THE CRYSTAL STRUCTURE

OF THE ADDUCT [$VO(ACA)_2 \cdot$4-PHENYLPYRIDINE]

by

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A C K N O W L E D G E M E N T S

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C O N T E N T S

1. INTRODUCTION

1.1 TRANSITION METAL β-KETOENOLATES

β-diketones, which exhibit keto-enol tautomerism [fig. (i)] react with metal cations to form six-membered chelate rings in which the metal replaces the enolic hydrogen. [fig. (ii)].

fig. (i)

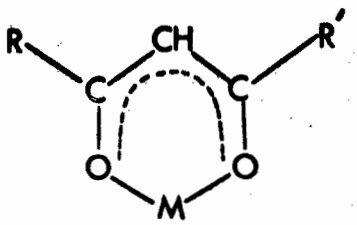


fig. (ii)

Divalent transition metal ions react with two enolate ions, each enolate ion carrying a single negative charge, to yield neutral molecules ML_2 (LH = β-diketone). In these complexes, the metal ion has a coordination number of four. (The quasi-aromatic character of these rings is indicated by the dotted curve.) [fig. (iii)].

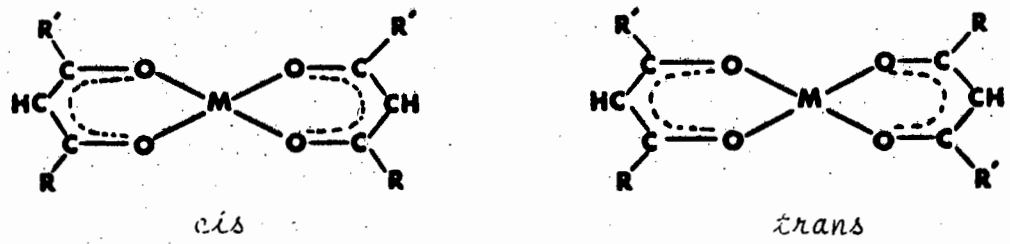


fig. (iii)

The three-dimensional arrangement of the oxygen atoms about the metal ion may be square planar or tetrahedral. It is noteworthy that, in both cases, either *cis*-or *trans*-isomers may result.

With relatively large metal ions, the neutral molecules ML_2 may behave as Lewis acids, forming adducts with bases such as ammonia, pyridine, water or additional enolate ions.

Many of these compounds form crystals whose molecular structures may be investigated by X-ray diffraction techniques.

1.2 TRANSITION METAL ACETYL ACETONATES

The β-diketone which has been studied most extensively is acetylacetone (ACAH), in which R = R' = CH_3 [fig.(i)].

The crystal structures of several metal acetylacetonates have been investigated.

X-ray single-crystal analysis has shown[1], for example, that bisacetylacetonatozinc(II) is trimeric in the solid state.

The crystal structure and molecular configuration of trisacetylacetonatomanganese(III), [fig.(iv)], have been determined by X-ray diffraction techniques[2]. Originally it was predicted (Dunitz & Orgel, 1957) that this Mn(III) complex, susceptible to a Jahn-Teller mechanism, might distort its immediate octahedral configuration to four shorter and two longer (or two shorter and four longer) metal-ligand bond lengths.

[1]M.J. Bennett, F.A. Cotton, R. Eiss and R.C. Elder, *Nature*, 213 (1967) 174.

[2]B. Morosin and J.R. Brathovde. *Acta Cryst.* (1964) 17, 705.

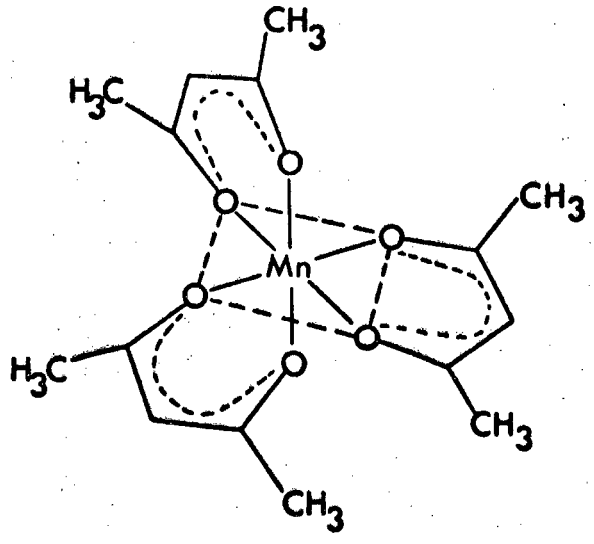


fig. (iv)

The X-ray analysis of this structure did reveal an interesting distortion from octahedral symmetry, but the conclusion reached was that this distortion may not be the result of a Jahn-Teller mechanism.

The distorted octahedral coordination found about the Mn atom appears to explain the compound's infrared absorption spectrum irrespective of whether a Jahn-Teller mechanism is operative or not. This is a typical example of how X-ray diffraction methods may be used to support or disprove particular structural features which may have been deduced from indirect evidence such as that obtained from infrared spectroscopy.

A three-dimensional X-ray diffraction analysis of crystalline vanadylbisacetylacetonate has shown[3] that there are two $VO(ACA)_2$ molecules in the crystal unit cell, these two molecules being related by a centre of inversion. The structure of this compound is of special interest as the

[3] Dodge, Templeton and Zalkin. *J.Chem.Phys.* 35 (1961) 55.

compound investigated in the present work is a derivative of $VO(ACA)_2$.

1.3 THE OXOVANADIUM(IV) ION OR VANADYL ION, VO^{++}

The species MO^{n+} and MO_2^{n+}, mononuclear oxycations, occur mainly among the lighter transition elements.

The uranyl ion UO_2^+ or dioxouranium(VI) ion is the most extensively studied and best characterised of these ions[4-6]. The next best characterised oxycation is the oxovanadium(IV) ion or vanadyl ion[6,7], in which vanadium has an oxidation number of four and is bound to an oxygen atom by a multiple covalent bond.

The cation VO^{++} may complex with a β-diketone (LH), to produce a neutral complex $[VOL_2]$.

Thus, in addition to the normal V-O bonds found in such a complex, there is the multiple bond between vanadium and oxygen. This bond is an additional feature, the study of which may lead to information regarding bonding and structure in these complexes.

That the VO^{++} species exists in solid complexes, has been clearly demonstrated by X-ray diffraction studies of the solid compounds $VOSO_4 \cdot 5H_2O$[8], vanadylbisacetylacetonate[3], vanadylbisbenzoylacetonate[9] and the 2:1 vanadylacetylacetonate : 1,4-dioxan complex[10]. The vanadium to oxygen bond distance in the vanadyl ion has therefore been determined in these cases.

[4]McGlynn, Smith and Neely., *J.Chem.Phys.* 35 (1961) 105.
[5]R.L. Belford and G. Belford., *J.Phys.Chem.* 34 (1961) 1330.
[6]J.M. Haigh *Ph.D. Thesis.* University of Cape Town (1970).
[7]J.Selbin and L.H. Holmes Jr. *J.Inorg.Nucl.Chem.* 24 (1962), 1111.
[8]C. Lundgren, *Rec.Trav.Chim.* 75 (1956) 585.
[9]Hon, Belford and Pfluger. *J.Chem.Phys.* 43 (1965) 1323.
[10]Dichmann, Hamer, Nyburg and Reynolds. *Chem. Comm.* (1970) 1295.

1.3(a) Infrared Spectral Data

It has been reported[11] that ν M=O, the stretching frequencies of metal-oxygen double bonds, may generally be located between 900 and 1100 cm^{-1}. The following V=O stretching frequencies were reported:

1020 cm^{-1} in $VOSO_4$, 995 cm^{-1} for $VO(ACA)_2$, 976 cm^{-1} for a complex vanadyloxinate and 967 cm^{-1} for a complex vanadyl malonate. Vanadium(IV) hydroxide had earlier been formulated as $VO(OH)_2$ on the basis of its infrared spectrum[12] which shows a strong band at 955 cm^{-1}, attributed to the V=O stretching vibration.

Clearly, the value of ν V=O is strongly dependent on the species to which the vanadium atom is attached. This is expected, since the V=O bond character and hence ν V=O would be expected to vary depending on the electron-withdrawing or electron-releasing nature of the coordinated species. By studying the variation in ν V=O in vanadyl complexes, as the ligands are varied, one might thus deduce important information regarding the structures of these compounds.

The vanadium atom in complexes of VO^{++} may be either five coordinate (as in $[VO(ACA)_2]$) or six coordinate (as in $[VO(ACA)_2 \cdot pyridine]$).

The vanadyl bond, V=O, in vanadyl complexes, is a multiple covalent bond formed by the donation of $p\pi$ electrons of oxygen to $d\pi$ orbitals of vanadium superimposed upon the V-O σ-bond. The extent of $p\pi \rightarrow d\pi$ donation depends both on the capacity of oxygen to donate and vanadium to accept electrons.

[11] C.G. Barraclough, J. Lewis and R.S. Nyholm., *J.Chem.Soc.* (1959) 3552.

[12] C.Cabannes-Ott. *Compt. rend;* 242 (1956) 2825.

Because the vanadium atom has a single d-electron, it is expected to be affected considerably by the presence of coordinated ligands. Thus, coordinated ligands which donate their electron-pairs will increase the electron density in the metal d-orbitals; $p\pi \rightarrow d\pi$ donation from the oxygen to vanadium will be reduced to an extent which depends on the donor ability of the ligand. As a consequence, the bond order of the V=O bond will be reduced and hence ν V=O will be reduced. That this argument is true is best illustrated by means of the following example. On adduction of a pyridine molecule to $[VO(ACA)_2]$ one would expect a decrease in the V=O bond order and hence in ν V=O. Comparison of the infrared spectra of $[VO(ACA)_2]$ and $[VO(ACA)_2 \cdot \text{pyridine}]$ shows that this is true, the values of the V=O stretching frequencies being 995 cm^{-1} and 964 cm^{-1} respectively[13]. A decrease in ν V-O is also expected. All bands assigned as ν V-O modes do show a decrease.

1.3(b) Vanadyl β-Ketoenolates : X-Ray Analyses

The crystal structure of vanadylbisacetylacetonate, $VO(ACA)_2$, has been elucidated by a three-dimensional X-ray diffraction analysis[3]. An idealised drawing of a single molecule is shown in fig. (v).

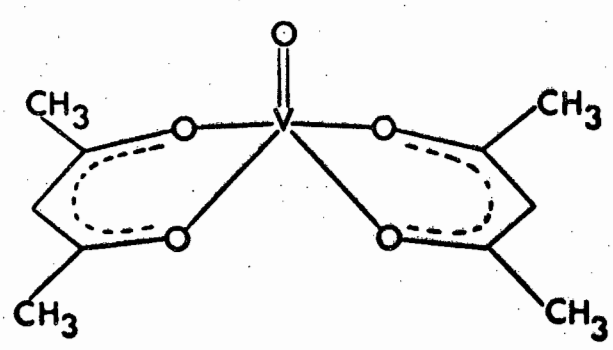


fig. (v)

[13] K. Nakamoto, Y. Morimoto and A.E. Martell. *J.Amer.Chem.Soc.* 83 (1961) 4533.

The purpose of the analysis was to establish the geometry of the bonds about the five-coordinate vanadium(IV) ion.

Previously, Jones[14] assumed a square planar arrangement of four oxygen atoms about the vanadium atom, with the fifth V to O bond presumably perpendicular to this plane. An alternative bipyramidal arrangement of the oxygen atoms about vanadium was suggested but was indicated as improbable from electron spin-resonance spectra[15] of $VO(ACA)_2$.

The X-ray analysis referred to above showed that the structure consists of discrete molecules and that there are two such molecules in the crystal unit cell. The five oxygen atoms are situated at the corners of an approximately square pyramid; the vanadium atom, however, is near the centre of gravity of this pyramid, rather than at the centre of its base.

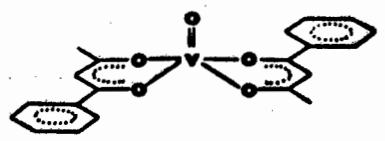
The bond distance of the vanadyl ion, that is the V=O distance, was found to be 1.56 ± 0.01 Å. This bond length had not been measured previous to this analysis and was therefore of special interest.

The average value of the other four V-O bonds, which are chemically identical, was found to be 1.97 Å.

More recently, the crystal structure of vanadyl-bisbenzoylacetonate, $[VO(BZA)_2]$, was established by X-ray diffraction techniques[9]. (In this complex, $R=CH_3$, $R' = C_6H_5$- fig.(i)). The possible isomers are drawn in fig. (vi).

[14] M.M. Jones. *J.Amer.Chem.Soc.* 76 5995 (1954).

[15] R.D. Feltham. *Ph.D. dissertation;* University of California, Berkeley (1957).



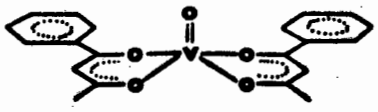


fig. (vi)

From steric considerations alone, one might expect the *trans*-form to be the preferred arrangement, but in this analysis, it was found that the two phenyl substituents are *cis* to one another.

A molecule of $VO(BZA)_2$ is structurally quite similar to one of $VO(ACA)_2$, except for the length of the V=O bond which is 1.61 ± 0.01 Å in the former compound and 1.56 ± 0.01 Å in the latter.

1.4 $VO(ACA)_2$: BASE ADDUCT FORMATION

1.4(a) Base Adducts of Vanadylbisacetylacetonate

The coordination number of the vanadium atom in a molecule of $VO(ACA)_2$ is five. This is increased to six on adduction of a single basic molecule B, such as water, ammonia or pyridine[14].

The reaction taking place may be written:

$$VO(ACA)_2 + B \rightarrow VO(ACA)_2 \cdot B$$

Garvey and Ragsdale[16] examined the solution infrared spectra of a series of 4- substituted pyridine N-oxide adducts

[16] R.G. Garvey and R.O. Ragsdale, *Inorg.Chem.Acta.* 2 (1968) 191.

of vanadylbisacetylacetonate, vanadylbistrifluoroacetylacetonate and vanadylbisbenzoylacetonate.

They found a linear relationship between ν V=O and $\bar{\sigma}$ (substituent parameters derived specifically for pyridine-N-oxides[17]) for the adducts of $VO(ACA)_2$ and of $VO(BZA)_2$ which indicated a decrease in the V=O bond strength with increasing electron-donating capacity of the substituent.

