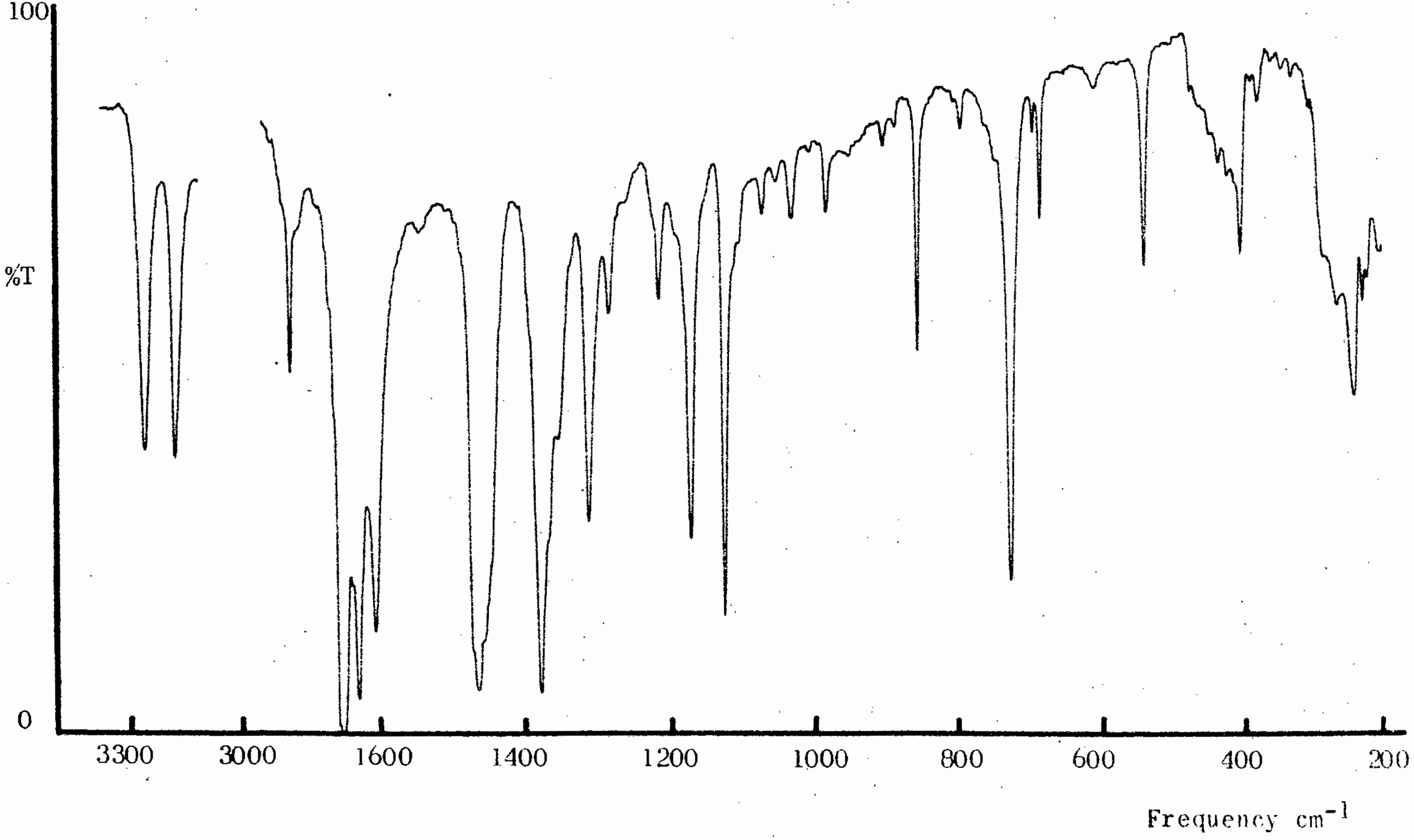


Fig. 14. Infrared spectrum of $[NiPhth_2(n\text{-butylamine})_2]$.

## (3) Amine adducts of nickel(II) acetylacetonate.

Acetylacetone was the first compound employed as a chelating agent by Werner[72]. Since then acetylacetone has proved to be one of the most versatile groups of ligands available in the study of coordination complexes. The bonding in these complexes e.g. tris(acetylacetonato)iron(III) has been established[73] by X-ray structural studies to occur via the oxygen atoms of the acetylacetone ligand.

Sqare planar complexes of nickel(II), $\left[NiL_4\right]$, may undergo an equilibrium with additional ligands, L′, in the following manner :

$$\left[NiL_4\right] + 2L' \rightleftharpoons \underline{trans} - \left[NiL_4L'_2\right]$$

If the adduct L′ is a good donor, then in many cases the equilibrium will lie far to the right, resulting in an isolable 6-coordinate complex. Examples of such ligands are water and nitrogenous bases.

Thus it would be expected that if bis(acetylacetonato)nickel(II) has monomeric square planar structure, diamine adducts of the form $\left[NiAcac_2Am_2\right]$ (see Diagram III, page 79) could be isolated. However X-ray analysis[74] of the crystal structure of bis(acetylacetonato)nickel(II) established the molecule as a trimer $\left[NiAcac_2\right]_3$. Some oxygen atoms of the acetylacetonate are thus shared between two nickel ions resulting in each nickel ion attaining octahedral configuration. The trimer is however readily cleaved by donors such as water and nitrogenous bases to yield 6-coordinate monomers.

Contrary to the behaviour of acetylacetone, certain other β-diketones do form square-planar complexes with nickel(II). If the methyl groups of acetylacetone are replaced by bulky substituents such as tertiary butyl groups, the nickel(II) complexes formed are monomeric and square-planar as a result of steric repulsion. The red bis(dipavaloylmethanoto)nickel(II) complex is diamagnetic but in the presence of water (or a nitrogenous base) the green paramagnetic dihydrate is formed.

Because the preparation of the green diaquo adduct of nickel(II) acetylacetonate is particularly straight forward it was considered practicable to use it as the starting material for synthesising the amine adducts. Amines are known[75] to displace some or all of the water molecules in the octahedral $\left[Ni(H_2O)_6\right]^{2+}$ ion, therefore it is not surprising that in an excess of amine replacement of water in the complex $\left[NiAcac_2(H_2O)_2\right]$ occurs, giving rise to the pale blue 6-coordinate complex of the form $\left[NiAcac_2Am_2\right]$.

The colour change from green to blue occurs because of shifts in the absorption bands when water is replaced by amine ligands which lie to the right of water in the spectrochemical series so producing a stronger ligand field.

As detailed in the Experimental Section, the adducts were synthesised by adding the appropriate solid aromatic amine in methanolic solution to a methanolic solution of $\left[NiAcac_2(H_2O)_2\right]$. Under these conditions only the solid amines with positive substituent constants yielded the required adduct; those with negative substituent constants gave the methanol adduct only undoubtedly because the reduced donor capacity of the nitrogen atom in the latter cases resulted in the methanol adduct being more stable.

A more direct and alternative method of preparation was devised for the aliphatic amine adducts, according to the following equation :

$$\mathrm{NiCl_2} + 2\ \mathrm{AcacH} + 2\ \mathrm{Am} \quad \left[\mathrm{NiAcac_2Am_2}\right] + 2\ \mathrm{HCl}$$

This method was not applicable to the aromatic amine adducts as mixed compounds were precipitated, these comprising a mixture of the amine hydrochloride, the amine complex of nickel(II) chloride and the required amine adduct. This method gave no precipitated complex for tertiary butylamine and even in the former method the adducted complex of this ligand formed with difficulty. Microanalysis indicated that this particular complex was in fact only 5-coordinated, (analysis, found : C, 50.34; H, 7.74; calculated for $C_{14}H_{25}O_4N_1Ni$ : C, 50.65; H, 7.59%) in contrast to all the others which were octahedrally coordinated.

The infrared spectra of acetylacetone derivatives have been summerised by Nakamoto[76] for a series of metal ions, including bis(acetylacetonato)nickel(II). The carbonyl and metal to oxygen vibrations are of particular interest. Some confusion exists in the literature concerning the assignment of the first two intense bands below 2000 $cm^{-1}$. Lecompte[77,78], by considering acetylacetone to be a combination of two molecules of acetone, has assigned the first band in the metal complexes (at approximately 1580 $cm^{-1}$) to the carbonyl stretching vibration and the second (at approximately 1520 $cm^{-1}$) to the C=C stretching mode. Bellamy and Branch[79] also assigned the band at 1580 $cm^{-1}$ to the carbonyl vibration. Nakamoto et. al.[80] reached the opposite conclusion on the basis of a normal coordinate treatment of copper(II) acetylacetonate. Subsequent revision[81] of his treatment led to a reversal of his earlier assignments and support for those by Lecompte. A recent infrared spectral study[83] with oxygen-18-labeled acetylacetone coordination compounds confirmed these assignments.

The infrared spectra of the diamine adducts of bis(acetylacetonato)nickel(II) exhibited two intense bands in the region 1600 - 1500 $cm^{-1}$. Unfortunately the first of these bands at approximately 1600 $cm^{-1}$(assigned to the carbonyl stretching vibration) was found to be quite broad probably due to overlap with the N-H bending vibration of the amine which is also expected to occur in this region.

The metal to oxygen vibrations are of particular interest in this problem as will be seen later. The infrared spectra of acetylacetone complexes contain three bands in the region of 650, 550 and 420 $cm^{-1}$ which have been assigned[80,82] to (M-O str. + $C-CH_3$ str.), (M-O str. + ring deformation) and (M-O str.) respectively. The infrared spectra of the diamine adducts exhibited bands of medium intensity corresponding to these three vibrations.

The N-H stretching frequencies of the free amines were found to be lowered on coordination as found in the spectra of amine complexes described elsewhere in this thesis (Section 1). Typical infrared spectra of these complexes appear in Figs. 17 and 18.

It has been found[41] that in a series of metal β-diketonates, the substituent on the β-diketone molecule has a direct bearing on the C-O and M-O frequencies. In a particular series of metal β-diketonates with constant metal ion, those with electron-releasing β-diketone substituents, _e.g._ tris(acetylacetonato)iron(III), were found to have low C-O and high M-O frequencies compared with those possessing electron-withdrawing substituents, e.g. tris(hexafluoroacetylacetonato)iron(III). This was explained as follows. The electronic effect of an electron releasing substituted β-diketone (R′ = $CH_3$) complex was assumed to take place as illustrated in Diagram IV, page 79. Thus the carbonyl frequency is lowered and the M-O frequency is raised. For an electron withdrawing substituted complex (R′ = $CF_3$) the illustrated electronic effect will be opposed or reversed causing the carbonyl frequency to be higher and the M-O frequencies to be lower than in the former case.

In the series of amine adducts of bis(acetylacetonato)nickel(II) examined, various amines of differing substituent effect were used. Thus instead of varying the β-diketone substituent, the nature of the amine adducts was varied.

It was found that two of the three M-O sensitive vibrations of the acetylacetonate were indeed affected by changing the amine in a set, as seen in Tables 16 and 17. On the other hand the M-O vibration at 650 $cm^{-1}$ was found to be relatively unaffected by this change. The assignment of this band has in fact been queried[83] on the basis of oxygen-18-labeled acetylacetone complexes. The infrared spectra of these complexes indicated that only the two lower frequency bands were M-O sensitive.

The carbonyl stretching vibration in the 1600 $cm^{-1}$ region of the spectrum was not affected to any great extent by the change of amine and was found to remain relatively constant at approximately 1605 $cm^{-1}$, probably because the effect of changing the amine was too weak to affect the carbonyl which is further removed from the amine than the M-O bond. In addition the precision with which the wavenumber of this band could be determined was poor due to its broad character and complications in that region of the spectrum resulting from aromatic ring vibrations (in the case of the aniline adducts).

Figs. 15 and 16 show the correlations between the two M-O sensitive vibrations and the substituent constants of the aliphatic amines. The basic trend indicates that strongly electron-releasing substituents lower the M-O frequencies and hence bond strengths, relative to weakly-electron releasing substituents in the case of aliphatic amine adducts. A similar trend in Table 17 for aromatic amine adducts indicate that electron-releasing substituents lower the M-O frequencies while electron withdrawing substituents have the reverse effect, relative to the aniline adduct.

These trends can be explained on the basis of the electronic effects existing in the molecule as shown in the illustrated diagram (IV). The electron-releasing substituents of the aromatic amines will tend to oppose the electronic effect shown i.e. assuming the electron drift from the amine to be transmitted through the metal ion. This will cause the M-O bond strength and thus the frequencies of the M-O sensitive vibrations to be lowered relative to the aniline adduct. The electron-withdrawing substituents will promote the effect illustrated, giving rise to higher M-O vibrations relative to the aniline adduct. The spectra of the aliphatic amine adducts receive a similar interpretation.

The M-O frequencies for the diaquo adduct were found to be the highest viz. 585 and 429 $cm^{-1}$. This fact supports the above explanation as water is a much weaker base than amines, thus the illustrated electronic effect will be relatively unopposed giving rise to the high observed M-O frequencies.

In support of the assumption that the electronic effects are transmitted through the metal ion, it has been found[41] that for instance bis(hexafluoroacetylacetonato)nickel(II) exists solely as a diadducted complex. Thus it appears that the strongly electron-withdrawing character of the β-diketonate promotes adduction to such an extent that adducted molecules cannot easily be removed again.

In conclusion it would appear that in a set of β-diketonate complexes, changing the substituent on the β-diketone molecule and changing the substituent on the adducted amine ion in the complex of a particular β-diketone produces a similar result. However the frequency shifts of the M-O vibrations are much more marked in the first case than in the second, presumably because in the former the substituent is part of the β-diketone molecule and therefore its effect is felt to a much greater extent for reasons of proximity.

The shifts observed in the N-H stretching frequencies on changing the aliphatic amine are shown in Table 16. There appears to be no obvious trend, this is probably due to the combination of electronic and mass effects and also possibly the steric hinderance imposed by bulky amines. The shifts observed in the N-H stretching frequencies of the aromatic amine adducts are shown in Table 17. The basic trend can be explained on the basis of electron increase and decrease on the nitrogen as shown in Section 1.

TABLE 16

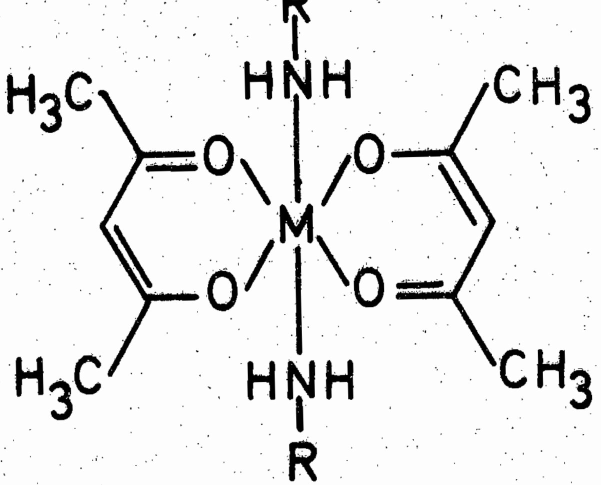
Infrared frequencies ($cm^{-1}$) of nickel(II) complexes, $[NiAcac_2(R\text{-}NH_2)_2]$

| σ | R | N-H stretching | | | M-O str. | M-O str. + ring def. |
|---|---|---|---|---|---|---|
| | Cx | 3316 | 3285 | 3265 | 414 | 565 |
| -0.19 | iso-Pr | 3314 | 3291 | 3270 | 415 | 564 |
| -0.13 | n-Bu | 3314 | 3280 | 3190 | 416 | 564 |
| -0.125 | iso-Bu | 3331 | 3277 | 3175 | 414 | 563 |
| -0.115 | n-Pr | 3318 | 3279 | 3190 | 416 | 564 |
| -0.10 | Et | 3321 | 3280 | 3192 | 415 | 565 |
| 0 | Me | 3328 | 3298 | 3208 | 417 | 567 |
| +0.08 | $CH_2CH_2Ph$ | 3318 | 3275 | 3190 | 417 | 576 563 |
| +0.215 | $CH_2Ph$ | 3317 | 3275 | 3177 | 418 | 567 |
| +0.49 | H | 3355 | 3276 | 3188 | 423 | 571 |
| | $CH_2CH_2OH$ | 3325 | 3278 | 3192 | 424 | 574 |
| +0.60 | Ph | 3289 | | 3183 | 425 | 576 |

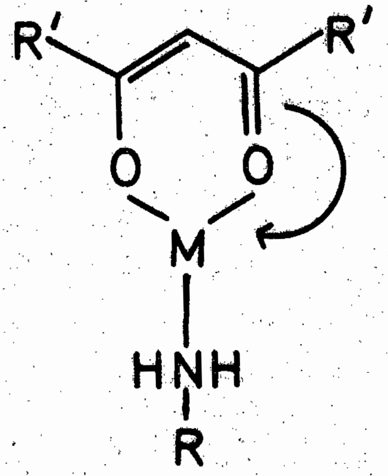
TABLE 17

Infrared frequencies (cm$^{-1}$) of nickel(II) complexes, $[NiAcac_2(R\text{-}C_6H_4\text{-}NH_2)_2]$

| σ | R | N-H stretching | | M-O str. | M-O str. + ring def. |
|---|---|---|---|---|---|
| | | asym. | sym. | | |
| -0.27 | 4-OMe | 3280 | 3188 | 420 | 571 |
| -0.25 | 4-OEt | - | 3188 | 422 | 571 |
| -0.24 | 3:4-diMe | 3280 | 3182 | 421 | 572 |
| -0,17 | 4-Me | 3276 | 3185 | 422 | 574 |
| -0.15 | 4-Et | 3270 | 3185 | 424 | 576 |
| -0.07 | 3-Me | 3269 | 3183 | 424 | 575 |
| 0 | H | 3269 | 3183 | 425 | 576 |
| +0.06 | 4-F | 3275 | 3183 | 425 | 576 |
| | | 3235 | | | |
| +0.115 | 3-OMe | 3268 | 3178 | 425 | 576 |
| +0.235 | 3-Cl, 4-Me | 3266 | 3176 | 426 | 577 |
| +0.34 | 4-F | 3265 | 3180 | 427 | 578 |
| +0.37 | 3-Cl | 3262 | 3178 | 428 | 578 |



(III)



(IV)

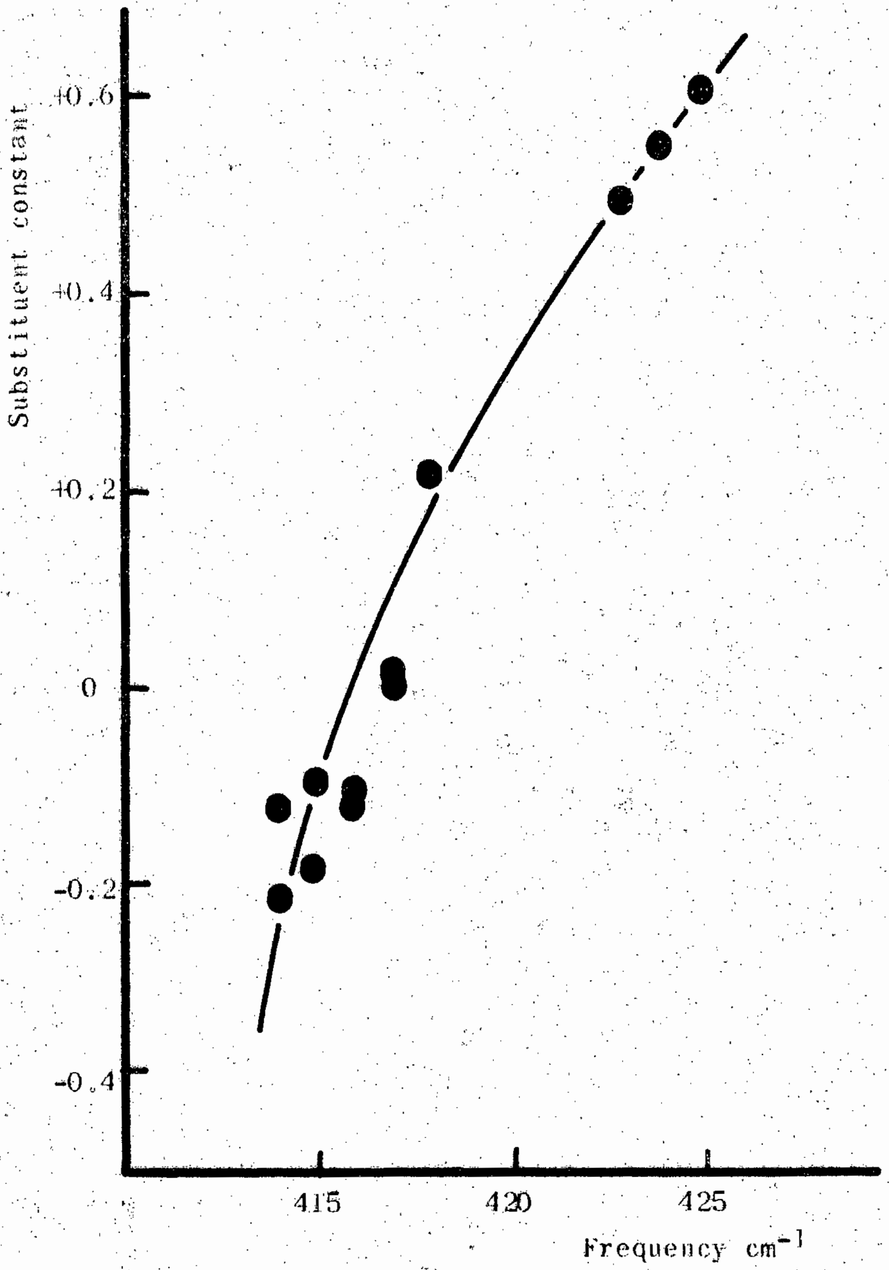


Fig. 15. Plot of M-O stretching frequency against substituent constant for $[NiAcac_2Am_2]$.