Increased electron donation by the substituent would reduce the amount of $p\pi \rightarrow d\pi$ donation possible from the vanadyl oxygen to the vanadium atom. Consequently, the V=O bond strength would be expected to decrease.

Since the present work deals with the structure of a substituted-pyridine adduct of vanadylbisacetylacetonate, complexes of this type are discussed below.

1.4(b) Substituted-pyridine adducts of Vanadylbisacetylacetonate: The Chemical Problem.

Haigh[6] considered it to be of interest to observe whether or not a series of substituted-pyridine adducts of $VO(ACA)_2$ would show similar results to those obtained from the pyridine-N-oxide adducts mentioned above. In this study, fourteen variously substituted pyridine complexes of $VO(ACA)_2$ were prepared and the infrared spectra of these adducts, $VO(ACA)_2 \cdot R\text{-}C_5H_4N$, were examined. The relevant infrared absorption bands are drawn up in Table 1. (Page 10.)

It is obvious from the infrared data that these compounds can be separated into two groups viz. one group of nine adducts for which ν V=O is lowered by 42 ± 4 cm^{-1} (relative to $VO(ACA)_2$) and a second group of five adducts for which ν V=O is lowered by 29 ± 4 cm^{-1}. ($\nu V{=}O$ in $VO(ACA)_2$ = 995 cm^{-1})

[17] Nelson, Garvey and Ragsdale, J. *Heterocyclic Chem.* 4 (1967) 591.

TABLE 1

$VO(ACA)_2 \cdot R\text{-}C_5H_4N$: infrared stretching frequencies

R	σx10^{2*}	νC=O	νV=O	νV-O		νV-O + νC-CH_3		δO-V-O	νV-O	
4-$CO_2C_2H_5$	+ 52	1590	955	591	554	456	436	416	363	333
4-COC_6H_5	+ 46	1580	957	589	554	453	437	414	358	357
4-C_6H_5	+ 1	1590	955	591	551	460	431	418	348	332
3,5-di-CH_3	- 14	1597	959	588	550	458	431	410	347	-
4-C_2H_5	- 15	1586	959	589	553	452	434	414	361	338
3-NH_2	- 16	1586	959	592	551	459	435	417	349	-
4-t-C_4H_9	- 20	1595	962	589	550	450	436	416	345	-
4-$N(CH_3)_2$	- 60	1595	953	589	555	455	434	406	348	336
4-NH_2	- 66	1572	958	593	551	458	438	418	349	338
4-CN	+ 63	1590	974	603	-	466	-	418	363	-
H	0	1586	973	601	-	465	-	422	362	-
4-n-C_3H_7	- 13	1588	971	606	-	465	-	423	363	-
4-CH_3	- 17	1575	971	605	-	465	-	421	363	-
3,4-di-CH_3	- 24	1570	965	602	-	462	-	421	363	-

*σ-values are those of Jaffe.
H.H. Jaffé. *Chem. Rev.* 53 (1953) 191.

If the electron-density on the nitrogen atom of the substituted pyridine were to increase, then the extent of $p\pi \rightarrow d\pi$ donation from oxygen to vanadium would be expected to decrease, resulting in a lowering of the V=O bond order and hence a reduction in ν V=O. This reduction was observed

for the group of five adducts, but in the case of the larger group of nine adducts, no such effect was observed.

In the larger group of nine adducts, the value of ν V=O had an almost constant value, independent of the basicity of the pyridine.

Haigh[6] then investigated the far infrared spectra of these adducts.

The four V-O modes at 611, 488, 426 and 367 cm^{-1} in $VO(ACA)_2$ were lowered to 601, 465, 422 and 362 cm^{-1} in $VO(ACA)_2 \cdot py$. These four V-O sensitive modes all occurred at approximately the same frequencies in the group of five substituted-pyridine adducts. In the group of nine substituted-pyridine adducts, showing the larger reduction in νV=O, these same four bands occurred at approximately 588, 456, 413 and 350 cm^{-1}. This was attributed to a greater decrease in the stability of these complexes.

In addition, the bands at 588, 456 and 350 cm^{-1} in this series were split, extra peaks appearing at around 552, 435 and 335 cm^{-1}. To quote Haigh[6]: "This would indicate a reduction in the degree of symmetry of these complexes, which would also explain the additional weakening of the V=O and V-O bonds. It is for this reason that it is suggested that these compounds exist as *cis* and *trans* isomers."

The structures suggested are shown in fig. (vii).

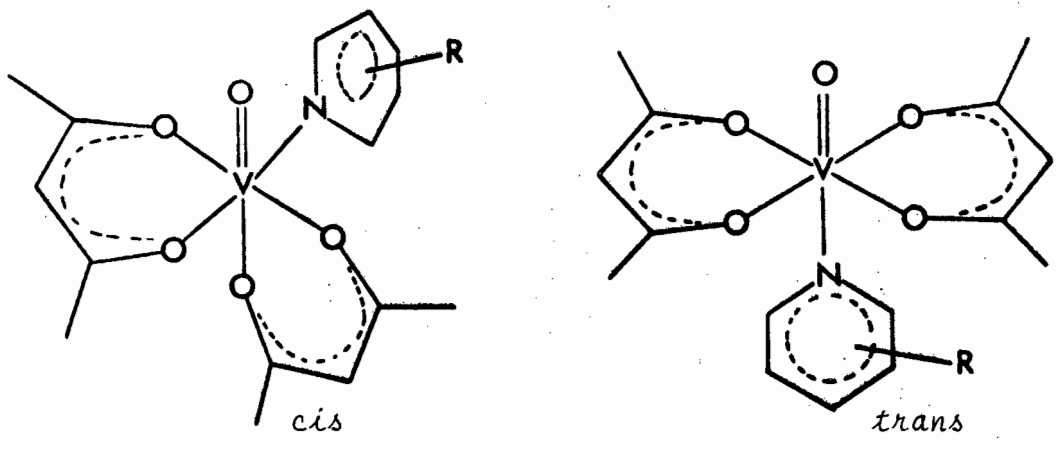


fig. (vii)

Haigh concluded that the series of complexes displaying greatest weakening of the V=O and V-O bonds are probably *cis*-isomers and the series of the five more stable complexes are *trans*- isomers. A *cis*- arrangement has been verified for the complex $Ni(ACA)_2 \cdot (py\ NO)_2$ and for some cobalt(II) complexes of acetylacetone[18] and is therefore not unreasonable.

Da Silva and Wootton[19] recorded the spectra of chloroform solutions of pyridines and $VO(ACA)_2$ in the approximate molar ratio of pyridine: $VO(ACA)_2$ = 5:1. Approximately fixed shifts of ν V=O of 31 ± 3 cm^{-1} or 51 ± 3 cm^{-1} were observed in all cases, the more basic pyridines giving only the ν V=O of larger shift. The observation of two shifted bands for some of the substituted pyridine adducts was interpreted as evidence for the existence of an equilibrium between two distinct types of complex in solution. The independence of this equilibrium of the ligand concentrations for a particular pyridine further suggested that these complexes are isomers. Thus, it was deduced that there is an equilibrium between geometrical isomers in chloroform solution, these isomers being those shown in fig (vii).

It was stated that the *trans*- coordination of the pyridine with respect to the V=O bond (i.e. in the *trans*-isomer) would be expected to have a larger effect on νV=O than the *cis*- coordination (i.e. in the *cis*-isomer).

These authors did not investigate the far infrared spectra and their final conclusion was that the complex in the *trans*- form is that with the lowest ν V=O value; that is, the opposite conclusion to that reached by Haigh[6].

[18]W.D.W. Horrocks, D.H. Templeton and A. Zalkin. *Inorg.Chem.* 7 (1968) 1552.

[19]J.J.R.F. Da Silva and R. Wootton. *Chem.Comm.* (1969) 421.

2. OBJECT OF RESEARCH

The aim of the present work was twofold.

In the first instance, structural investigation by X-ray diffraction techniques of vanadyl complexes has been made in a few cases only. It was thought to be of interest to determine the effect on the geometry of the 'oxygen pyramid' referred to above, on the adduction of a substituted-pyridine to $VO(ACA)_2$.

Secondly, X-ray diffraction being the ultimate means of structural investigation, it was decided to use this method to establish the structure of a substituted-pyridine adduct of $VO(ACA)_2$, in order to resolve the controversy regarding *cis*- *trans*- isomerism, mentioned above.

Samples of several of these adducts were examined. It was found that the 4-phenylpyridine adduct of vanadylbis-acetylacetonate yielded crystals suitable for X-ray analysis.

For this particular adduct, a *cis*- configuration was predicted by Haigh[6]. [fig.(viii)]. (R = 4-C_6H_5, Table 1).

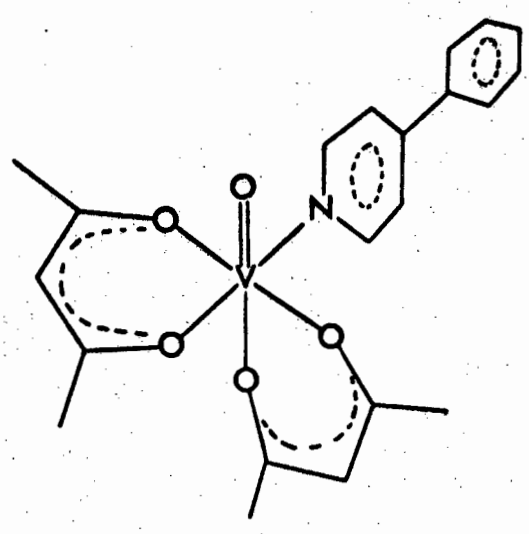


fig. (viii)

While the present work was being undertaken, it was noted further that there is a possibility of enantiomorphism in the *cis*- structure. That is, if the adduct were to exist in the *cis*- form, it might assume either of the enantiomorphous structures [fig. (ix)] in the crystalline state. Alternatively, the crystal might consist of equal numbers of both enantiomorphs arranged in a centrosymmetric fashion.

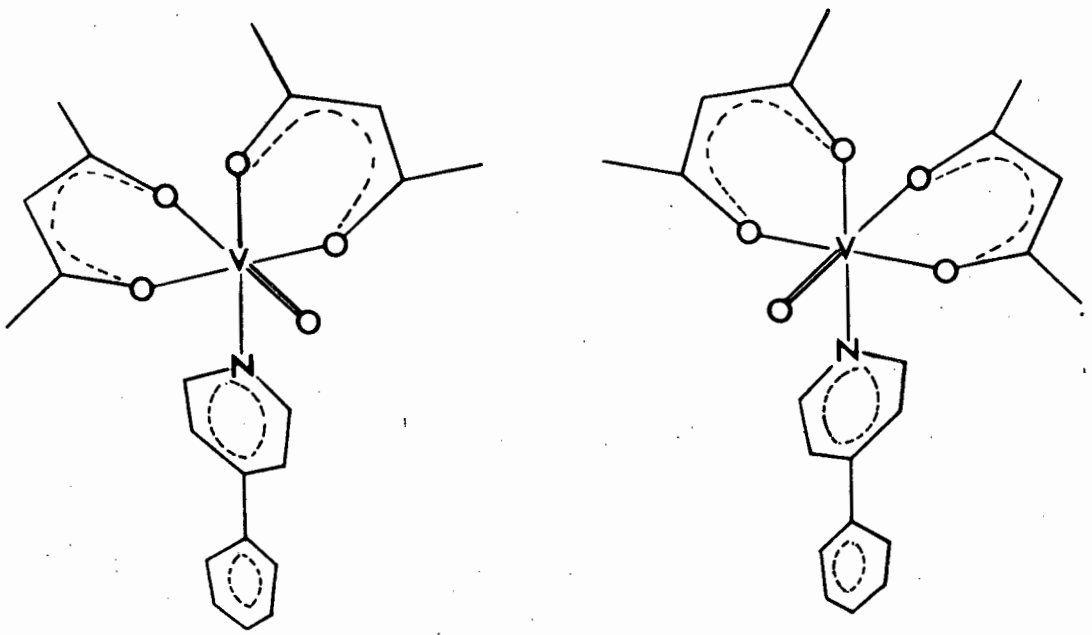


fig. (ix)

There are thus three stereochemically feasible structures for this adduct viz. a *trans*- structure and two enantiomeric *cis*- structures.

This work was directed towards determining the crystal structure of the complex by X-ray diffraction methods.

3. PREPARATION AND CHARACTERISATION OF THE COMPLEX

3.1 PREPARATION

Vanadylbisacetylacetonate (0.0026 mole) was dissolved in chloroform (10 ml). It was necessary to heat the solvent in order to obtain complete dissolution of the solid. The solid compound, 4-phenylpyridine (0.0026 mole) was dissolved in chloroform (10 ml). No heating was necessary. To the mixture obtained by adding the two solutions together, excess diethyl ether was added. The reaction vessel was left to stand for twenty-four hours during which time the level of the ether in the vessel was kept constant. After this period, dark-green crystals were obtained. These crystals adhered to the sides of the vessel. The supernatant liquid was decanted and the crystals were washed several times with ether until the washings were clear. The crystals were filtered off at the pump, washed with ether and air dried.