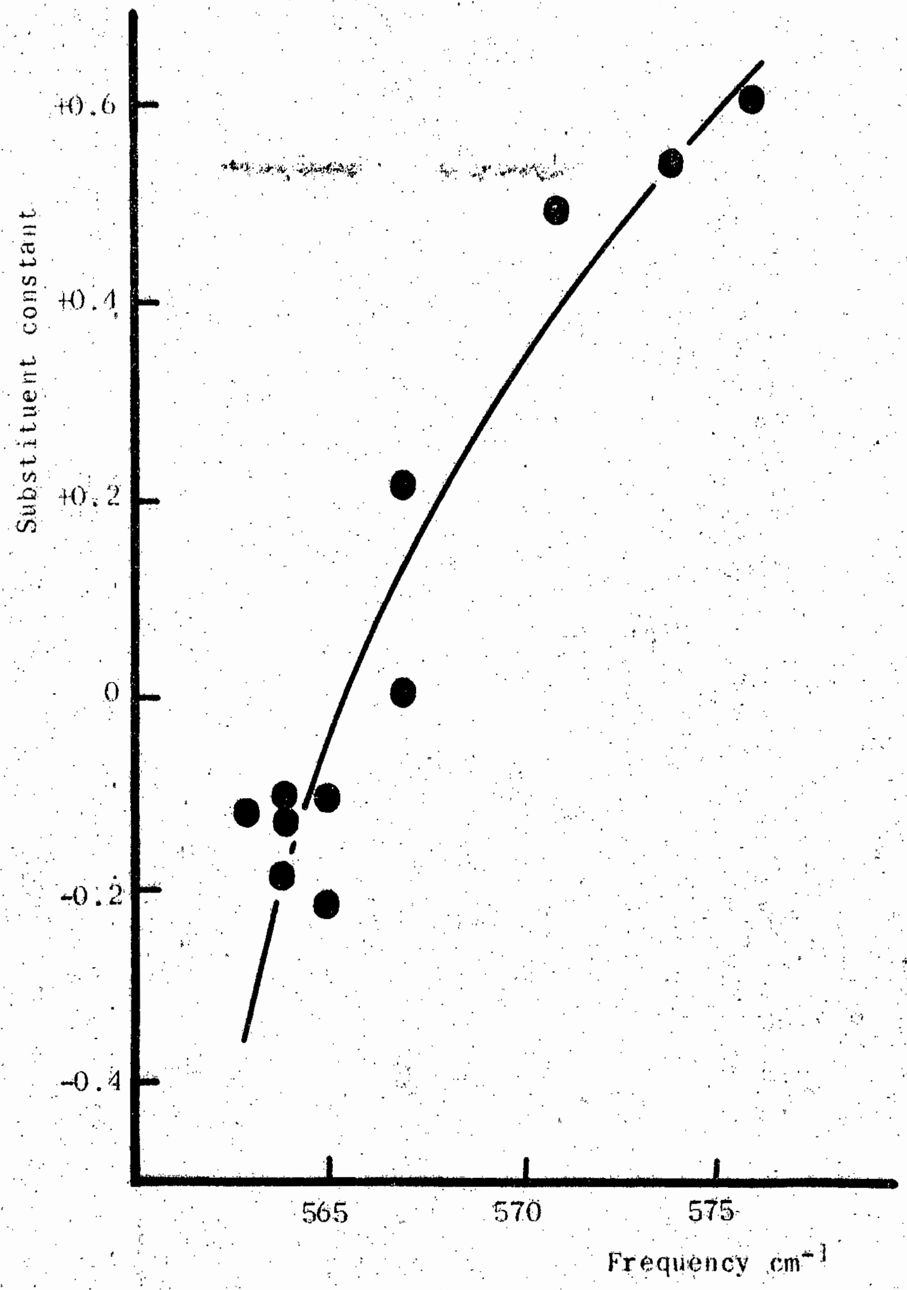


Fig. 16. Plot of M-O + ring deformation frequency against substituent constant for $[NiAcac_2Am_2]$.

Fig. 17. Infrared spectrum of $[NiAcac_2(ammonia)_2]$.

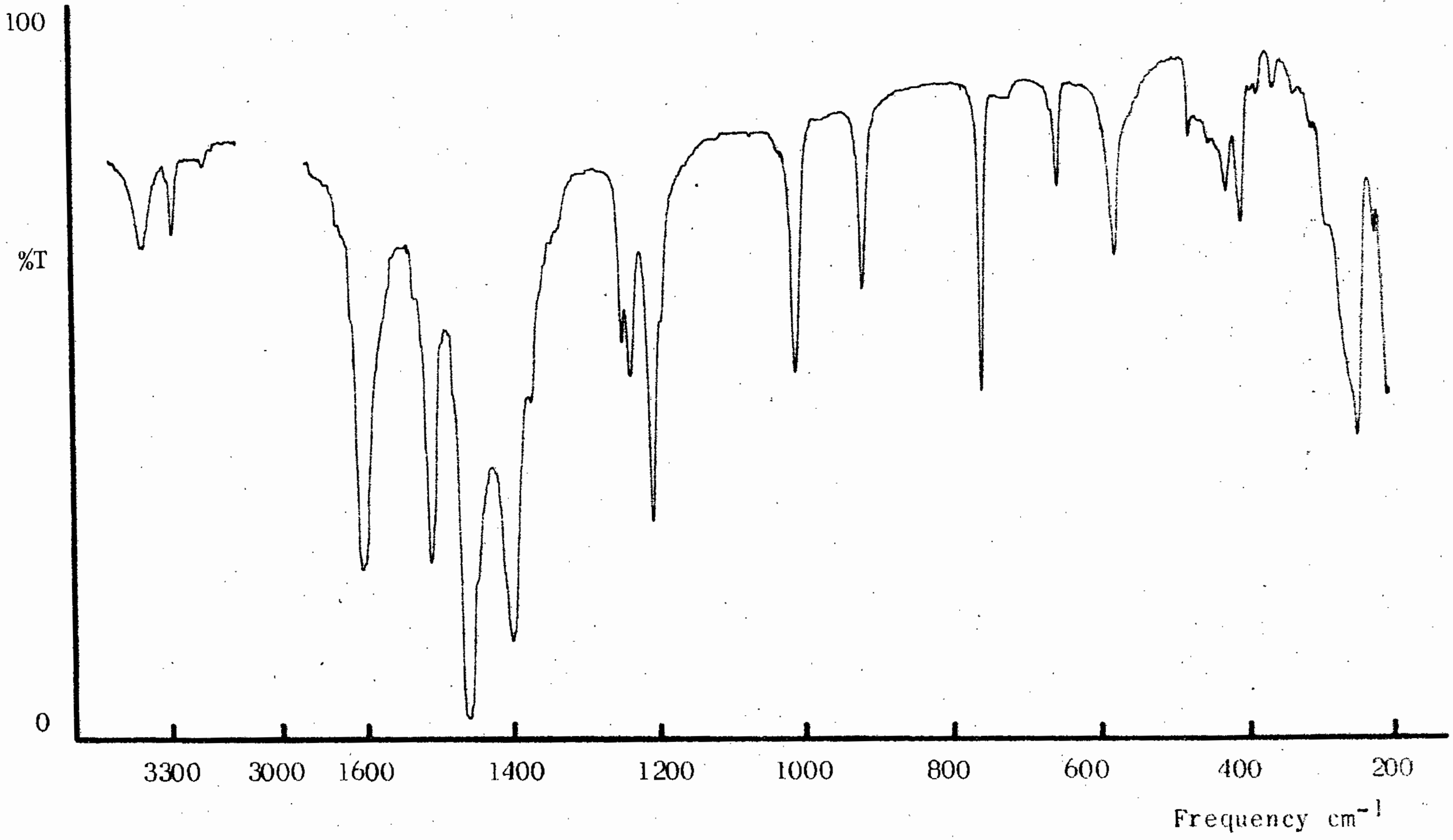
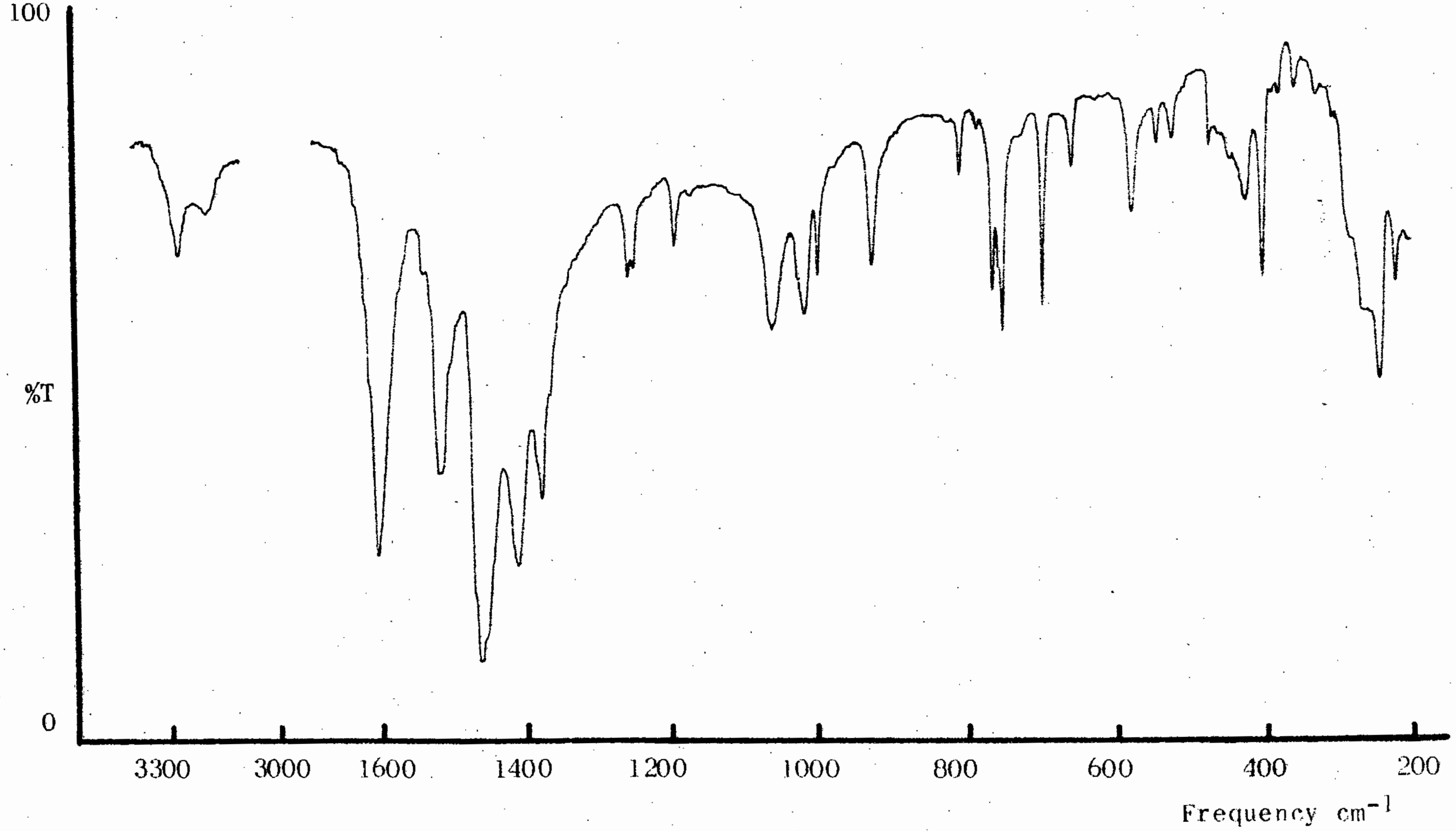


Fig. 18. Infrared spectrum of [$NiAcac_2(aniline)_2$].