3.2 CHARACTERISATION

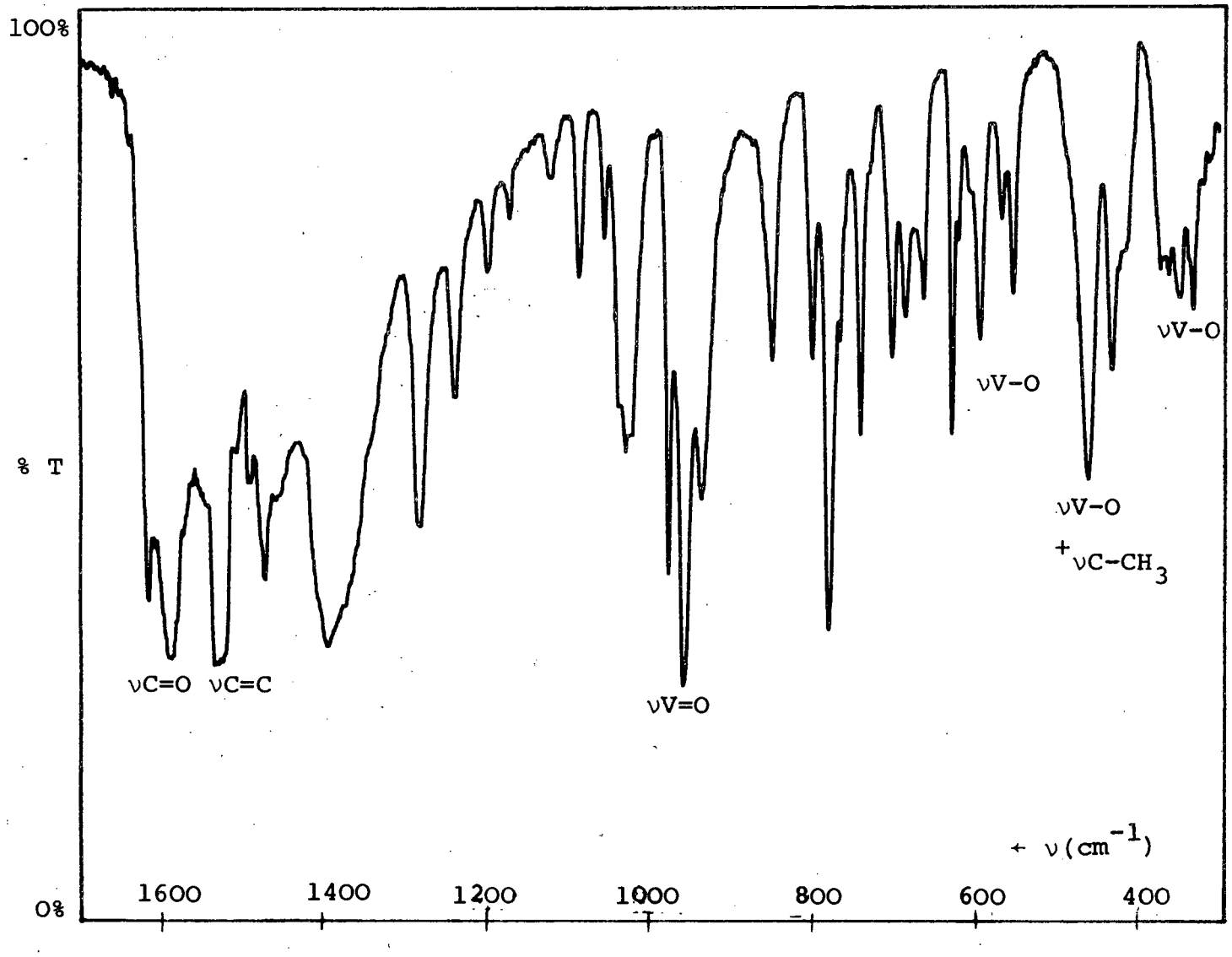
For the complex $[VO(C_5H_7O_2)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N]$, composition analysis gave the following results.
(Microanalysis was performed by Dr. K.G. Fuhr of this department).

	% C	% H	% N
Found :	60.2	5.4	3.4
Calculated:	60.0	5.5	3.3

The complex appeared to lose the adducted pyridine on heating; the remaining solid then sublimed.

The infrared spectrum of the adduct is reproduced in fig. (x).

Fig. (x). Infrared Spectrum of $[VO(ACA)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N]$



4. THE X-RAY GENERATORS AND ACCESSORIES

The generator used in this project was a Philips PW 1120/00/60 generator capable of supplying an X-ray tube up to 60 kV, 80mA, 3000 watts. The generator was operated at 40mA and 30 kV and a copper target was used.

Weissenberg photographs were taken using a non-integrating Stoe (Heidelberg) goniometer.

Precession photographs were taken using a Stoe (Heidelberg) Precession goniometer.

In the collection of intensity data, Kodak "Kodirex" film was used. The film was developed in Kodak X-ray developer for 5 minutes at 20°C, immersed for 5 seconds in a stop bath containing 3% acetic acid and was fixed for 5 minutes with agitation in Kodak X-ray fixer. The film was suspended in the fixer for a further 10 minutes, washed in running water for 20 minutes and left to dry in air.

5. PRELIMINARY INVESTIGATION

5.1(a) Linear constants of the unit cell

The compound crystallised in dark-green plates of average dimensions 0.08 x 0.04 x 0.02 cm. A single crystal was selected and was mounted along the needle axis. With the crystal rotating about this axis, a rotation photograph was taken using Ni-filtered Cu K_α radiation. From measurements of the layer-line spacings on this photograph, the value of the cell constant *b* was determined using the formulae[20]

[20] C.W. Bunn *Chemical Crystallography* 2nd Ed., p. 149 (Oxford University Press 1961.)

$$b = \frac{n\lambda}{\cos \phi_n} \quad \ldots\ldots \quad \ldots\ldots \quad (5.1)$$

and

$$\tan \phi_n = {}^{r}/_{Yn} \quad \ldots\ldots \quad (5.2)$$

where n is the number of the layer line,

λ is the wavelength of the X-radiation used (1.5418 Å),

r is the camera radius (3.00 cm),

y is the layer-line spacing

and ϕ_n is the semi-vertical angle of the n^{th} cone of diffracted rays.

Analysis of a zero-layer Weissenberg photograph taken with the crystal rotating about the needle axis allowed the calculation of a and c. These parameters were evaluated in the following way: The above photograph was taken using unfiltered X-rays. The axial reflections in the directions of a^* and c^* were identified. For each axial row, the film coordinates x_1 and x_2 of corresponding pairs of reflections on either side of the centre line of the photograph were recorded. Owing to K_α and K_β splitting (λ_α = 1.5418 Å, λ_β = 1.392 Å), the use of unfiltered X-rays made it possible to obtain a larger number of individual measurements of the film coordinates than would have been the case in the absence of filtering. The values of the Bragg angle, θ, corresponding to each reflection were calculated and the reciprocal lattice constants a^* and c^* were evaluated from the Bragg equation

$$d^* = \frac{2 \sin \theta}{n\lambda} \quad \ldots\ldots \quad (5.3)$$

where d^* is the interplanar distance in reciprocal space.

Upper-layer Weissenberg photographs confirmed that the space group was monoclinic with b the unique axis. The following relations therefore hold:

$$\left.\begin{aligned} a &= \frac{1}{a^*}\sin\beta \\ b &= \frac{1}{b^*} \\ c &= \frac{1}{c^*}\sin\beta \\ \beta &= 180^\circ - \beta^* \\ V &= abc\sin\beta \end{aligned}\right\} \quad \text{(Monoclinic 2nd setting)} \qquad \ldots\ldots \qquad (5.4)$$

In the calculation of d^*, the measured θ-values ranged from 10° to 53°. Through this range, no systematic trend in the corresponding values of d^* was apparent, these values being distributed randomly about the mean. Hence, refinement of d^* by extrapolation techniques was not applicable.

5.1(b) The determination of β

(i) From reciprocal lattice plots drawn by means of a Weissenberg template, the average value of β was found to be $71 \pm 1^\circ$.

(ii) From the zero-layer Weissenberg photograph, the method of ω-separations[21] yielded a value, $\beta = 72^\circ \pm 1^\circ$.

(iii) An accurate value of β was determined by direct measurement on the a^*c^* reciprocal lattice net, the latter having been photographed with a single crystal precessing about b.

Five measured values of β yielded an average β of 71.4° with a corresponding standard deviation of $\pm 0.2^\circ$.

[21] M.J. Buerger *X-Ray Crystallography* p. 372 (John Wiley 1942).

The final values of the unit cell parameters were:

$a = 24.29 \pm 0.01$ Å

$b = 8.14 \pm 0.02$ Å

$c = 21.66 \pm 0.01$ Å

$\alpha = 90^{\circ}$, $\beta = 71.4 \pm 0.2^{\circ}$, $\gamma = 90^{\circ}$

(The errors are standard deviations).

5.2 SPACE GROUP DETERMINATION

Precession photographs were used in conjunction with zero- and upper- layer Weissenberg photographs in the examination of the $h\ k\ \ell$ data for systematically-present reflections, all of which had been assigned Miller Indices.

The conditions for non-extinction were found to be:

$h\ k\ \ell$: $h + k = 2n$ → C-centred lattice.

$h\ o\ \ell$: $\ell = 2n$; $(h=2n)$ → (010) glide plane, component $^{c}/_{2}$.

$o\ k\ o$: $k = 2n$ → [010] screw axis, component $^{b}/_{2}$

Two possible space groups viz. C_c No. 9 (non-centrosymmetric) and C2/c No. 15 (centrosymmetric) were indicated by these conditions[22]. There are four equivalent positions in the former space group and eight in the latter. The space group C2/c was suggested by the fact that there were eight molecules in the unit cell. A three-dimensional Patterson analysis and the subsequently successful structure-analysis determined the space group unambiguously as C2/c.

[22] *International Tables for X-Ray Crystallography* 1. 89 and 101. (1959).

5.3 THE NUMBER OF MOLECULES IN THE UNIT CELL

The flotation technique and a modification of this technique were used to determine the density of the crystals.

In the first instance, the crystals were suspended in an aqueous solution of potassium iodide, in which they were insoluble. This method yielded a value of ρ, the crystal density, of 1.36 g cm^{-3}.

Secondly, a density-gradient column[23] containing an equilibrated mixture of carbon tetrachloride (ρ = 1.604 g cm^{-3}) and chlorobenzene (ρ = 1.107 g cm^{-3}) was set up. The column was calibrated with minute drops (c. 0.01 ml) of potassium iodide solutions of measured density. The immersed crystals settled at a position in the column liquid corresponding to a density of ρ = 1.360 ± 0.005 g cm^{-3}.

The number of molecules per unit cell, Z, was calculated from the formula[24]

$$Z = \frac{V\rho \times 0.6023 \times 10^{24}}{M} \qquad \ldots\ldots \qquad (5.5)$$

where $V = abc \sin\beta$ is the volume of the monoclinic unit cell,

ρ, the measured density (1.360 ± 0.005 g cm^{-3})

M, the gram molar mass of the compound $C_{21}H_{23}O_5$ NV (420 g $mole^{-1}$).

From equation (5.5), n = 7.90, indicating that there are eight molecules in the unit cell.

For n = 8, the calculated density is 1.37 g cm^{-3}.

[23] Low and Richards. *J. Amer. Chem. Soc.* 74 1660(1952).

[24] C.W. Bunn *Chemical Crystallography* 2nd Ed., p.198 (Oxford University Press 1961).

6. INTENSITY DATA COLLECTION

6.1 THE SELECTION OF A CRYSTAL SUITABLE FOR X-RAY ANALYSIS

All matter absorbs X-rays, of incident intensity I_o, according to the equation[25]: $I = I_o e^{-\mu t}$ ..... (6.1)

where I is the intensity of the beam after it has passed through a thickness t of absorber and μ is the linear absorption coefficient. A different absorption coefficient may be defined by rewriting equation (6.1) in the form

$$I = I_o e^{-\rho \mu_m t} \quad . \qquad \ldots\ldots \qquad (6.2)$$

where μ_m is defined as the mass absorption coefficient for the particular wavelength of X-radiation and ρ is the density of the absorber.

The linear absorption coefficient μ, of the hypothetical compound ABC is calculated from the individual mass absorption coefficients of the elements A, B and C.

Thus: $\mu = \rho \Sigma p(\mu/\rho) = \rho \Sigma p \mu_m$

$$= \rho \{p_A(\mu/\rho)_A + p_B(\mu/\rho)_B + p_C(\mu/\rho)_C\} \ldots (6.3)$$

where ρ is the density of the compound, p is the proportion of each element by weight in the compound and μ/ρ is the mass absorption coefficient of each element.

For the complex investigated and using Cu K_α radiation of wavelength 1.5418 Å, $\rho = 1.360 \pm 0.005$ g cm^{-3},

$$\mu_m \text{ (V)} = 233 \text{ cm}^2\text{g}^{-1}$$
$$\mu_m \text{ (N)} = 7.52 \text{ cm}^2\text{g}^{-1}$$
$$\mu_m \text{ (O)} = 11.5 \text{ cm}^2\text{g}^{-1}$$
$$\mu_m \text{ (C)} = 4.60 \text{ cm}^2\text{g}^{-1}$$
$$\mu_m \text{ (H)} = 0.44 \text{ cm}^2\text{g}^{-1}$$

[25] *X-ray Crystallography* M.J. Buerger. Chapter 9 (John Wiley 1942).

Application of the formula (6.3) yields a value of $\mu = 45.4\ cm^{-1}$ for the complex $[VO(C_5H_7O_2)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N]$ and an optimum crystal radius for rotation photographs given by $2/\mu = 0.44$ mm.

The cross-sections of the plate-like crystals prepared were generally parallelograms in which the length of one side was approximately twice the length of the adjacent side. In order to minimise absorption effects, it was necessary to select a crystal whose cross-section was as near a rhombus as possible. Such a crystal was chosen and its size was accurately measured. The cross-section had the dimensions 0.006 x 0.012 cm which resulted in an average radius, R, of the crystal, equal to 0.009 cm. with the corresponding value $\mu R = 0.40$.

The absorption correction A* for $\mu R = 0.40$ for cylinders varies[26] from 1.95 to 1.81 for θ varying from 0° to 90°. Correction of the measured intensity data for absorption was not undertaken as the variation in A* was thought to be sufficiently small over the range of θ-values.

In the final collection of intensity data at room temperature, the above crystal was used.

Attempts at crystal grinding and shaping failed, since the crystals showed pronounced cleavage.

Efforts to cut them with a razor-blade also failed because they were extremely brittle and invariably shattered.

[26] *International Tables for X-Ray Crystallography* Vol. II. p295. (1959).

6.2 ATTEMPTS TO OBTAIN LOW-TEMPERATURE DATA

Initially it was decided to analyse the crystal at low temperature at which molecular thermal vibrations would be reduced. It was feared that the thermal vibration, at room-temperature, of the relatively heavy Vanadium atom (Z = 23) might cause adjacent peaks (due to lighter atoms) in the Fourier map to be overshadowed by the Vanadium peak. The cooling apparatus used[27] consisted of two 10-ℓ. Dewar-flasks filled with liquid-nitrogen, sealed with rubber bungs and connected by means of copper tubing. A heating coil in one flask caused the liquid-nitrogen to boil and pass into the second flask from which nitrogen-vapour was emitted through a spiral (condensing) copper tube.

The nitrogen-vapour was allowed to flow through a double-walled glass tube at the end of which a thermocouple was situated. The crystal under analysis was made to oscillate in the nitrogen-vapour stream. Using this system, constant temperatures as low as -130^{o}C were recorded. Under these conditions, however, much difficulty was encountered in attempts to collect $h\ k\ \ell$ Weissenberg data by the equi-inclination technique. It was found that the crystals contracted and shattered at low temperatures. This procedure was therefore abandoned and it was decided to proceed with data collection at room-temperature.

6.3 THE ACCURATE ALIGNMENT OF CRYSTALS FOR X-RAY ANALYSIS

A two-circle optical-goniometer was used to align well-formed crystals. The advantages of the relatively long

[27] A. Rodgers. *Ph.D. Thesis*, (unpublished) (University of Cape Town)

needle-axis and the presence of near-perfect external faces permitted quick and accurate alignment of these crystals. In cases where crystals were malformed, the alignment technique developed by Weisz and Cole[28] was used. This consisted of irradiating the stationary, misaligned crystal with unfiltered radiation with one goniometer arc parallel to the X-ray beam. This was followed by a second irradiation made with the crystal at 180° from its initial orientation.

From the composite zero-layerline photograph obtained in this way, both arc errors were deduced. The arcs were then adjusted by the appropriate angles in the appropriate directions. Excellent rotation photographs were obtained in this manner.

6.4 WEISSENBERG DATA COLLECTION AT ROOM-TEMPERATURE (20°C)

The crystal selected (6.1) was mounted at the end of a glass rod and was accurately aligned as described above. It was then set with the needle axis, Y, parallel to the oscillation axis. A non-integrating Weissenberg camera was used to collect zero- and upper-layer Weissenberg data by the equi-inclination technique.

The standard multiple-film technique[29] was used in order to record a maximum range of measurable intensities. For each Weissenberg layer, two exposures were necessary. Using four superimposed films, an average forty-hour exposure provided three usable films. The top film was discarded since the dark background on this film would have led to inaccurate intensity measurements. The second exposure of three hours

[28] O.Weisz and W.F. Cole. *J.Sci. Instr.* 25 213 (1948).

[29] G.H. Stout and L.H. Jensen. *X-Ray Structure Determination* p160 (MacMillan 1968).

(average) for each Weissenberg layer provided another four films from which intensities could be measured.

Thus, for each layer, seven Weissenberg photographs were available for intensity measurements.

Data from the layers $h0\ell$, $h1\ell$, $h2\ell$, $h3\ell$, $h4\ell$ and $h5\ell$ were recorded.

6.5 MEASUREMENT OF INTENSITIES

A standard intensity-strip was prepared in the following manner: spots of the same average magnitude as the reflections on the Weissenberg photographs were produced on film using an X-ray collimator and Ni-filtered CuK_α radiation in the absence of a crystal.

Twenty-four accurately timed exposures were taken, the times of these exposures being successively increased[30] by a factor of $\sqrt[3]{2}$', as this was considered to yield a finer comparison scale than one in which the factor was $\sqrt{2}$'.

The actual densities of the spots on the final scale had the relative values: 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.5, 8.0, 10.0, 13.0, 16.0, 20.0, 25.0, 32.0, 40.0, 51.0, 64.0, 81.0, 102.0, 128.0, 161.0, 200.0, 256.0, corresponding as closely as the measurement of time permitted to a geometrical progression of common ratio approximately 1.26 and first term 1.0. The accuracy involved in the timing procedure (± 0.5 sec.) obviously prevented the achievement of a ratio equal to $\sqrt[3]{2}$' exactly, so that the theoretical times were rounded off to the figures listed above.

The intensities of the Weissenberg reflections were

[30] G.H. Stout and L.H. Jensen. *X-Ray Structure Determination* p.166. (Macmillan 1968).

then estimated by visual comparison of the reflection with the spots on the intensity scale. Any one reflection was measured on each of the films on which it appeared. The film factor between every pair of films was calculated by taking the average of all the film factors obtained for individual reflections. Most of the individual intensity values therefore represented an average of 3 or 4 measurements.

Generally, for each layer, most of the reflections whose intensities were estimated were of the type $h\ell$, $\bar{h}\ell$, $\overline{h\ell}$, the first and last sets of reflections being equivalent, from Friedel's Law[31] viz. $I_{hk\ell} = I_{\overline{hk\ell}}$ ..... (6.4).

Thus, taking into account also the symmetry relations, it was found that about 3000 measured intensities reduced to 1595 independent reflections of the type $hk\ell$ and $\bar{h}k\ell$.

Many of these reflections were, however, of very low intensity (e.g. 1.0, 1.5, 2.0, 3.0 on the intensity strip) and an error in the measurement of such reflections would have amounted to a fifty - or even a one - hundred percent error in the intensity estimate.

These reflections were discarded and the number of unique reflections finally used was 1412.

In order to facilitate computing, the reflections with Miller Indices $\bar{h}k\ell$ were relabelled $hk\bar{\ell}$ in accordance with the condition[32] $F(\bar{h}k\ell) = F(hk\bar{\ell})$ obtained from the space-group symmetry.

[31] M.J. Buerger *X-Ray Crystallography* p. 55. (John Wiley 1942).

[32] *International Tables for X-Ray Crystallography* Vol. III p.384 (1959).

Thus, 1412 reflections of the type $hk\ell$, $hk\bar{\ell}$ (k = 0, 1, 2, 3, 4, 5) were used in the eventual refinement of the structure.

6.6. SCALING OF THE INTENSITY DATA

It was necessary to bring the sets of intensity data for the reflections $h0\ell$, $h1\ell$, $h2\ell$, $h3\ell$, $h4\ell$ and $h5\ell$ onto a common scale.

To a first approximation, this end was achieved by making all the exposure times roughly equal (viz. 40 hours) and by making no changes in the experimental conditions during or between exposure times.

However, accurate scaling by means of cross-level photographs[33] was attempted.

A second crystal was selected and was mounted along a non-needle axis. A rotation photograph obtained from this crystal gave a value of 23.0Å for the unit cell length, in fair agreement with the value of 21.66Å obtained for c by accurate measurement (5.1(a)). A zero layer Weissenberg photograph taken with this crystal oscillating about the Z - axis yielded reflections of the type $hk0$.

An average of ten reflections from each layer $hk\ell$ (k = 0 to k = 5) were selected and the corresponding reflections on the $hk0$ photograph were measured. It was found, however, that for a set of reflections from any one $hk\ell$ layer, the ratio of the intensity of a reflection measured on the $hk\ell$ film and

[33] G.H. Stout and L.H. Jensen *X-Ray Structure Determination* p.202. (Macmillan 1968).

that of the corresponding reflection on the *hk*O film was not constant, as expected, but varied with the Bragg angle, θ. This variation was attributed to severe absorption effects which arose because the crystal was made to oscillate about a non-needle axis. Further attempts at scaling the *hkl* data by photographic methods were not made; instead, it was decided to allow the scaling to be performed automatically in the least squares refinement.

6.7. CORRECTION OF INTENSITY DATA

The measured intensities were corrected for geometrical and physical factors[34] by means of the C.S.I.R. Crystallographic programme "CØRRECT". The unscaled reflections were corrected for spot-splitting and for spot-shape.

The Lorentz-Polarization correction was then applied and finally, the square-root $|F_o| = |F_{observed}|$ of the observed intensities, I, were computed.

Thus, 1412 observed structure factors $|F_o|$ and their corresponding *hkl* values were available for the structural analysis. (Initially, computing was performed on the I.B.M. 1130 computer and later, on the UNIVAC 1106 system at the Computer centre of the University of Cape Town.)

[34] *International Tables for X-Ray Crystallography* Vol. III. 3.1. p.133 (1959)

and hence eight Vanadium atoms in the unit cell. The possible space groups indicated by reflection conditions were Cc (non-centrosymmetric) or C2/c (centrosymmetric).

The eight Vanadium atoms were placed in the general atomic positions as required by the space group[36] C2/c. The 8 x 8 positions of the vector peaks arising from the V-V interactions are tabulated [Table 2. (Page 33)]. The origin has a multiplicity eight, since there are eight vector peaks at (0,0,0). The multiplicities of all the other peaks are derived in the same manner.

The Vanadium in the molecule investigated was assumed to be in the state V^{2+}, for which Z = 21. (The assignment of Z = 21 is discussed in chapter 8.) A single V-V vector peak was expected to have a height (21 x 21) = 441; a double V-V vector peak, a height of (2 x 441) = 882, and so on, while the height of the origin was expected to be $\sum_n Z_n^2$ = 1589. The Patterson synthesis was computed for one eighth of the unit cell volume only and therefore not all of the peaks listed in Table 3 (Page 34) were expected in the map. The expected peaks are marked with asterisks.

The Patterson map obtained was generally featureless except for the major peaks listed in Table 4 (Page 34). Peak heights are scaled so that the origin height has a value $\sum_n Z_n^2 = 1589$.

A peak of height 1764 was expected at 0, 2y, ½ [Table 3]. Corresponding to this position, the highest observed

[36] *International Tables for X-Ray Crystallography* 1 101 (1959).

TABLE 2

ATOMIC POSITION	1 x y z	2 $\bar{x}$ $\bar{y}$ $\bar{z}$	3 $\bar{x}$ y ½-z	4 x $\bar{y}$ ½+z	5 ½+x ½+y z	6 ½-x ½-y $\bar{z}$	7 ½-x ½+y ½-z	8 ½+x ½-y ½+z
1 x y z	1-1 0 0 0	1-2 2x 2y 2z	1-3 2x 0 2z-½	1-4 0 2y -½	1-5 -½ -½ 0	1-6 2x-½ 2y-½ 2z	1-7 2x-½ -½ 2z-½	1-8 -½ 2y-½ -½
2 $\bar{x}$ $\bar{y}$ $\bar{z}$	2-1 -2x -2y -2z	2-2 0 0 0	2-3 0 -2y -½	2-4 -2x 0 -2z-½	2-5 -2x-½ -2y-½ -2z	2-6 -½ -½ 0	2-7 -½ -2y-½ -½	2-8 -2x-½ -½ -2z-½
3 $\bar{x}$ y ½-z	3-1 -2x 0 ½-2z	3-2 0 2y ½	3-3 0 0 0	3-4 -2x 2y -2z	3-5 -½-2x -½ ½-2z	3-6 -½ 2y-½ ½	3-7 -½ -½ 0	3-8 -½-2x 2y-½ -2z
4 x $\bar{y}$ ½+z	4-1 0 -2y ½	4-2 2x 0 ½+2z	4-3 2x -2y 2z	4-4 0 0 0	4-5 -½ -½-2y ½	4-6 2x-½ -½ ½+2z	4-7 2x-½ -½-2y 2z	4-8 -½ -½ 0
5 ½+x ½+y z	5-1 ½ ½ 0	5-2 ½+2x ½+2y 2z	5-3 ½+2x ½ 2z-½	5-4 ½ ½+2y -½	5-5 0 0 0	5-6 2x 2y 2z	5-7 2x 0 2z-½	5-8 0 2y -½
6 ½-x ½-y $\bar{z}$	6-1 ½-2x ½-2y -2z	6-2 ½ ½ 0	6-3 ½ ½-2y -½	6-4 ½-2x ½ -½-2z	6-5 -2x -2y -2z	6-6 0 0 0	6-7 0 -2y -½	6-8 -2x 0 -½-2z
7 ½-x ½+y ½-z	7-1 ½-2x ½ ½-2z	7-2 ½ ½+2y ½	7-3 ½ ½ 0	7-4 ½-2x ½+2y -2z	7-5 -2x 0 ½-2z	7-6 0 2y ½	7-7 0 0 0	7-8 -2x 2y -2z
8 ½+x ½-y ½+z	8-1 ½ ½-2y ½	8-2 ½+2x ½ ½+2z	8-3 ½+2x ½-2y 2z	8-4 ½ ½ 0	8-5 0 -2y ½	8-6 2x 0 ½+2z	8-7 2x -2y 2z	8-8 0 0 0

TABLE 3

PEAK POSITION	PEAK MULTIPLICITY	EXPECTED PEAK HEIGHT
0, 0, 0 *	8	1589
½, ½, 0 *	8	1589
0, 2y, ½ *	4	1764
0, -2y, ½	4	
2x, 0, ½+2z	4	
-2x, 0, ½-2z	4	
½, ½+2y, ½	4	
½, ½-2y, ½ *	4	1764
½+2x, ½, ½+2z	4	
½-2x, ½, ½-2z *	4	1764
2x, 2y, 2z *	2	882
-2x, -2y, -2z	2	
2x, -2y, 2z	2	
-2x, 2y, 2z	2	
½+2x, ½-2y, 2z	2	
½+2x, ½+2y, 2z	2	
½-2x, ½-2y, -2z	2	
½-2x, ½+2y, -2z	2	

TABLE 4

Peak Number	Map Coordinates (hundredths of the unit cell lengths)	Peak Height Scaled to ORIGIN height = 1589	General Coordinates
1	0, 0, 0	1589	0, 0, 0
2	50, 50, 0	1589	½, ½, 0
3	50, 20, 50	340	½, ½-2y, ½
4	0, 10, 50	340	0, 2y, ½
5	28, 50, 32	202	½-2x, ½, ½-2z
6	22, 10, 17	103	2x, 2y, 2z

peak [peak No.4, Table 4] of height 340 occurred at 0, 10, 50. Hence $2y = {}^{10}/_{100}$. At the section $2y = {}^{10}/_{100}$, the highest observed peak (height = 103) occurred at 2x = 22, 2z = 17.

The satellite peaks at ($\frac{1}{2}$ - 2x, $\frac{1}{2}$, $\frac{1}{2}$ - 2z) and ($\frac{1}{2}$, $\frac{1}{2}$ - 2y, $\frac{1}{2}$) were found in the expected positions and therefore served as confirmation of the correct location of the rotation peak at (2x, 2y, 2z).