## (4) Amine adducts of zinc(II) acetylacetonate

The stereochemistry of zinc(II) complexes is not affected by ligand field stabilisation effects, owing to the spherical symmetry of the full 3d shell and is thus solely determined by considerations of size, electrostatic interaction and covalent bond strengths.

Zinc(II) has usually been regarded as exhibiting two alternative stereochemistries; octahedral with relatively long zinc-ligand bonds and tetrahedral with shorter bonds. However 5-coordinate zinc(II) complexes are known <u>e.g.</u> where amines form 1 : 1 complexes with zinc(II) dialkyldithiocarbamates[84]. It has been found[34] that several alternative syntheses of bis(acetylacetonato)zinc(II) lead to the formation of the 5-coordinate monohydrate. X-ray analysis[85] of this compound shows it to have trigonal bipyramidal structure. The complex can be dehydrated but it has been shown[86] that the anhydrous form is analogous to the nickel(II) complex is existing as a trimer in the solid state. Nevertheless in non-donor solvents it is monomeric and therefore presumably tetrahedral[34].

Like the nickel(II) analogues, it may be anticipated that zinc(II) acetylacetonate would also form adducts with nitrogenous bases. Some adducts of bis(acetylacetonato)zinc(II) have been reported[87]. In these cases chelating bases such as 2,2'-bipyridine form 6-coordinate complexes of the form $\left[ZnAcac_2Bipy\right]$. However monodentate nitrogenous base adducts of zinc(II) β-diketonates have been shown[34,35] to exist as both 5- and 6-coordinated species.

The monohydrate of bis(acetylacetonato)zinc(II) was used as the starting material for the preparation of the primary amine adducts. Most of the amines displaced the water fairly rapidly simply by recrystallisation of the hydrate from the appropriate amine to give colourless plate- or needle-like complexes. On the basis of percentage composition the amines reacted with bis(acetylacetonato)zinc(II) to yield either 2 : 1 (see III, page 79) or 1 : 1 adducts, these being respectively 6-coordinate octahedral and 5-coordinate trigonal bipyramidal complexes.

Most of the 6-coordinate complexes lost amine slowly if left in the atmosphere; presumably they would decompose to the mono-amine adduct if left for a sufficient period. The benzylamine adduct was found to be the most stable; even at reduced pressure it remained virtually unchanged.

Both basicity and steric requirements of the amine are factors in determining which of the two structures is the more stable. Tertiary butyl- and isopropylamine (strong bases) formed mono-adducts, whereas aniline (relatively weak base) formed a diadduct. This could also be attributed to steric factors since triethylamine and dibenzylamine failed to adduct at all. Furthermore, it has been found[34] that 4-methylpyridine forms a stable diadduct, whereas pyridine forms a relatively unstable diadduct and decomposes rapidly to the monopyridine complex. Because 4-methylpyridine is a stronger base than pyridine the above stabilities are in accordance with expectations. 2-methylpyridine was found to form only the mono-adduct, presumably because of steric inhibition.

Methylamine and ammonia were both found to form only the mono-adduct, probably because on preparation of these complexes both amine ligands were used in the form of alcoholic solutions as compared to the other ligands which were used as pure ligands. This would reduce the concentration of the amine and consequently favour mono-adduction.

The formally 5-coordinate amine complex, $\left[ZnAcac_2NH_3\right]$ was found to be insoluble in chloroform, whereas all other complexes were extremely soluble in this solvent and it is presumed that this complex is polymeric, the coordination number of the zinc ion being increased to six. This is contrary to what was found by Graddon[34], the diammine adduct of bis(acetylacetonato)zinc(II) was prepared and found to be very unstable. The mono-ammine adduct could not be prepared. However it is similar to what was found[35] for the ammine adduct of bis(benzoylacetonato)zinc(II).

The infrared spectrum of bis(acetylacetonato)zinc(II) has been shown[79] to be analogous to the other metal acetylacetonates and the band due to the carbonyl stretching vibration has been assigned to the first intense band observed below 2000 $cm^{-1}$ (at approximately 1600 $cm^{-1}$) The M-O vibrations have been assigned[80,82] to the three bands observed in the far infrared region at approximately 650, 550 and 420 $cm^{-1}$ ascribed to the (M-O str. + $C-CH_3$ str.), (M-O str. + ring deformation) and (M-O str.) vibrations respectively.

Both the 5- and 6-coordinated complexes gave bands corresponding to these frequencies. A representative spectrum of each type appear in Figs. 21 and 22. However there was found to be a small but discernable difference in the spectra of the mono-adducts compared with those of the di-adducts. Only two bands due to the N-H stretching vibrations were found in the former in the region of 3160 $cm^{-1}$ (weak) and 3260 $cm^{-1}$ (medium), whereas an additional weak band was observed in the latter spectra in the region of 3315 $cm^{-1}$. In addition the M-O vibrational frequencies were found to be higher by approximately 10 $cm^{-1}$ in the mono-adducts as might be expected on the basis that stabilities (which are related to the bond strengths and hence frequencies of the M-O bond) of the 5-coordinate complexes are greater than those of the 6-coordinate species[34].

On changing the amine adduct in the 6-coordinate series two of the M-O sensitive vibrations were observed to shift in a regular manner (data in Table 18). The fact that the third M-O sensitive and the carbonyl vibration shifted hardly at all is in accord with the nickel(II) analogues. (Section 3).

The trends observed in the two M-O sensitive frequencies of the 6-coordinate species, $[ZnAcac_2Am_2]$, with changing amine substituent constant are shown in Figs. 19 and 20. The basic trends are similar to those observed for the nickel(II) analogues of the previous section; obviously the affects of varying basicity are comparable and thus the same explanations would also be applicable to the zinc(II) complexes. The shifts observed for the N-H stretching vibrations of the various amines are evident from Table 18. The most intense band (in the region of 3275 $cm^{-1}$) shows a slight trend, which is the expected one on the basis of electron density increase and decrease on the nitrogen as shown in Section 1. This is contrary to what was found for the nickel(II) analogues, where no regular trend was observed.

In the case of the 5-coordinated complexes, $\left[ZnAcac_2Am\right]$ conclusions were limited by the limited number of examples available. Nevertheless it appears that the M-O sensitive vibrations show the same basic trend as observed in the 6-coordinate series e.g. the band assigned to (M-O str. + ring deformation) shifted with decreasing electron releasing character of the amine as follows, 554, 556 and 557 $cm^{-1}$ for tertiary butyl-, isopropyl- and methylamine respectively. The same band had the highest value for the mono-aquo complex, which is in accordance with the nickel(II) series.

The fact that the ammine complex has frequencies which fit the observed trends in the 6-coordinate series shown in Figs. 19 and 20, supports the assumption that it is an octahedral polymer. The distinguishing fact that the 6-coordinate series gave three N-H stretching vibrational bands and the 5-coordinate series only two, could not be used in the case of the ammine complex as a stereochemical distinguishing feature because the presence of ammonia produces a change in the N-H stretching vibrational pattern as a result of the additional hydrogen atom.

Zinc(II) complexes are particularly suitable for nuclear magnetic resonance spectrometry as there are no complications due to paramagnetism, because of its $d^{10}$ configuration. The N.M.R. spectrum bis(acetylacetonato)zinc(II) in $CDCl_3$ was found to consist of 2 signals, with chemical shifts of 2.0 and 5.4 p.p.m. corresonding to the 12 methyl protons and the 2 ring protons respectively. It may be expected that because of the changing electronic effects in the various amine adducts of bis(acetylacetonato)zinc(II), the ring protons would be either shielded or deshielded giving rise to upfield or downfield shifts respectively in their N.M.R. spectra. In practice it was found that the position of this signal remained virtually unchanged throughout the series of both the 5- and 6-coordinated complexes (see Table 19). This is probably a result of the fact that the changes in electronic environment are too small to cause a noticeable shielding or deshielding of the ring protons. Another possible reason is that the adducts dissociate from the complexes in solution viz. in $CDCl_3$, thus giving rise to a spectrum which represents a superimposition of the spectra of the bis(acetylacetonato)zinc(II) and the free amine. This is supported by the observation[35] that the dipyridine and di-4-methylpyridine adducts of bis(benzoylacetonato)zinc(II) dissociate completely into the anhydrous complex and free base in dilute triphenylmethane solutions. However the chemical shifts of the amino protons of the free amines are known[88,89] for n-butylamine, tertiary butylamine and aniline, viz. 1.10, 1.23 and 3.48 p.p.m. respectively. The corresponding values for the amino protons in the complexes were found to be 1.87, 2.29 and 3.88 p.p.m. The downfield nature of the shifts on coordination suggests that the adducts are not dissociated in solution, as the reduction in the electron density on the nitrogen atom on coordination reduces the shielding of the amino protons causing the observed downfield shift.

The intergrated N.M.R. spectra were useful in determing whether a complex was 5- or 6-coordinated, as the number of protons could be calculated with sufficient precision. In fact this method of determining the structures agreed in all cases with those indicated on the basis of percentage composition. A typical N.M.R. spectrum is represented in Fig. 25.

The chemical shifts of the amino protons in the 6-coordinated complexes vary from one amine to another as seen in Table 19. However these variations are not necessarily due to the electronic effects of the amine substituents. The chemical shift of the aniline amino protons are far downfield relative to the other amines, however these protons lie more or less in the plane of the aromatic ring and the chemical shift is more likely to be as a result of deshielding from the induced magnetic field of the aromatic ring. Similarly this effect will shield the amino protons of β-phenylethylamine which could lie above or below the aromatic ring, thus producing a relative upfield shift, as observed.