Table 4 shows that the peaks occurred in the correct positions. Correspondence between the heights, however, was not good. This is not easy to explain but must be due to the wrong assumption that the origin peak height is $\sum_n Z_n^2$. The latter assumption is only true for point atoms at $\frac{\sin\theta}{\lambda} = 0$. However, since no other peaks of large magnitude were found, the only reasonable solution to the vector map was the one outlined above. This was later vindicated by the successful solution of the structure. From the position (22, 10, 17) of the Patterson rotation-peak (2x, 2y, 2z) the position of the Vanadium atom in the unit cell was therefore found to be x = 0.11, y = 0.05, z = 0.085.

7.2 THE UNAMBIGUOUS DETERMINATION OF THE SPACE GROUP

The four equivalent positions of the space-group Cc[37] are x, y, z; $\frac{1}{2}$ + x, $\frac{1}{2}$ + y, z; x, -y, $\frac{1}{2}$ + z; $\frac{1}{2}$ + x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z, (Cc being a subgroup of the space group C2/c).

A similar analysis to that shown in Table 2 for the space-group Cc yields no vector peak at ($\frac{1}{2}$ - 2x, $\frac{1}{2}$, $\frac{1}{2}$ - 2z), which was actually found in the Patterson map computed. [Table 4, peak 5.]

This analysis showed therefore that the space group of the structure investigated is C2/c and not Cc.

[37] *International Tables for X-Ray Crystallography* 1 89 (1959).

8. LOCATION OF THE LIGHT ATOMS BY FOURIER METHODS

8.1 ATOMIC SCATTERING FACTORS; ANOMALOUS DISPERSION

The scattering factor, f, for a real atom is given by[38]

$$f = f_o e^{-B(\frac{\sin\theta}{\lambda})^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (8.1.1)$$

where B, the isotropic temperature factor, is related to the mean-square amplitude $(\overline{u^2})$ of atomic vibration by

$$B = 8\pi^2 \overline{u^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8.1.2)$$

and f_o is the scattering factor when thermal motion is neglected. (Thermal agitation causes each atom of a crystal structure to execute vibrations about its equilibrium position. The magnitude of the thermal motion is expressed by the factor B. If the restoring forces are the same in all directions of vibration, then the field of restoring forces is said to be 'isotropic'.)

If the atom has an atomic number near to that of the element used to generate the incident X-rays, an anomalous phase change occurs during scattering by the electrons associated with the absorption edge. This effect, 'anomalous scattering' or 'anomalous dispersion' causes the scattering factor of the atom to be complex. It can be represented by

$$f_o^{anom} = f_o + \Delta f' + i\Delta f'' = f' + i\Delta f'' \quad \ldots \quad (8.1.3)$$

where f_o is the normal scattering factor, $\Delta f'$ is a real correction term (usually negative) and $\Delta f''$ is the imaginary component.

In this investigation, the scattering factors for

[38] G.H. Stout and L.H. Jensen *X-Ray Structure Determination* Ch. 7 (MacMillan 1968)

V^{2+} were corrected for anomalous dispersion, by applying equation (8.1.3), using $\Delta f''$ values for Sc^{0} (Z = 21)[39].

For the carbon, nitrogen and oxygen atoms, atomic scattering factors[40] were employed. The effect of scattering by hydrogen atoms was not taken into account at any stage of the analysis.

8.2 STRUCTURE FACTORS

The structure factor, $F_{hk\ell}$ is the resultant of j waves scattered in the direction of the reflection $hk\ell$ by the j atoms in the unit cell. In the exponential form[41], it is written

$$F_{hk\ell} = \sum_j f_j e^{2\pi i(hx_j + ky_j + \ell z_j)} \quad \ldots\ldots \quad (8.2.1)$$

where x_j, y_j, z_j are the positional coordinates of the jth atom.

The degree of agreement between observed and calculated structure factors is usually assessed by evaluating the residual factor, R, given by[42]

$$R = \frac{\Sigma\,||F_{obs}|-|F_{calc}||}{\Sigma|F_{obs}|} \quad \ldots\ldots\ldots \quad (8.2.2)$$

A value of R = 0.20 usually indicates that there is little doubt that the atoms employed in the structure factor calculation have been properly located.

In the present analysis, structure factors were calculated (using the C.S.I.R. programme "CENTRØSY") with the Vanadium atom alone, situated at the position x = 0.11, y = 0.05,

[39] *International Tables for X-Ray Crystallography* 214 3 (1962).

[40] Ibid 3 201 (1962).

[41] G.H. Stout and L.H. Jensen *X-Ray Structure Determination* Ch. 9 (Macmillan 1968).

[42] C.W. Bunn *Chemical Crystallography* 432 (Oxford, 1961).

z = 0.085 in the crystal unit cell. The value obtained for R in this computation was 0.524.

8.3 THE FOURIER SYNTHESIS

The general expression for the calculation of the electron-density $\rho(x, y, z)$ in the unit cell is[41]

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_\ell F_{hk\ell}\, e^{-2\pi i(hx + ky + \ell z)} \qquad \ldots\ldots\ldots (8.3.1)$$

where V is the volume of the unit cell and $F_{hk\ell}$ is the structure factor.

The coefficients in this series are not merely the moduli of the structure factors which are available as the $|F_o|$ values, but rather the moduli plus the unobservable phases.

Since a heavy atom in the unit cell governs the majority of these phases, the correct location of the heavy atom and subsequent calculation of $F_{hk\ell}$ will provide not only $|F_{hk\ell}|$ but will assign a + or a - sign to the modulus.

By combining the observed structure amplitudes, $|F_o|$, with the calculated phases and using these as the coefficients in the Fourier series, the electron-density $\rho(x, y, z)$ may be calculated. [Eqn. 8.3.1]

In the present analysis, a three-dimensional Fourier map was computed for one-eighth of the unit cell ($0 \rightarrow \frac{1}{2}$ along a, $0 \rightarrow \frac{1}{2}$ along b and $0 \rightarrow \frac{1}{2}$ along c).

The map was sectioned at intervals of $^1/_{50}$ of the unit cell lengths along each axis. This map was based on the $F_{hk\ell}$ coefficients calculated by locating only the Vanadium

[41] G.H. Stout and L.H. Jensen *X-Ray Structure Determination* Ch. 9 (Macmillan 1968).

atoms (see section 8.2). The map was drawn on glass sheets and peaks of high electron-density were sought. From the map, 17 major peaks were found in chemically feasible positions. The atoms corresponding to these positions were tentatively identified and their coordinates were read from the map. The labelling system for the atoms is shown in fig.(xi) (page 40). A typical section of the Fourier synthesis, showing atoms O2, C1, C2, C3 and C5 of the first acetylacetonate ring is reproduced in fig. (xii) (page 41). The second acetylacetonate ring was sought in a position *trans* - to the first, but was not found. However, there were high electron-density peaks in positions *cis* to the first ring. This was the first indication that the molecule is in the *cis* - configuration.

Structure factors were calculated with the 17 atoms which had been located. The initial atomic coordinates and the isotropic B factors for each atom are tabulated [Table 5].

TABLE 5

ATOM LABEL	FRACTIONAL COORDINATES x	y	z	INITIAL ISOTROPIC TEMPERATURE FACTOR, B($Å^2$)
V	0.11	0.05	0.085	2.5
O1	0.12	0.24	0.12	4.0
O2	0.084	-0.18	0.06	3.0
O3	0.108	-0.06	0.16	3.0
O4	0.116	0.16	0.00	3.0
O5	0.20	-0.05	0.04	3.0
N	0.02	0.10	0.12	3.0
C1	0.064	-0.28	0.08	3.0
C2	0.066	-0.35	0.16	3.0
C3	0.086	-0.20	0.18	3.0
C4	0.044	-0.42	0.06	4.0
C5	0.08	-0.24	0.26	4.0
C11	-0.02	0.06	0.08	3.0
C12	-0.08	0.14	0.10	3.0
C13	-0.10	0.21	0.16	3.0
C14	-0.08	0.14	0.20	3.0
C15	-0.02	0.14	0.18	3.0

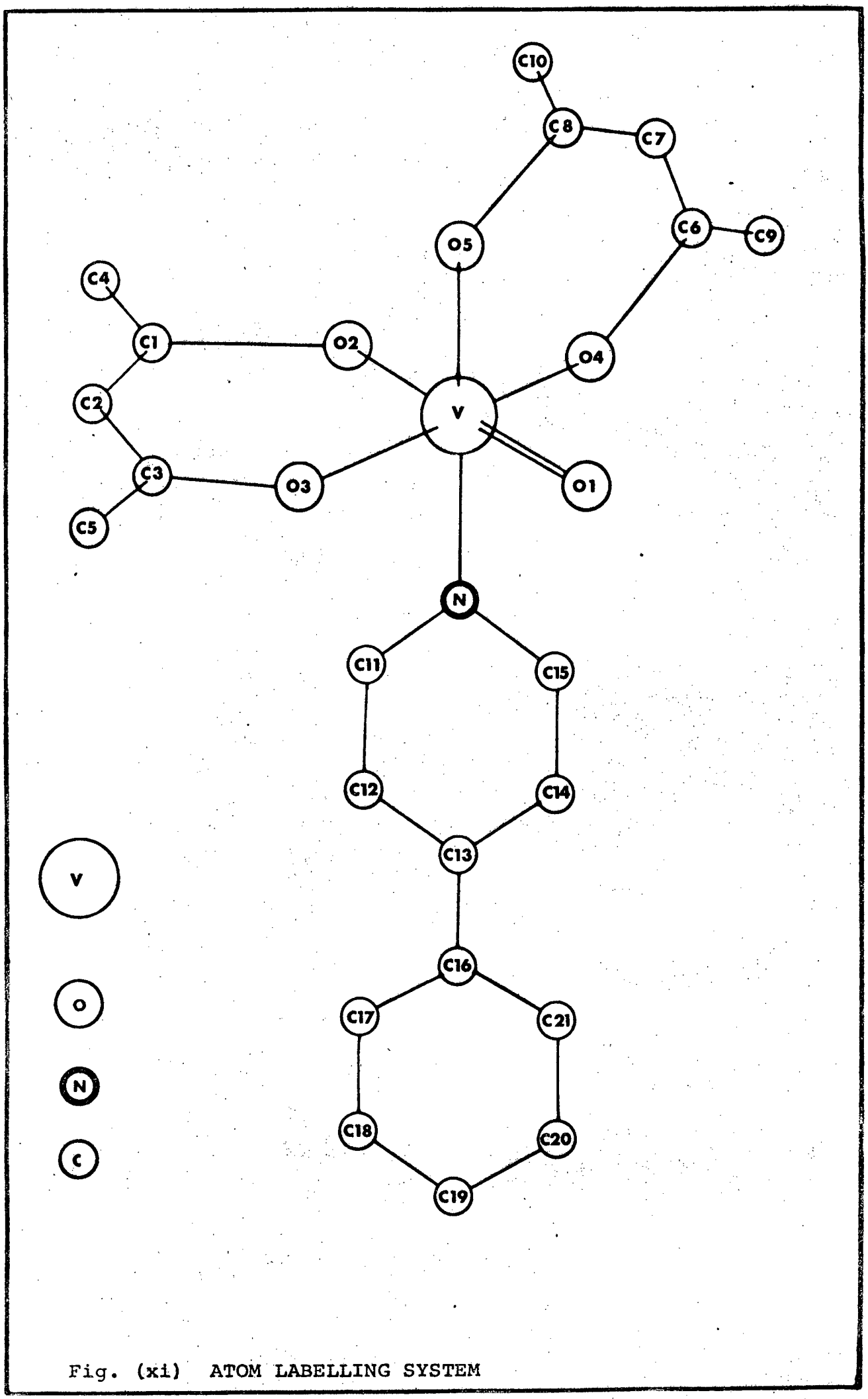


Fig. (xi) ATOM LABELLING SYSTEM

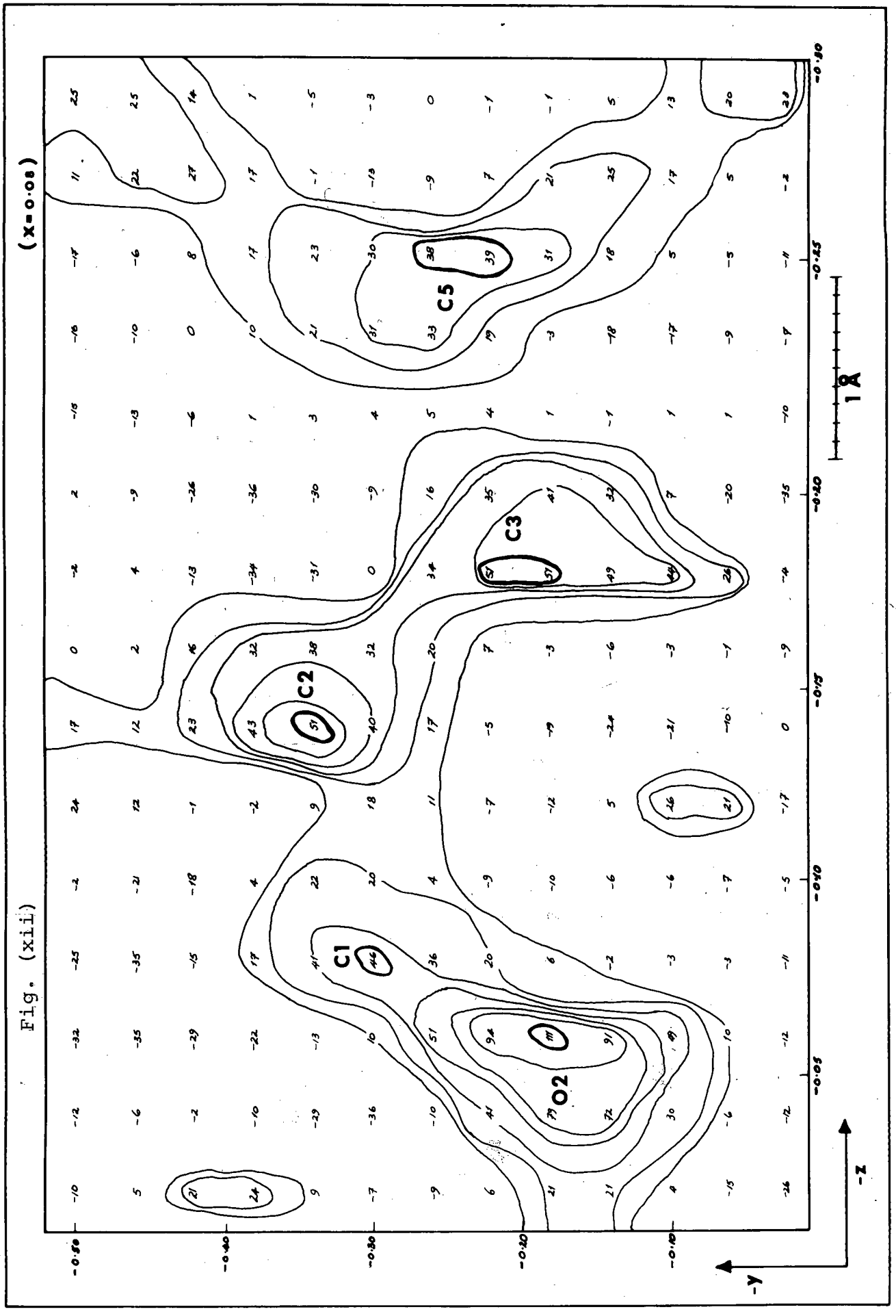


Fig. (xii)

The value of R at this stage was 0.409, which was still rather high.