The overall electronic effect on the amino protons can be better seen in the N.M.R. spectra of the three 5-coordinated complexes where there are no problems due to aromatic ring effects; here the chemical shifts for the amino protons were found to be 2.29, 2.35 and 2.45 p.p.m. for tertiary butyl-, isopropyl- and methylamine respectively. This is in the order of reduced electron release by the amine substituent. The trend is the expected one as the electron density at the nitrogen will shield the amino protons most in tertiary butylamine and least in methylamine.

Disregarding the two exceptional cases of aniline and β-phenyethylamine there appears (Table 19) to be a regular trend in the chemical shifts of the amino protons with changing substituent constant for the 6-coordinate series. The trend indicates that the above explanation for the 5-coordinate series holds in this case as well.

TABLE 18

Infrared frequencies ($cm^{-1}$) of zinc complexes, $[ZnAcac_2(R-NH_2)_2]$

| σ | R | N-H stretching | | | M-O str. | M-O str. + ring def. |
|---|---|---|---|---|---|---|
| | Cx | 3313 | 3285 | 3190 | 407 | 543 |
| | | | 3264 | | | |
| -0.13 | n-Bu | 3310 | 3279 | 3188 | 407 | 543 |
| -0.125 | iso-Bu | 3330 | 3278 | 3160 | 408 | 544 |
| -0.115 | n-Pr | 3317 | 3280 | 3196 | 409 | 544 |
| -0.10 | Et | 3318 | 3278 | 3194 | 408 | 544 |
| +0.08 | $CH_2CH_2Ph$ | 3314 | 3275 | 3188 | 409 | 544 |
| +0.215 | $CH_2Ph$ | 3315 | 3275 | 3180 | 410 | 545 |
| +0.49 | H | 3355 | 3277 | | 412 | 549 |
| | $CH_2CH_2OH$ | 3322 | 3272 | 3184 | 415 | 551 |
| +0.60 | Ph | | 3270 | 3160 | 421 | 556 |

TABLE 19.

Chemical shifts (p.p.m.) in $CDCl_3$ of zinc complexes, $\left[ZnAcac_2(R\text{-}NH_2)_2\right]$

| $\sigma$ | R | Me protons | ring protons | amino protons |
|---|---|---|---|---|
| | Cx | 1.94 | 5.27 | 1.83 |
| -0.13 | n-Bu | 1.95 | 5.28 | 1.87 |
| -0.125 | iso-Bu | 1.97 | 5.28 | 1.80 |
| -0.115 | n-Pr | 1.95 | 5.28 | 1.88 |
| -0.10 | Et | 1.95 | 5.28 | 1.92 |
| +0.08 | $CH_2CH_2Ph$ | 1.95 | 5.28 | 1.77 |
| +0.215 | $CH_2Ph$ | 1.93 | 5.29 | 2.21 |
| | $CH_2CH_2OH$ | 1.95 | 5.28 | 2.80 |
| +0.60 | Ph | 1.95 | 5.31 | 3.88 |

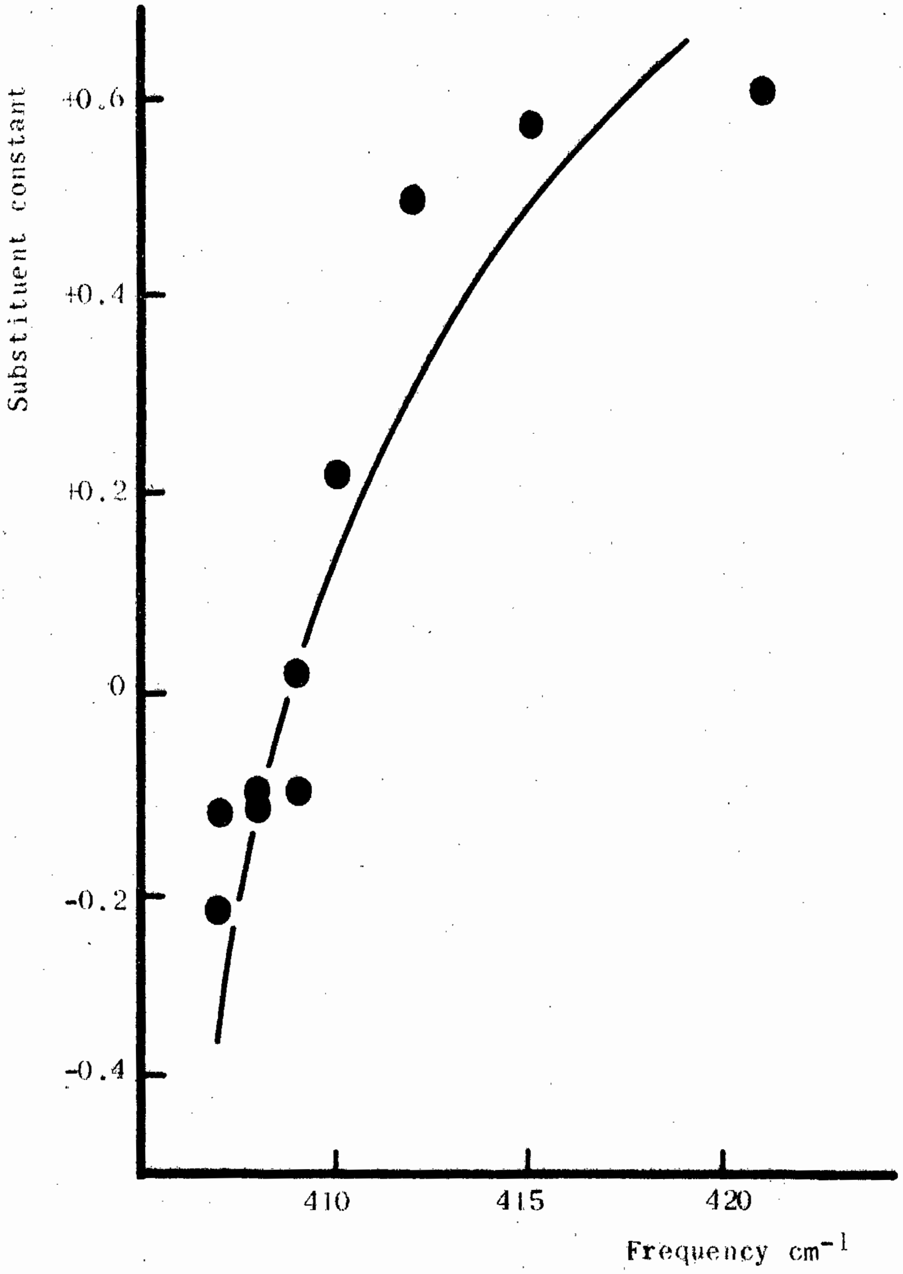


Fig. 19. Plot of M-O stretching frequency against substituent constant for $[ZnAcac_2Am_2]$.

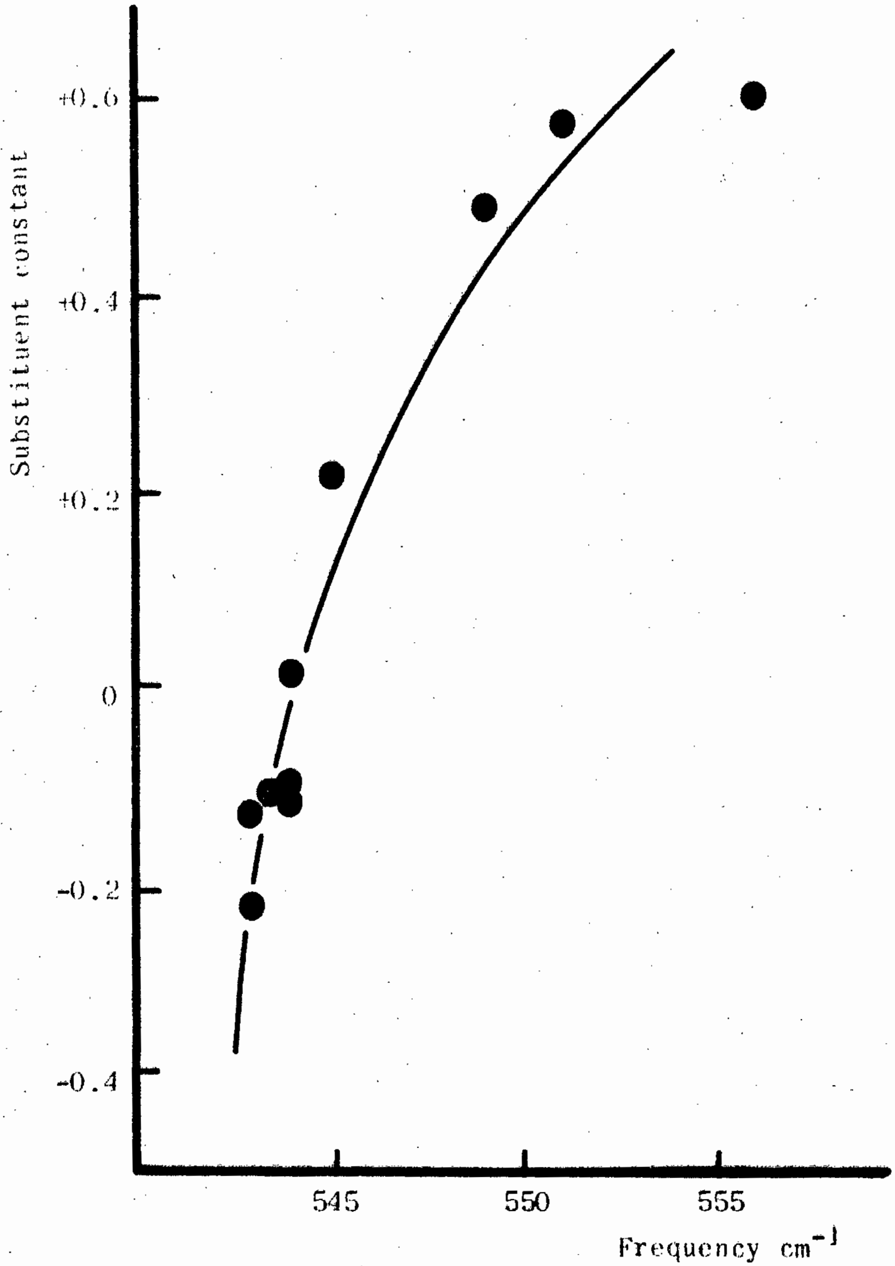


Fig. 20. Plot of M-O + ring deformation frequency against substituent constant for $[ZnAcac_2Am_2]$.

Fig. 21. Infrared spectrum of $[\mathrm{ZnAcac_2(benzylamine)_2}]$.

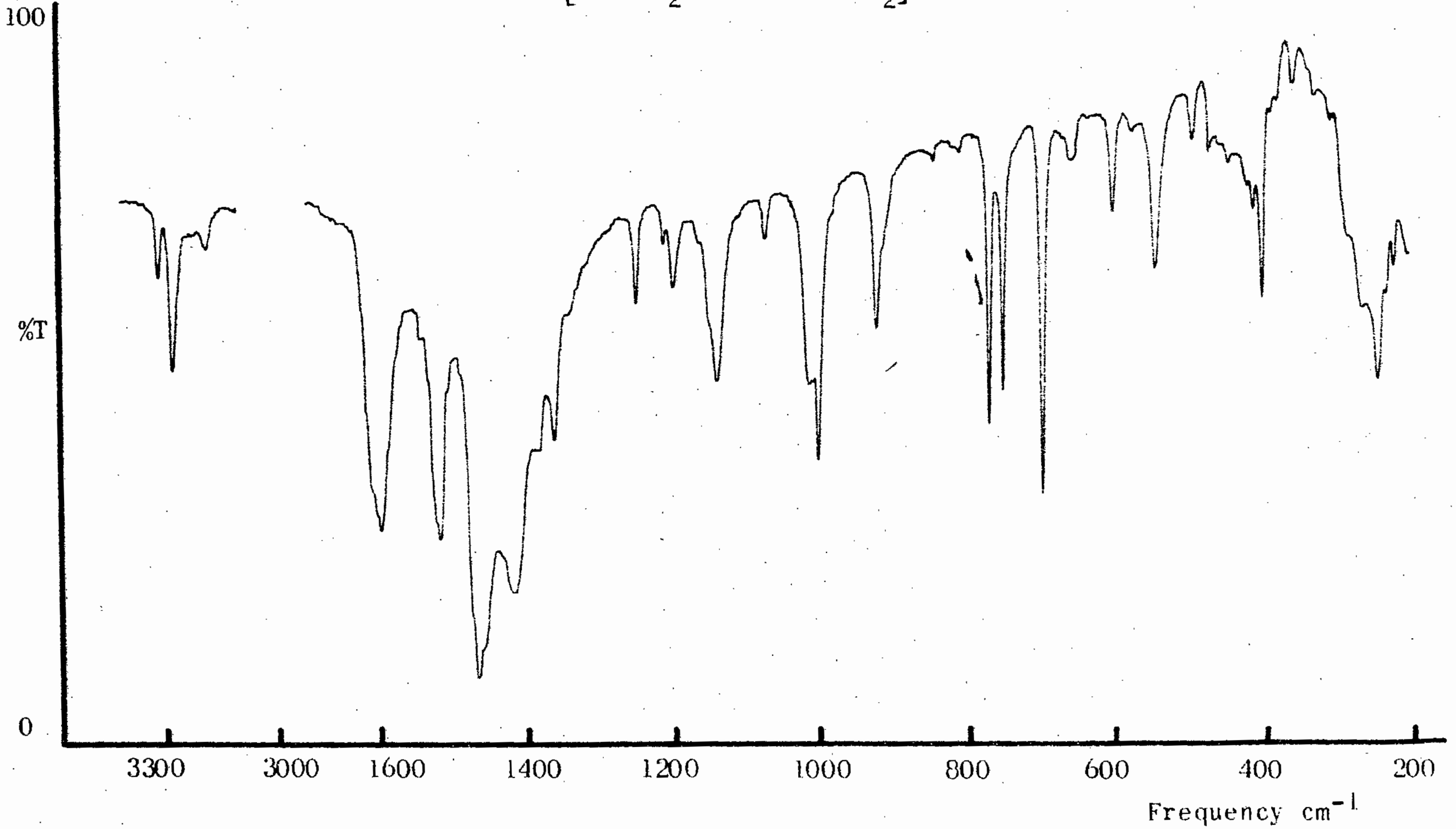


Fig. 22. Infrared spectrum of [ZnAcac$_2$(iso-propylamine)].

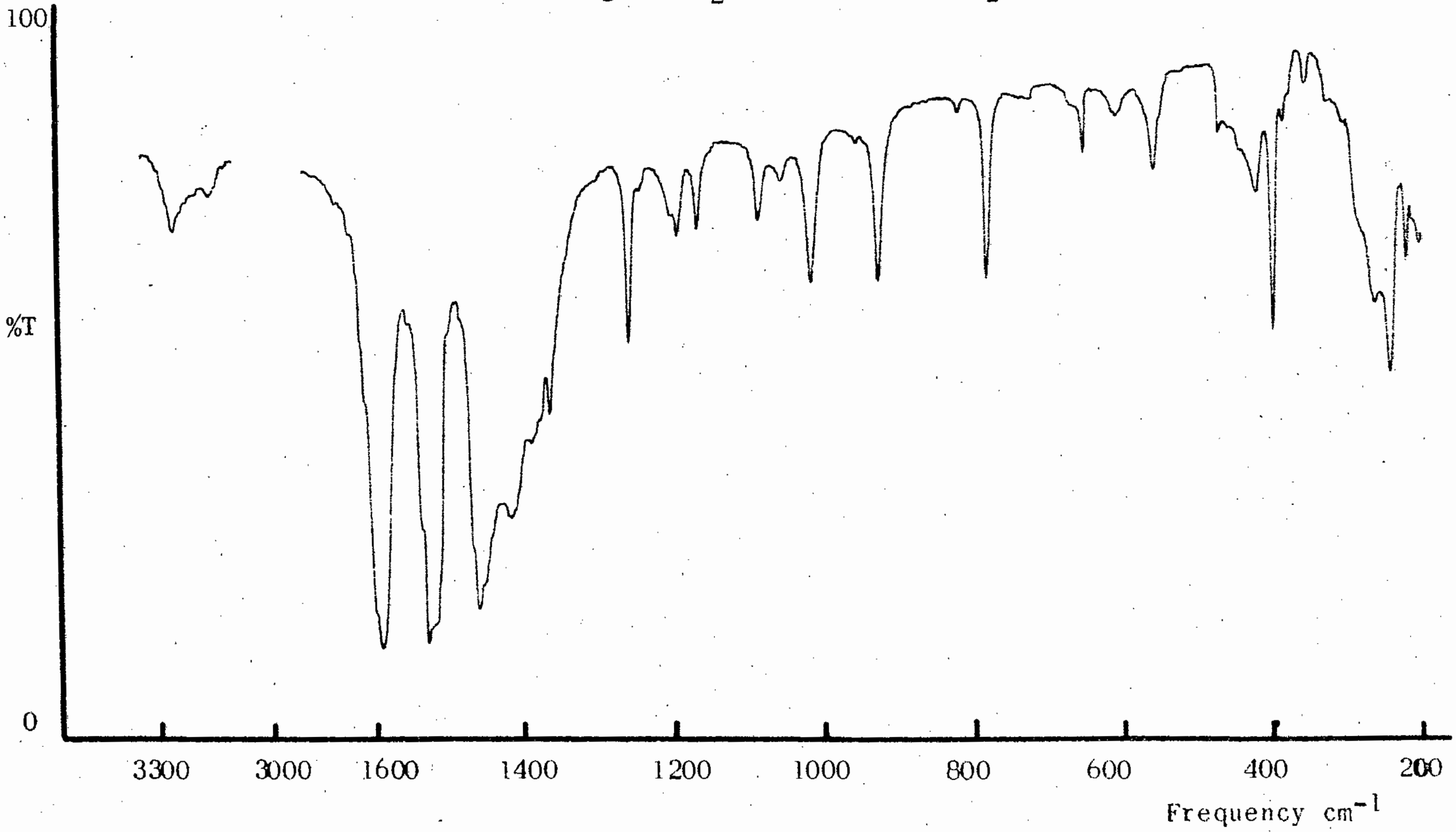
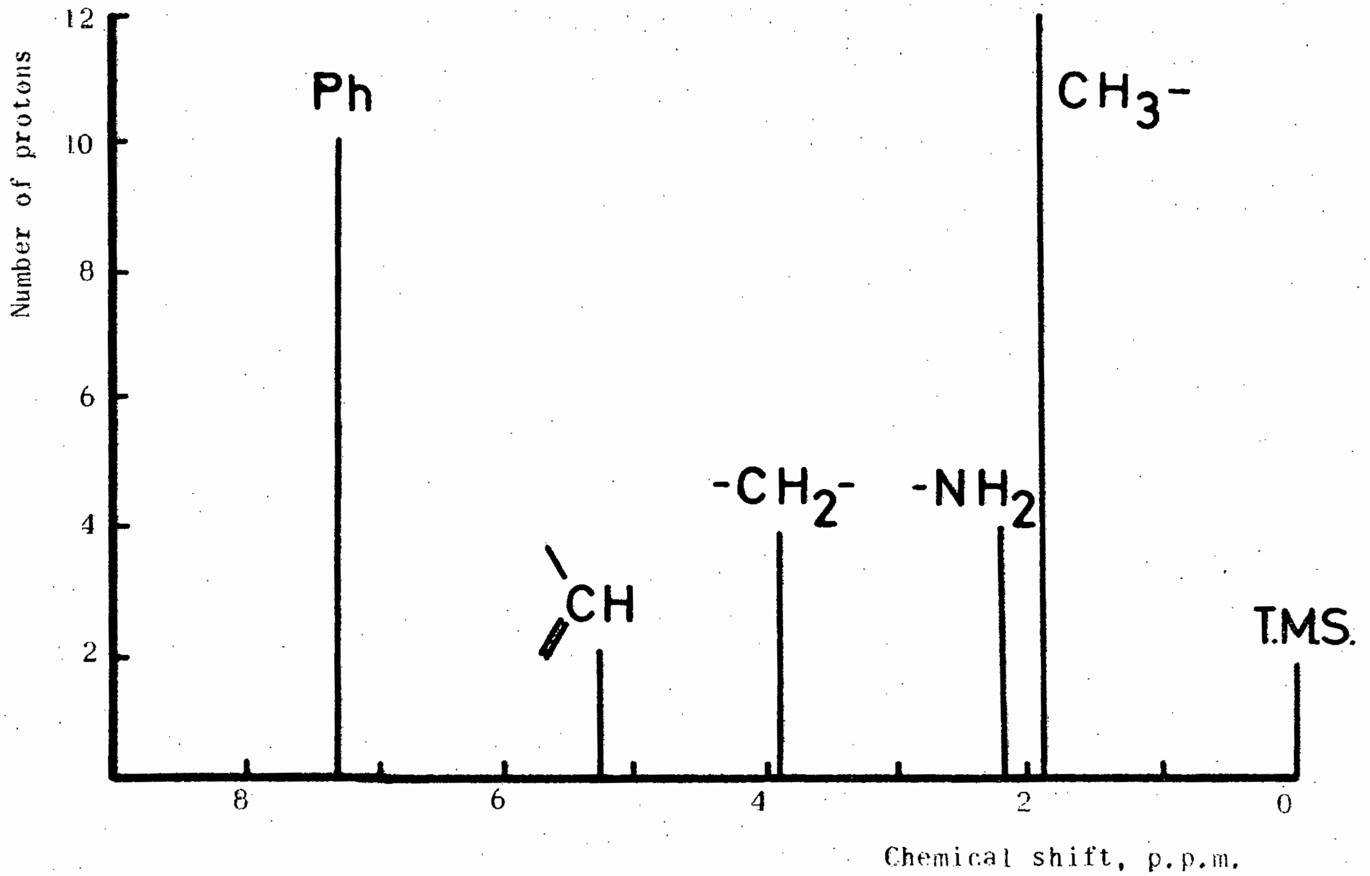


Fig. 25. Nuclear magnetic resonance spectrum of [ZnAcac$_2$(benzylamine)$_2$].