8.4 THE DIFFERENCE FOURIER SYNTHESIS

The ΔF or difference synthesis may be expressed[43] in the form

$$\Delta\rho = \frac{1}{V} \sum_h \sum_k \sum_\ell (|F_o| - |F_c|)e^{i\alpha_c} e^{-2\pi i(hx + ky + \ell z)} \quad \ldots\ldots\ldots \quad (8.4.1)$$

where $\Delta\rho$ is now the difference in electron-density and α_c is the phase of F_c.

As a first approximation, correctly placed atoms will not appear in the synthesis, completely misplaced ones will be in "holes" and missing ones will appear as peaks. These peaks should correspond to ones appearing in the Fourier map, but are usually much more distinct and obvious.

A difference Fourier synthesis was computed with the first 17 atoms subtracted. All the remaining (11) non-hydrogen atoms were then revealed and their atomic coordinates were read from the map. On examining the positions of the 17 previously-located atoms, it was found that, in general, "holes" had appeared in the difference map. This phenomenon is usually observed when temperature factors, B, which are too small are used. It was decided, therefore, to increase all the isotropic temperature factors before proceeding with further calculations. The coordinates of atom O3 were changed as this atom appeared to have been misplaced.

The trial values of the atomic coordinates and the isotropic temperature factors of all 28 non-hydrogen atoms in the asymmetric unit are shown in Table 6, (Page 43).

[43] G.H. Stout and L.H. Jensen *X-Ray Structure Determination* Ch. 15 (Macmillan 1968).

TABLE 6

ATOM LABEL	FRACTIONAL COORDINATES x	y	z	ISOTROPIC TEMPERATURE FACTOR, B(Å^2)
V	0.11	0.05	0.085	5.0
O1	0.12	0.24	0.12	6.0
O2	0.084	-0.18	0.06	5.0
O3	0.108	-0.03	0.18	5.0
O4	0.116	0.16	0.00	5.0
O5	0.20	-0.05	0.04	5.0
N	0.02	0.10	0.12	5.0
C1	0.064	-0.28	0.08	5.0
C2	0.066	-0.35	0.16	5.0
C3	0.086	-0.20	0.18	5.0
C4	0.044	-0.42	0.06	6.0
C5	0.08	-0.24	0.26	6.0
C6	0.16	0.18	-0.06	5.0
C7	0.21	0.14	-0.06	5.0
C8	0.224	0.10	0.00	5.0
C9	0.145	0.27	-0.105	6.0
C10	0.28	-0.09	-0.02	6.0
C11	-0.02	0.06	0.08	5.0
C12	-0.08	0.14	0.10	5.0
C13	-0.10	0.21	0.16	5.0
C14	-0.08	0.14	0.20	5.0
C15	-0.02	0.14	0.18	5.0
C16	-0.155	0.28	0.18	5.0
C17	-0.19	0.28	0.12	5.0
C18	-0.248	0.34	0.14	5.0
C19	-0.27	0.42	0.22	5.0
C20	-0.238	0.42	0.26	5.0
C21	-0.176	0.34	0.24	5.0

Structure factors based on all 28 atomic positions were then calculated. The value of R was 0.378 which was still disturbingly high. This was thought to be due to the fact that some of the atoms had been misplaced. A second difference Fourier was again computed; in this case, 27 atoms were subtracted, leaving only one atom (viz. C2) in the map as a reference peak.

No major peaks appeared in this synthesis. Small changes in the atomic coordinates and in the isotropic temperature factors were evidently necessary.

Since the Vanadium atom was situated near the edge of the unit cell (x = 0.11, y = 0.05, z = 0.085), it was necessary to extend the original Fourier map beyond the limits 0 → ½ along each axis. Using the 28 atomic positions, corresponding peaks were then drawn on glass sheets. The resulting three-dimensional picture was a very convincing representation of an entire molecule of the adduct investigated. This drawing showed, without ambiguity, the molecule in the *cis* - configuration, as drawn in fig. (xi).

Each of the six-membered rings in the 4-phenylpyridine ligand was not exactly planar, as expected, so it appeared that the high value of R was due to small errors in the atomic coordinates and errors in the isotropic temperature factors.

It seemed certain, therefore, that the value of R would decrease in the refinement process.

8.5 REFINEMENT OF THE STRUCTURE

The structure was refined by the method of least squares[44] using the C.S.I.R. computer programme "ØRFLS". In the isotropic refinement of the structure, there were 118 variables to be taken into account in the minimisation process. These consisted of 6 scale-factors, K, relating the *hkl* (*k* = 0 to *k* = 5) observed structure factors, 28 x 3 atomic coordinates (x, y, z) and 28 isotropic temperature factors, B.

[44] C.W. Bunn *Chemical Crystallography* 399 (Oxford, 1961).

In the first two cycles of refinement, only the scale-factors and the overall B (tentatively taken as 3.0 $\mathring{A}^2$) were allowed to vary. A new value of the residual index, R, of 0.382 was obtained. A further 7 cycles of refinement varying the scale-factors, all of the atomic coordinates and the individual isotropic temperature factors, brought the value of R down to 0.159. At this stage, some of the B parameters were still oscillating slightly but the changes in the atomic coordinates were, on the average, only ± 0.0005 $\mathring{A}$. The variations in the isotropic temperature factors, B, as a function of the number of least squares cycles of refinement for all the atoms are plotted in fig. (xiii) (page 46).

Finally, four cycles of least-squares refinement were carried out and R was reduced to 0.128. At this stage, it was observed that further isotropic refinement would not reduce R below this value.

In the final stage of refinement, anisotropic thermal motion[45] of the atoms was considered. The form of the anisotropic temperature correction, $T_{hk\ell}$, is

$$T_{hk\ell} = e^{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{23}k\ell + \beta_{31}\ell h)}.$$

Here, the B factors for a set of atoms were themselves refined, each B resolving into six parameters viz. β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}. These parameters define an ellipsoid which is traced out by the mean-square displacement of the vibrating atom.

Three cycles of anisotropic least-squares refinement, reduced the value of R from 0.128 to 0.106, which was taken as

[45] M.J. Buerger *Contemporary Crystallography* 327 (McGraw-Hill, 1970).

the final agreement factor. For this value of R, the observed and calculated structure factors for 1412 independent reflections are listed in the Appendix.

The final atomic coordinates and temperature factors are listed in Table 7 (page 48). Standard deviations in these parameters are also listed.

8.6 CALCULATION OF INTERATOMIC BOND LENGTHS AND ANGLES

The computer programme "ØRFFE" (C.S.I.R.) is a function and error programme which allows the calculation of interatomic bond lengths and angles. The unit cell parameters a, b, c, α, β, γ and their appropriate errors [section 5.1(b)] constitute the input data. The atomic positional parameters x, y, z are read from the magnetic-tape output of the programme "ØRFLS".

For the compound investigated, all interatomic bond lengths (excluding hydrogen atoms) and their standard errors were calculated. These are tabulated. [Table 8, page 49.]

In addition to bonded-distances, several relevant non-bonded separations were computed, the latter distances involving the bipyramidal atomic arrangement about the Vanadium atom.

All interatomic bond angles, including those about the Vanadium atom were computed. The bond angles in each separate ring of the molecule are also grouped together. These are tabulated. [Table 9, page 50.] Bond lengths and bond angles are drawn in figs. (xiv) page 55, and (xv) page 60 respectively.

TABLE 7

FINAL ATOMIC FRACTIONAL COORDINATES AND THERMAL PARAMETERS

(STANDARD DEVIATION is shown below each parameter; $B_{ij} \equiv 10^5 \beta_{ij}$ where β_{ij} = anisotropic temp. factor.)

ATOM	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Bisotropic
V	.11140	.06095	.08594	148	1309	191	- 95	- 56	182	3.15
	11	49	13	4	75	5	18	4	20	
O1	.12463	.22523	.11748	208	1070	310	-144	-128	37	4.18
	47	191	54	23	323	32	67	22	78	
O2	.08414	-.16338	.05328	179	1551	175	91	- 51	- 28	3.54
	44	188	51	20	307	24	66	18	69	
O3	.10287	-.06549	.16580	145	1238	167	- 88	- 60	107	3.00
	40	186	45	18	312	22	68	17	72	
O4	.11163	.14046	-.00015	175	1404	243	-174	-.60	357	3.92
	46	180	52	21	323	29	64	20	74	
O5	.19074	-.01797	.04443	169	1539	269	28	- 73	88	3.99
	46	186	53	21	348	30	64	21	75	
N	.01897	.11235	.11769	119	647	148	22	- 61	46	2.18
	47	189	54	21	370	27	62	20	68	
C1	.06848	-.28817	.08415	(164	1317	206	0	58	0)*	3.49
	69	291	80	-	-	-	-	-	-	
C2	.07272	-.32084	.14677	229	394	376	135	- 62	- 68	4.77
	78	322	91	38	498	56	109	38	128	
C3	.08684	-.21168	.18511	82	322	228	15	6	85	2.62
	62	274	71	25	500	41	77	26	100	
C4	.04966	-.43717	.04727	442	3496	688	- 93	-263	-736	9.20
	116	479	131	66	823	102	215	68	252	
C5	.08789	-.26250	.25221	247	2525	235	-139	- 91	520	4.95
	79	324	91	41	625	46	127	35	133	
C6	.15451	.18504	-.04742	198	871	214	-191	- 43	206	3.74
	71	286	81	34	479	40	102	31	108	
C7	.21069	.12896	-.05689	260	1877	251	180	- 24	63	5.35
	86	319	96	42	627	48	122	37	128	
C8	.22495	.03826	-.01108	338	1694	303	-209	- 64	263	5.75
	87	361	102	52	592	54	146	43	149	
C9	.14251	.26829	-.10203	318	2834	178	4	- 68	341	5.41
	82	342	93	48	667	43	143	37	131	
C10	.28842	-.04053	-.02782	153	2441	613	93	- 7	274	7.05
	98	409	112	36	680	81	135	144	198	
C11	-.01320	.10630	.07916	221	2819	277	129	-130	-581	4.39
	77	299	85	36	691	47	120	35	139	
C12	-.07187	.15306	.09722	140	2522	317	257	- 78	-562	4.03
	74	298	83	30	596	50	109	32	138	
C13	-.09640	.21822	.15607	(101	816	128	0	- 36	0)*	2.16
	57	238	66	-	-	-	-	-	-	
C14	-.06695	.21563	.20114	201	5847	329	723	-116	-457	5.95
	92	364	101	39	997	58	162	39	186	
C15	-.00790	.16999	.17739	269	5510	263	623	-145	-661	5.70
	89	350	98	44	951	52	168	40	175	
C16	-.15739	.28398	.17607	113	939	220	-107	- 68	231	2.59
	61	250	68	27	463	40	84	27	99	
C17	-.18825	.27640	.13172	176	653	299	- 73	- 96	137	3.67
	70	285	80	33	472	46	93	33	110	
C18	-.24312	.34996	.14869	165	1920	310	117	- 83	15	4.09
	73	300	82	34	569	52	109	35	133	
C19	-.26670	.42943	.20881	201	1740	434	-208	-110	164	5.25
	81	344	91	36	583	64	130	40	164	
C20	-.23499	.43578	.25266	158	1787	385	137	- 17	144	4.95
	76	340	91	35	563	56	120	36	152	
C21	-.18076	.35582	.23660	159	884	232	- 97	- 20	-106	3.44
	69	277	77	30	459	42	93	29	105	

* Signifies that these parameters were not refined.

TABLE 8

INTERATOMIC BOND LENGTHS, (Å)

STANDARD ERRORS $x10^2$ ARE GIVEN IN PARENTHESES

(Chemically equivalent bonds are grouped together)

BONDED-SEPARATIONS		NON-BONDED SEPARATIONS	
BOND	LENGTH (Å)	ATOMS	LENGTH (Å)
V-O1	1.58 (1)		
		O1-O4	2.76 (2)
V-O2	2.14 (1)	O4-O2	2.72 (2)
V-O3	1.97 (1)	O2-O3	2.74 (1)
V-O4	1.97 (1)	O3-O1	2.57 (2)
V-O5	1.96 (1)		
O2-C1	1.21 (2)	O1-O5	2.71 (2)
O3-C3	1.28 (2)	O4-O5	2.74 (2)
O4-C6	1.26 (2)	O2-O5	2.80 (2)
O5-C8	1.31 (2)	O3-O5	2.82 (2)
C1-C2	1.42 (2)		
C2-C3	1.33 (3)	O1-N	2.72 (2)
C6-C7	1.39 (2)	O4-N	2.80 (2)
C7-C8	1.37 (3)	O2-N	2.84 (2)
		O3-N	2.96 (2)
C1-C4	1.60 (4)		
C3-C5	1.52 (2)		
C6-C9	1.47 (3)		
C8-C10	1.60 (3)		
V-N	2.17 (1)		
N-C11	1.31 (2)		
N-C15	1.33 (2)		
C11-C12	1.40 (2)		
C12-C13	1.33 (2)		
C13-C14	1.38 (2)		
C14-C15	1.41 (3)		
C13-C16	1.50 (2)		
C16-C17	1.40 (2)		
C17-C18	1.40 (2)		
C18-C19	1.40 (3)		
C19-C20	1.40 (2)		
C20-C21	1.41 (2)		
C16-C21	1.38 (2)		

TABLE 9

INTERATOMIC BOND ANGLES, θ, IN DEGREES AND THEIR STANDARD ERRORS

ANGLE	θ	ANGLE	θ
O1-V-O2	173.1° (0.5°)	V-N-C11	124.1° (1.1°)
O3-V-O4	166.2 (0.6)	V-N-C15	120.3 (1.1)
O1-V-O3	92.3 (0.6)	C15-N-C11	115.2 (1.5)
O1-V-O4	101.1 (0.6)	N-C11-C12	125.0 (1.7)
O4-V-O2	82.7 (0.5)	C11-C12-C13	118.1 (1.6)
O2-V-O3	83.7 (0.5)	C12-C13-C14	119.8 (1.6)
		C13-C14-C15	116.5 (1.8)
O1-V-O5	99.6 (0.6)	C14-C15-N	124.5 (1.8)
O4-V-O5	88.7 (0.5)	C12-C13-C16	120.6 (1.4)
O2-V-O5	86.1 (0.5)	C14-C13-C16	119.4 (1.5)
O3-V-O5	92.0 (0.5)		
		C13-C16-C17	119.1 (1.4)
O1-V-N	92.1 (0.6)	C13-C16-C21	119.1 (1.3)
O4-V-N	85.2 (0.5)	C21-C16-C17	121.7 (1.5)
O2-V-N	82.4 (0.5)	C16-C17-C18	118.7 (1.6)
O3-V-N	91.4 (0.5)	C17-C18-C19	120.5 (1.6)
		C18-C19-C20	119.9 (1.9)
V-O2-C1	127.6 (1.2)	C19-C20-C21	119.5 (1.9)
O2-C1-C2	125.4 (1.9)	C20-C21-C16	119.4 (1.5)
C1-C2-C3	125.7 (2.2)		
C2-C3-O3	121.9 (1.6)		
C3-O3-V	135.1 (1.0)		
O2-C1-C4	116.8 (1.8)		
C4-C1-C2	117.3 (2.2)		
C2-C3-C5	120.1 (2.1)		
C5-C3-O3	117.8 (1.6)		
V-O4-C6	127.7 (1.1)		
O4-C6-C7	122.6 (1.9)		
C6-C7-C8	122.7 (1.9)		
C7-C8-O5	128.5 (1.9)		
C8-O5-V	123.0 (1.4)		
O4-C6-C9	117.4 (1.5)		
C9-C6-C7	118.5 (1.6)		
C7-C8-C10	120.5 (1.9)		
C10-C8-O5	110.1 (2.0)		

The computer programme "L S PLANE" (i.e. Least-squares plane) was used to determine the best planes through certain sets of atoms. If any two planes have the equations[46]

$$\ell_1 X + m_1 Y + n_1 Z - p_1 = 0 \text{ and } \ell_1^2 + m_1^2 + n_1^2 = 1$$

and $\ell_2 X + m_2 Y + n_2 Z - p_2 = 0$ and $\ell_2^2 + m_2^2 + n_2^2 = 1$

then the angle θ between these planes has the value

$$\theta = \text{Arc cos } (\ell_1\ell_2 + m_1m_2 + n_1n_2) \quad \ldots\ldots\ldots \quad (8.6.1)$$

The programme output listed the parameters ℓ, m and n for any one plane specified and hence interplanar angles, θ, could be calculated using equation (8.6.1). These angles are dealt with in the discussion.

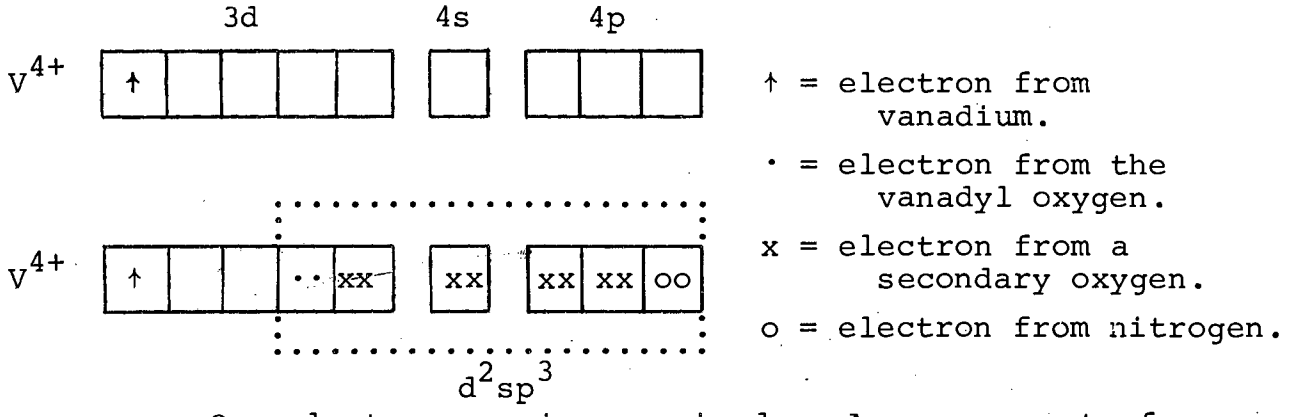
[46] *International Tables for X-Ray Crystallography* Vol. II p.43 (1952).

9. DISCUSSION

9.1 BONDING IN THE ADDUCT; OCTAHEDRAL SYMMETRY

The Vanadium atom (Z=23) has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ in the ground state. In the Vanadyl ion, VO^{2+}, the species present is V^{4+} which has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$. The environment about the vanadium in the adduct studied is octahedral and this can be explained by invoking d^2sp^3 hybridisation of the 3d, 4s and 4p orbitals of vanadium. The six hybrid orbitals so formed are octahedrally oriented and each may accommodate a pair of electrons. These hybrid orbitals are filled by electrons donated by the ligands.

Diagramatically, this may be represented as follows:



One electron remains unpaired. A measurement of the magnetic susceptibility of the adduct showed it to be paramagnetic as predicted.

The above analysis does not take into account π-bonding which is known[47] to occur in the vanadyl system. This π-bonding occurs by overlap of a doubly-filled p-orbital on the sp^2-hybridised O^{2-} ion and an unfilled t_{2g} orbital of vanadium. This $p\pi \rightarrow d\pi$ donation of electrons is therefore superimposed on the V-O σ-bond. The resulting increased bond strength is manifested in the relatively short V=O bond (e.g. 1.56 ± 0.01 Å

[47] Selbin, Holmes and McGlynn *J. Inorg. Nucl. Chem.* 25 1359 (1963)

in $VO(ACA)_2$ compared with the mean secondary V-O bond length of 1.97 ± 0.005 Å). In the adduct whose structure was investigated in this work, the V=O bond length was found to be 1.58 ± 0.01 Å while the V-O secondary bond lengths have a mean value of 1.97 ± 0.01 Å; these results support the hypothesis of the electron-rich Vanadyl bond.

Considering the vanadyl ion VO^{2+}, in which the Vanadium has a formal valence of 4 and regarding the adduct molecule as being purely ionic, then the effective scattering power of the Vanadium is 19 electrons. If the bonding is regarded as being purely covalent, then the species V^{o} (Z=23) would be considered. In reality, the bonding in the adduct is at neither extreme. A reasonable compromise is to assign 21 electrons to Vanadium, effectively regarding the scattering species as V^{2+} (Z=21). In the X-ray crystal structure analysis[3] of $VO(ACA)_2$, scattering factors for V^{2+} were also employed.

The 4-phenylpyridine ligand is strongly coordinating and hence electron donation from the nitrogen atom to vanadium is expected in the adduct $[VO(ACA)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N]$ whose structure was elucidated in the present work. Because of the possibility of π-bonding between the nitrogen atom and vanadium by back-donation of electrons from vanadium to the nitrogen atom, the extent of the N → V electron donation is effectively reduced. The extent of the back-donation process is impossible to estimate quantitatively. In this analysis, therefore, the effect on the scattering power of Vanadium (II) by electron donation from the ligand was neglected and scattering factors for V^{2+} (Z=21) were used. (These were corrected for anomalous dispersion; see section 8.1.)

[3] Dodge, Templeton and Zalkin
J. Chem. Phys. 35 (1961) 55.

9.2 THE CRYSTAL STRUCTURE OF THE ADDUCT

The analysis undertaken has shown that there are eight discrete molecules of the adduct [$VO(ACA)_2$·4-phenylpyridine] in the monoclinic crystal unit cell. Each molecule has the *cis* - configuration (as predicted by Haigh[6]) and is therefore asymmetric. The essential condition for optical isomerism[48] in coordination compounds is the same as for organic molecules; viz. that the structure be non-superimposable on its mirror image. Because the space group to which the crystal belongs (viz. C2/c) is centrosymmetric, it is necessary that four of the molecules in the cell be "left-handed" enantiomorphs while the other four molecules be "right-handed" enantiomorphs. The symmetry elements in a centrosymmetric space group require the presence of both left and right-handed asymmetric species in the crystal. This condition cannot be fulfilled by a single enantiomorph. The molecular model drawn in fig. (xi) and its non-superimposable mirror image represent the two enantiomorphs present in the crystal. Details of the intramolecular and intermolecular structures are discussed below.

9.2(a) Intramolecular Structure
Vanadium to Oxygen and Vanadium to Nitrogen Bond Lengths

Table 8 lists bond distances and non-bonded separations and Table 9 lists interatomic bond angles. The bond distances are drawn in Fig. (xiv), page 55 and the bond angles in Fig. (xv), page 60.

Probably the most significant bond lengths in the molecule are those of the vanadyl bond V=O (V-O1) and the

[48] Dwyer and Mellor *Chelating Agents and Metal Chelates* Ch. 5 (Academic Press Inc. New York 1964).

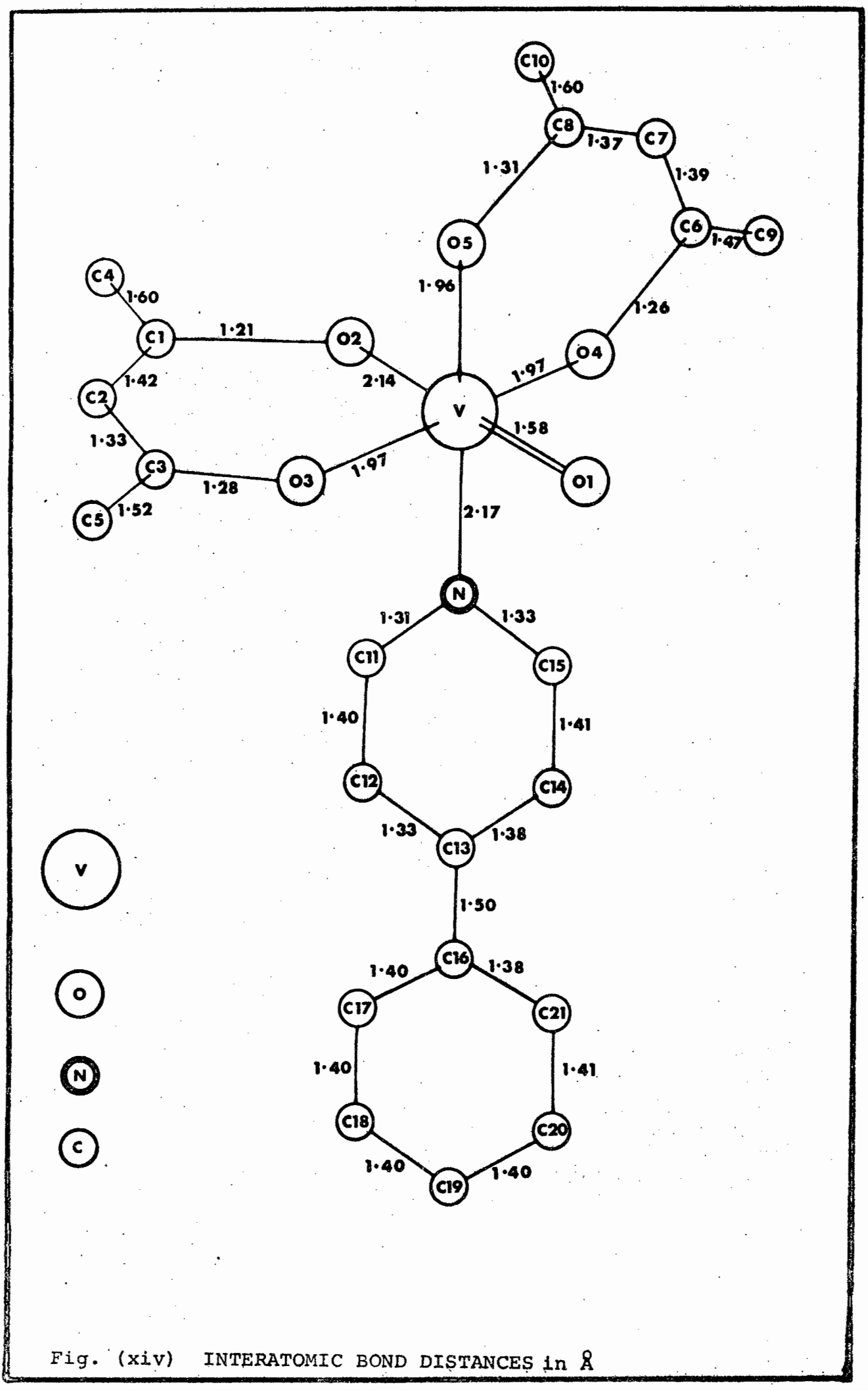


Fig. (xiv) INTERATOMIC BOND DISTANCES in Å

Vanadium to nitrogen (V-N) bond. In the adduct studied, the value of the V=O distance was found to be 1.58 ± 0.01 Å.

This estimate is in good agreement with known vanadyl bond lengths. In the complex $VO(ACA)_2$, the V=O distance was initially[3] found to be 1.56 ± 0.01 Å. Here, the vanadium atom has a coordination number of five. In vanadylbisbenzoylacetonate [fig. (vi), page 8], $VO(BZA)_2$, the vanadyl bond length was initially[9] determined to be 1.61 ± 0.01 Å. Further refinement of the two latter structures have since been undertaken[49] to establish whether the difference in these bond lengths was significant or not. Final estimates were 1.57 ± 0.01 Å for V=O in $VO(ACA)_2$ and 1.61 ± 0.01 Å for V=O in $VO(BZA)_2$.