## (5) Amine complexes of uranyl acetylacetonate

The spectroscopic properties of pyridine adducts of uranyl acetylacetonate have been extensively studied[42-44]. However no similar studies of the corresponding aliphatic and aromatic amine analogues have been made. A series of primary aromatic amine complexes with uranyl acetylacetonate were therefore prepared with a view to studying their infrared and N.M.R. spectra.

It was at first considered that the amines would form 1 : 1 adducts with uranyl acetylacetonate analogous to the pyridine adducts (see Diagram V, page 105). However the infrared spectra of the amine complexes did not show any N-H stretching bands in the region 3350 - 3150 $cm^{-1}$ characteristic[90] of coordinated N-H groups. Clearly, therefore, the structure of the complexes is not analogous to that of the pyridine adducts. Microanalysis results also suggest that the structures differ as the C and H percentages found were all too high for the latter structure.

To account for the absence of N-H stretching vibrations an alternative structure was proposed (see Diagram VI, page 105). Here it was assumed that the amine condensed with one of the "oxo" groups (U=O) with the loss of $H_2O$ to produce the grouping U=N-, similar to the condensation of a carbonyl group with an amine to form a Schiff base, $>C=N-$[93]. Although this would explain the absence of N-H stretching vibrations, the characteristic intense band in the region of 900 $cm^{-1}$ due to the U=O stretching vibration was relatively unaffected on formation of the amine complex, whereas according to this proposed structure conversion to a U=N bond would be expected to influence the frequency. In addition microanalysis showed that this structure was incorrect because of the high percentages of C and H found. Even if both "oxo" groups are assumed to react these values are still too high for the bis(imido) complex.

In an earlier reference[91] to the products formed from amines and uranyl acetylacetonate, the amine complexes were reported to differ from the pyridine adducts in that an additional acetylacetone molecule is incorporated in the complex along with one molecule of the amine. It was proposed that the additional acetylacetone molecule in the form of the enol-tautomer ($CH_3$-C(OH)=CH-CO-$CH_3$) was adducted to the metal through the keto-carbonyl group while the enol-group remained free. The acidic character of this enolic group was supposed to induce the formation of a quarternary ammonium salt with the basic amine molecule to form an isolable 7-coordinate complex (see Diagram VII, page 106).

This structure satisfied the microanalysis figures of the studied aromatic amine complexes fairly well (Table 9) and also satisfied the absence of coordinated N-H stretching vibrations (in the range 3350 - 3150 $cm^{-1}$) in their infrared spectra, because now the amine exists as a quarternary ammonium salt. A comparison was made of the infrared spectrum of the acetylacetone adduct of uranyl acetylacetonate, $[UO_2acac_2(AcacH)]$ with the spectra of the amine complexes in the range 1700 - 200 $cm^{-1}$. They were found to be very similar with the expected additional bands in the latter spectra due to the amine present. This comparison favoured the salt structure. However the infrared spectra of the amine complexes failed to show any N-H stretching vibrations in the range 3100 - 2900 cm$^{-1}$ (as hexachlorobutadiene mulls) characteristic[90] of quarternary ammonium salts.

The N.M.R. spectra of the amine complexes could be explained on the basis of the salt structure, except for the farthest downfield signal, e.g. the unsubstituted aniline complex $[UO_2Acac_2(AcacH)(aniline)]$, which gave the signals with chemical shifts of 2.19 (3), 2.25 (12), 2.68 (3), 5.60 (1), 5.75 (2), 7.25 (5) and 13.25 (1) p.p.m. The figures in brackets represent the number of protons obtained by intergration, the signal at 2.25 p.p.m. being due to the 12 methyl protons of the coordinated acetylacetonate, those at 2.19 and 2.68 p.p.m. to the 6 methyl protons of the adducted acetylacetone (the seperation of the signals being due to the fact that the acetylacetone molecule is in the enol-tautomer, the one methyl group is thus in a different environment from the other). The signal at 2.60 p.p.m. results from the one ring proton of the adducted acetylacetone molecule and that at 2.75 p.p.m. to the two ring protons of the coordinated acetylacetonate molecules. The signals in the region of 7.25 p.p.m. arise from the five aromatic ring protons of aniline.

In an ammonium salt the positive charge on the nitrogen would considerably deshield the amino protons. The chemical shifts would be found far downfield. The N.M.R. spectra of all the amine complexes of uranyl acetylacetonate did in fact give a signal far downfield in the region of 13.20 p.p.m.. However on intergration this signal only represented one proton whereas the proposed salt structure requires three amino protons. This anomaly of the downfield signal remained temporarily unexplained but it was clear that this signal is in some way associated with the amino protons as these were the only protons unaccounted for in the N.M.R. spectra.

The salt structure satisfied most of the spectroscopic evidence but failed to explain the anomalous absence of N-H stretching vibrations in the infrared and the downfield signal in the N.M.R. spectra. The deciding factor which indicated that the salt structure was incorrect was the conductance measurements. Because of the ionic character of the salt structure it would be expected that the complex would be a relatively good electrolyte. However the molar conductances in methanol were found to be very small (less than 0.5 mho) indicating that they are in fact non-electrolytes.

Aniline is known[92] to react with the enol-tautomer of acetylacetone with loss of $H_2O$ to form 4-anilino-3-penten-2-one. It is thus likely that on formation of the complex, the acetylacetone adduct (enol-tautomer) of uranyl acetylacetonate could be formed initially and the aniline could then react with the enol group of the acetylacetone adduct to form the 4-anilino-3-penten-2-one adduct of uranyl acetylacetonate (see Diagram VIII, page 106 ). This structure in fact satisfies the microanalysis figures fairly well, (Table 9) although for some of the amine complexes the salt structure is in better agreement. Of greater significance is the fact that both the infrared and N.M.R. spectra can be completely interpreted on the basis of this structure.

The absence of sharp N-H stretching vibrational bands in the infrared spectra of the complexes can now be rationalised on the basis that the single hydrogen atom of the amino nitrogen is hydrogen bonded to the carbonyl oxygen as in acetylacetone itself. This hydrogen bonding will cause the band due to the N-H stretching vibration to become broader and to be considerably reduced in intensity as is observed, for instance for the O-H stretching vibration in strongly hydrogen bonded hydroxylic compounds such as nickel(II) dimethylglyoximate[94]. This band must actually be very broad because of the complete absence of any significant bands in the expected N-H stretching vibrational region. The rest of the infrared spectrum was found to be very complex. However, the intense $U=O$ stretching vibrational band in the region of 900 $cm^{-1}$ was very characteristic in all the spectra. The carbonyl stretching frequency of the coordinated acetylacetonate ligands was found to be at approximately 1580 $cm^{-1}$ for all the complexes. In all the spectra a band of medium intensity was observed in the region of 1610 $cm^{-1}$, which in a few spectra appeared as a shoulder on the high frequency side of the intense carbonyl band. This band could be assigned to the carbonyl stretching frequency of the adducted 4-anilino-3-penten-2-one. In the acetylacetone adduct of uranyl acetylacetonate a similar band was observed, as expected. In the infrared spectrum of uranyl acetylacetonate itself this band is absent, which supports the above assignment. A typical infrared spectrum appears in Fig 24.

The downfield signal representing one proton in the N.M.R. spectra of all the complexes in the region of 13.20 p.p.m. can now also be explained by the proposed structure arising from the single proton on the nitrogen of the 4-anilino-3-penten-2-one adduct. The assignment of this signal was confirmed by the fact that on $D_2O$ exchange this signal disappeared. Amino protons are known to be active and are easily replaced by the deuterium atom, which does not give a signal in proton magnetic resonance spectrometry, having integral nuclear spin. A similar signal is found in the N.M.R. spectrum of acetylacetone at 15.35 p.p.m. which has been assigned to the enol hydrogen. This signal is found at 14.82 p.p.m. in the acetylacetone adduct of uranyl acetylacetonate. The reason for this signal being so far downfield is that in the above three compounds, the active hydrogen is hydrogen bonded to the carbonyl group of the same molecule (as illustrated in Diagram VIII, page 106).

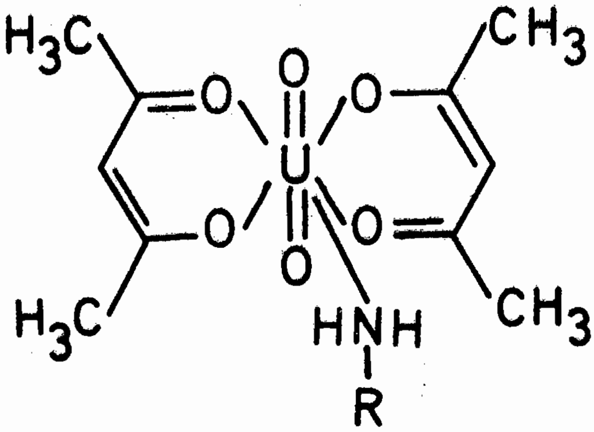
The rest of the N.M.R. spectrum can be interpreted in the same manner as in the previously proposed salt structure, as the environment of the remainder of the complex molecule is closely similar in both structures. A typical N.M.R. spectrum is represented in Fig. 26.

The fact that these complexes were found to be non-electrolytes in methanol is expected on the basis of this structure.

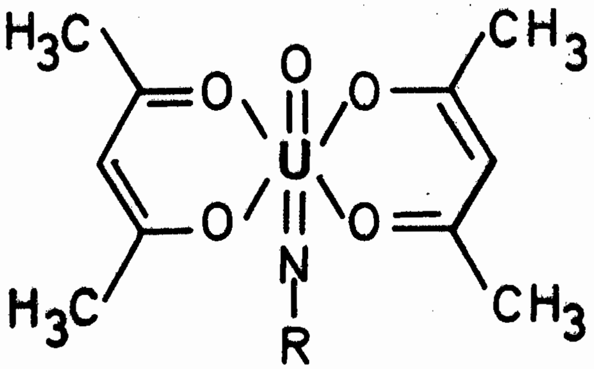
The final structure (Diagram VIII) is the most favourable as it satisfies all the observed microanalytical, spectroscopic and conductance data.

Many of the aromatic amines did not form complexes at all, but non-formation of certain complexes does not appear to be associated with the electronic effects of the substituents as both meta- and para-substituted anilines and both electron-withdrawing and electron-releasing substituents formed isolable complexes.

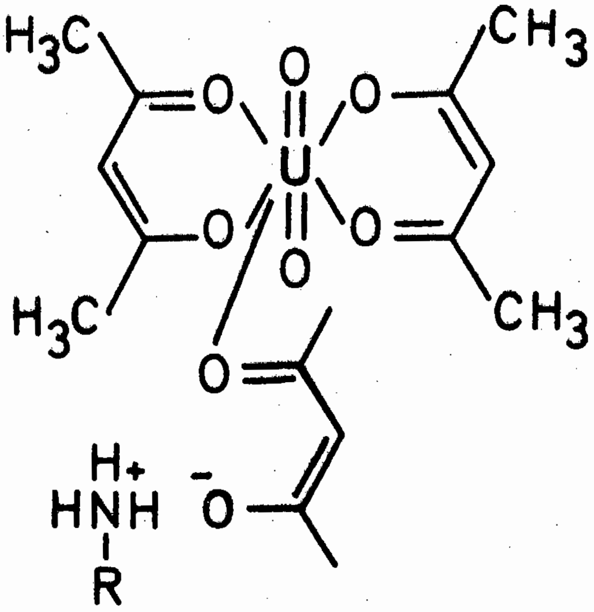
The effect of varying the substituent on the amine was found to have a negligable effect on the U=O and carbonyl frequencies in the infrared spectra and on the chemical shifts of the amino proton, the ring protons and methyl protons in the N.M.R. spectra of the complexes.



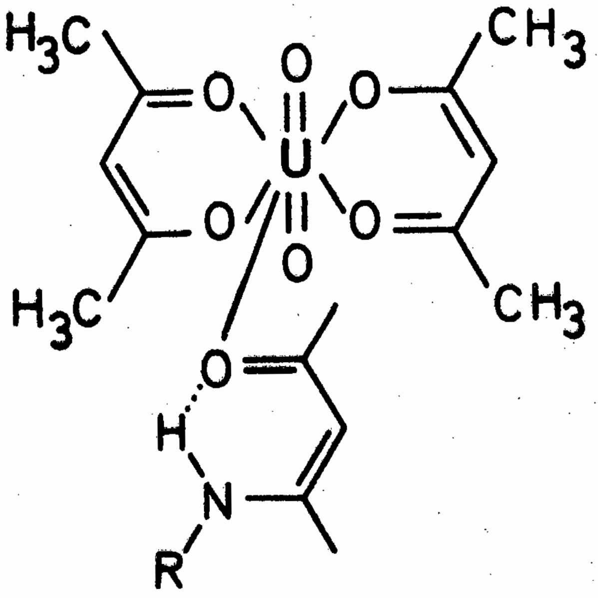
(V)



(VI)



(VII)



(VIII)

Fig. 24. Infrared spectrum of $[UO_2Acac_2(4\text{-anilino-3-penten-2-one})]$.

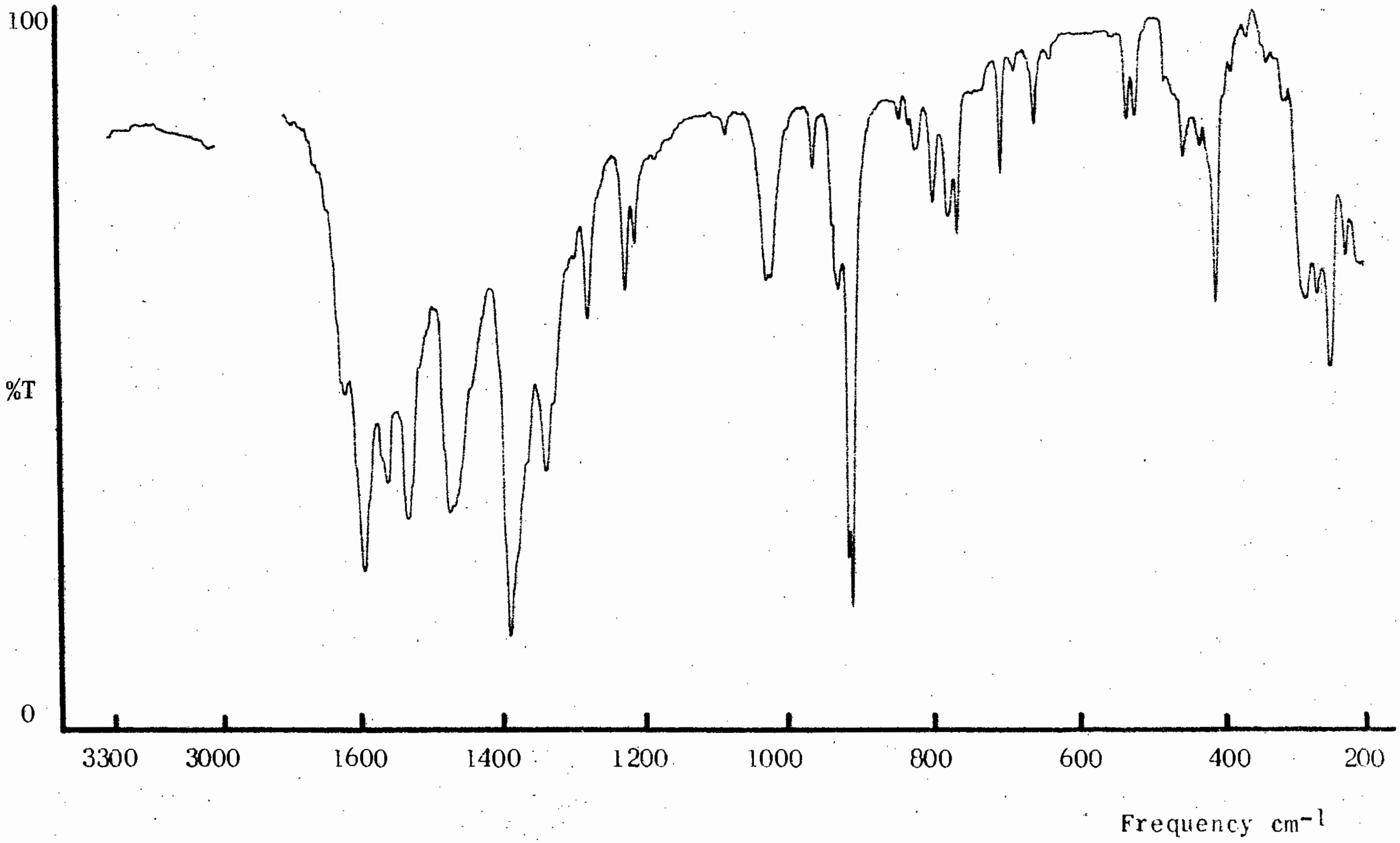
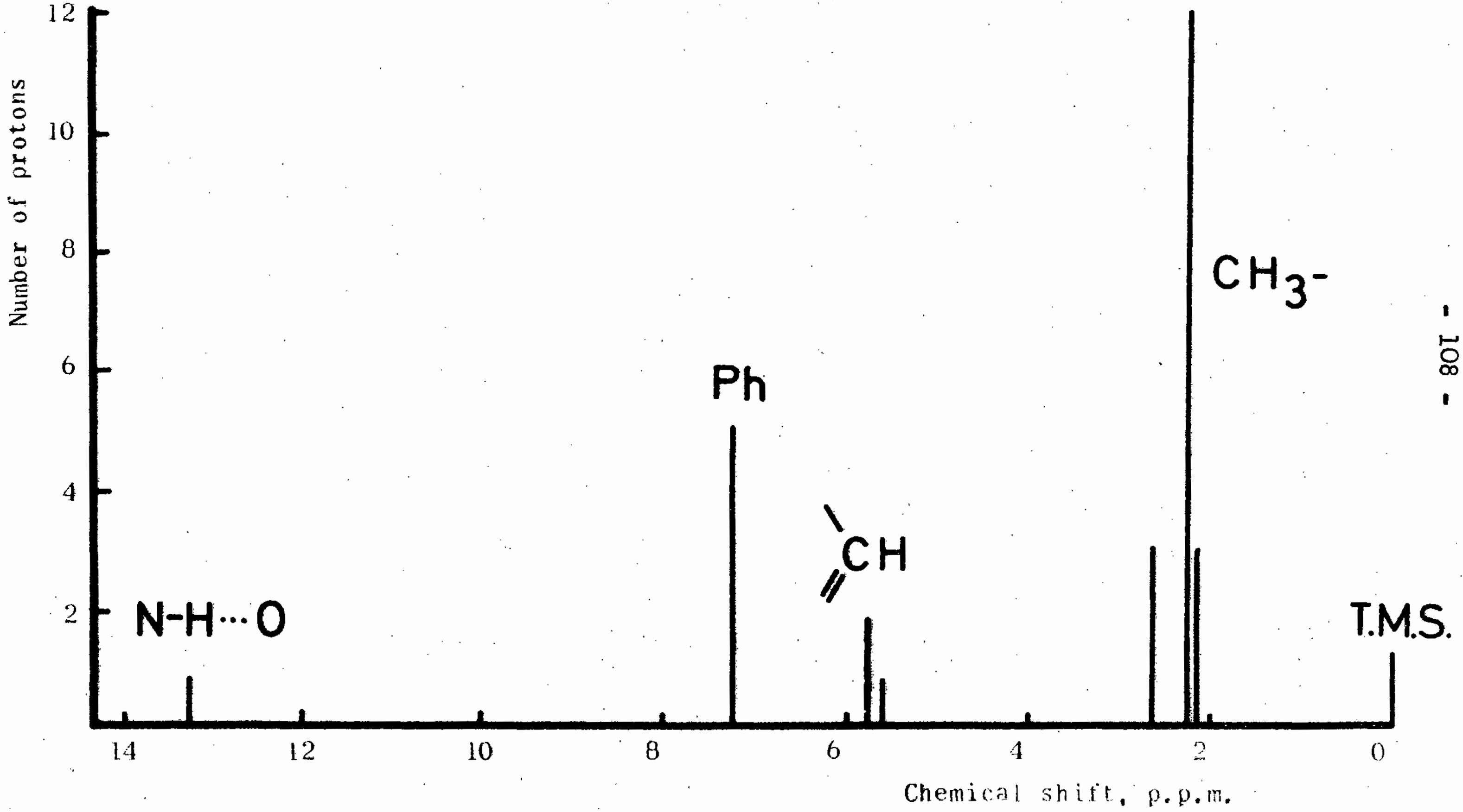


Fig. 26. Nuclear magnetic resonance spectrum of [$UO_2Acac_2$(4-anilino-3-penten-2-one)].



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