These values of the primary vanadyl linkage differ by three to four standard deviations and this difference was thought[49] to be significant. The interpretation of this result was that bonding in the vanadyl ion is not extremely sensitive to bond length. Recently[10], a nuclear magnetic resonance and X-ray crystal structure study of the 2:1 $VO(ACA)_2$: 1,4-dioxan complex was undertaken. In this adduct, $[VO(ACA)_2]_2$ (dioxan), a dioxan molecule bridges two $VO(ACA)_2$ groups by coordination to the sixth unoccupied site of the vanadium atom. In any one of the $VO(ACA)_2$ groups, the acetylacetonate rings are *trans*- to one another as in $VO(ACA)_2$ itself and as in $VO(BZA)_2$. The V=O bond length was reported as 1.62 Å (no error quoted).

[9] Hon, Belford and Pfluger *J. Chem. Phys.* 43 (1965) 1323.

[10] Dickmann, Hamer, Nyburg & Reynolds *Chem. Comm.* (1970) 1295.

[49] Hon, Belford and Pfluger *J. Chem. Phys.* 43 No. 9 3111 (1965).

The value of the V-N bond distance was found to be 2.17 ± 0.01 Å in the adduct studied. This compares favourably with a value[50] of 2.10 ± 0.03 Å for the V-N distance in the complex V(2,2'-bipyridyl)$_3$, in which Vanadium is in the zero-valent state. This interatomic distance of 2.17 ± 0.01 Å is, in fact, the longest bond length in the molecule. (See Table 8, page 49.)

The V-O secondary bonds are of interest. In VO(ACA)$_2$, these four bonds have the lengths 1.97, 1.96, 1.98, 1.96 Å (average error = ± 0.008 Å) while in VO(BZA)$_2$, these bond lengths are 1.95, 1.95, 1.97, and 1.97 Å (average error = ± 0.007 Å). For the dioxan adduct, a value of 1.99 Å is quoted for these lengths. This is presumably an average of the four V-O bond lengths.

In the analysis reported here, the values obtained for the secondary V-O distances were 1.97, 1.97, 1.96 and 2.14 Å (σ = ± 0.01 Å in each case). Here, however, the stereochemical arrangement of these oxygen atoms about the vanadyl entity, VO^{2+}, is somewhat different to the arrangements found in the other known complexes. In the latter structures, the four secondary V-O bonds lie in a plane, with the vanadyl V=O bond lying perpendicular to this plane.

In the 4-phenylpyridine adduct reported here, three of the V-O bonds (viz. V-O3, V-O4 and V-O5) and the V-N bond lie perpendicular to the vanadyl V=O (V-O1) bond, while the fourth V-O bond (V-O2) is collinear with the V=O bond. The character of the V-O2 bond would therefore be expected to be somewhat different from those of the bonds V-O3, V-O4 and V-O5. This was indeed found to be so, the V-O2 bond distance of 2.14 ± 0.01 Å

[50] W.R. McWhinnie and J.D. Miller *Advances in Inorganic Chemistry and Radiochemistry* p. 135 (1969).

being greater than the mean (1.97 Å) of the other three V-O bond distances by several standard deviations. This difference can be attributed to the multiple bonding in the V=O bond, which is strong, resulting in a relative weakening and hence lengthening of the collinear , but oppositely directed V-O2 bond.

The appearance of extra infrared peaks (detected by Haigh[6]) in the region of the secondary V-O absorption bands in the far infrared spectrum of this adduct suggested asymmetry of the V-O bonds. The relatively long V-O2 bond would have a smaller force constant compared with the bonds V-O3, V-O4 and V-O5 (which have about equal length), and hence the stretching frequency ν for the bond V-O2 should appear at a lower value than νV-O for the other three secondary bonds.

As discussed in the Introduction, a peak at a lower frequency was observed and this can presumably be attributed to the anomalously long V-O2 distance which was found in the solution of the present structure.

Bond Distances and Bond Angles in the Acetylacetonate Rings

The average value of the four C-O distances in the acetylacetonate rings in the 4-phenylpyridine adduct is 1.27 ± 0.02 Å, in good agreement with the average value of 1.29 ± 0.003 Å for the equivalent bond lengths in the $VO(ACA)_2$ molecule and with the average value of 1.29 ± 0.007 Å for these distances in $VO(BZA)_2$.

Carbon-carbon distances in the acetylacetonate rings have a mean value of 1.38 ± 0.02 A in the adduct studied, while these distances have a mean value of 1.40 ± 0.01 Å in both $VO(ACA)_2$ and $VO(BZA)_2$.

For the methyl substituents, the mean length of the four C-C bonds, C1-C4, C3-C5, C6-C9 and C8-C10, is 1.55 ± 0.03 Å conforming with the well established C-C single bond distance of 1.54 Å. In $VO(ACA)_2$, these bond lengths have a mean value of 1.518 ± 0.001 Å.

The following table (Table 10) lists the mean values of comparable O-C-C and C-C-C bond angles in the acetylacetonate rings in the molecules $VO(ACA)_2 \cdot 4$-phenylpyridine, $VO(ACA)_2$ and $VO(BZA)_2$.

TABLE 10

$VO(ACA)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N$		$VO(ACA)_2$	$VO(BZA)_2$
Angles	Mean Value Max.error = ±2°	Comparable Bond Angles, Max. error = ±1°	Comparable Bond Angles, Max. error = ±1°
O2-C1-C2, O3-C3-C2, O4-C6-C7, O5-C8-C7.	124.6	124.0	124.3
O2-C1-C4, O3-C3-C5, O4-C6-C9, O5-C8-C10.	115.5	115.9	114.3
C4-C1-C2, C5-C3-C2, C10-C8-C7, C9-C6-C7.	119.1	120.4	121.4
C1-C2-C3, C6-C7-C8.	124.2	123.9	122.8

Good agreement is found in all three cases. It is unrealistic to compare the V-O-C bond angles in the three molecules, since these angles depend on the degree of planarity of the

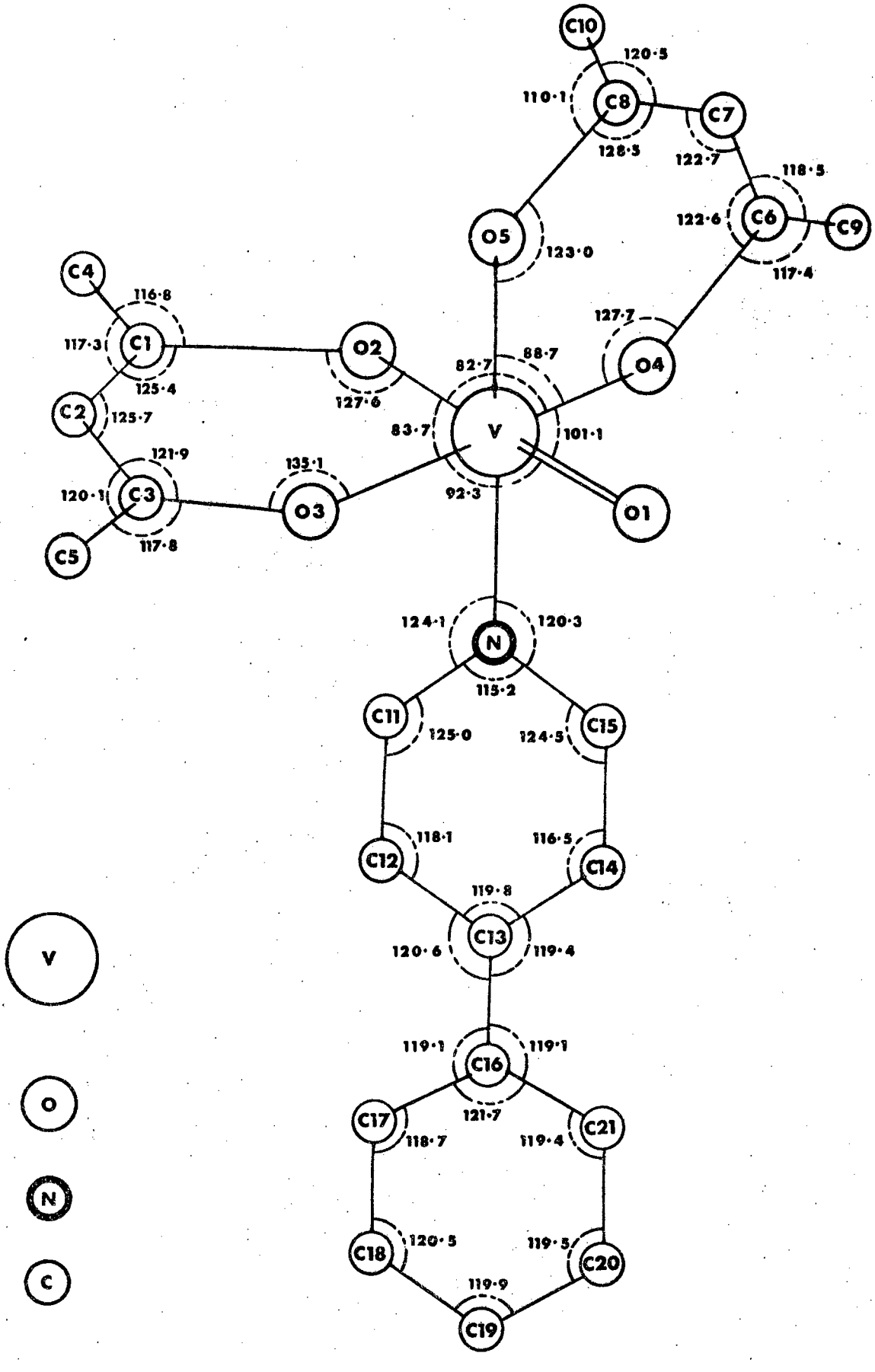


Fig. (xv) INTERATOMIC BOND ANGLES in degrees

chelate ring containing the Vanadium atom, which in turn depends on the stereochemistry of the V to O bonds. (This is dealt with later.) It is interesting however, to note that, in the present structural investigation, the angles V-O2-C1, C3-O3-V, V-O5-C8 and V-O4-C6 were found to have the respective values 127.6°, 135.1°, 123.0° and 127.7° (Max. error = ±2°), the angle C3-O3-V being larger than the mean of the other three by approximately 9° (see fig. (xv)), which is significant. This can be explained if one remembers that the V-O2 bond is anomalously long; this lengthening distorts the chelate ring containing the atoms V, O2, C1, C2, C3 and O3, causing the angle C3-O3-V to be larger than the angle V-O2-C1. The magnitude of the angle C3-O3-V should strictly be compared with that of angle V-O2-C1 only; this is so since the angle of intersection of the planes containing atoms V, O2, O3 and C1, C2, C3, C4, C5, O2 and O3 is different from the angle of intersection of the planes containing atoms V, O4, O5 and C6, C7, C8, C9, C10, O4 and O5. (This is dealt with below.)

The Structure of the Phenylpyridine Substituent

The bond lengths and angles discussed above are essentially those for the system $[VO(ACA)_2]$ in the adduct $[VO(ACA)_2 \cdot 4\text{-}C_6H_5\text{-}C_5H_4N]$. The structure of the 4-phenylpyridine ligand in the adduct is also of interest. (See figs (xiv) and (xv)). The carbon-nitrogen distances (C11-N and C15-N) of 1.31 ± 0.02 Å and 1.33 ± 0.02 Å respectively are in very good agreement with the C to N distance of 1.34 Å in pyridine itself. The latter[51] estimate was obtained from calculations based on the microwave spectrum of pyridine. Generally,

[51] M.H. Palmer *The Structure and Reactions of Heterocyclic Compounds* p.12 (Edward Arnold, London, 1967)

the shortened C to N partial double bond in heterocyclic systems has a length[52] of 1.352 ± 0.005 Å. In the adduct analysed, the average of the carbon-carbon distances in the pyridine ring is 1.38 ± 0.05 Å, the distances C11-C12 and C14-C15 being slightly longer than the distances C12-C13 and C13-C14. In pyridine itself, these two sets of lengths have average values of 1.39 Å and 1.40 Å respectively. The pyridine ring is known[51] to be a rather distorted hexagon and this is confirmed by the present analysis. The deviation of the bond angle C11-N-C15 (115 ± 1.5°) from the usual 120° bears this out. Connecting the phenyl and pyridine rings, the bond C13-C16 has a length of 1.50 ± 0.02 Å, which is shorter than the single C-C bond length of 1.54 Å. For a C-C single bond which is shortened in the presence of a C to C double bond (e.g. in C_6H_5-CH_3), the length of the single bond[52] is 1.53 ± 0.01 Å. The estimate of 1.50 ± 0.02 Å for the bond length C13-C16 is reasonable, in that it is slightly less than the C to C distance in C_6H_5-CH_3 since the former distance is effectively shortened by the presence of two double bonds, one from each six-membered ring.

In the phenyl nucleus itself, the average C to C bond distance is 1.40 ± 0.005 Å in this adduct, in accord with carbon-carbon bond distances in aromatic compounds (1.395 ± 0.003 Å). Individual agreement is also very good, as may be seen from Table 8 (page 49).

For the C-C-C bond angles in the phenyl nucleus, the mean value is 120.0 ± 0.5° as expected.

[52] *International Tables for X-Ray Crystallography* Vol. III p.276 (1962)

The sum of the interatomic angles about C13 is 359.8° demonstrating the trigonal coplanarity of the bonds to C13. This is also true for atom C16, for which the sum of the equivalent angles is 359.9°.

PLANARITY OF THE STRUCTURE

Normal Distances from Least-squares Planes

As mentioned in chapter 8, least-squares planes were computed for various sets of atoms. In addition, the perpendicular distances of the atoms from the best planes were calculated. The results are shown in Table 11, page 64. The equation used in this calculation is[53]

$$D = \ell X_1 + mY_1 + nZ_1 - p \quad \ldots\ldots\ldots \quad (9.1)$$

where D is the normal distance of the point whose orthogonalized coordinates are X_1, Y_1, Z_1, from the plane whose parameters are ℓ, m, n and p.

Planes 1 and 2 together contain the first chelate ring, including the Vanadium atom while planes 3 and 4 contain the second chelate ring including the Vanadium atom. The ligand atoms equatorially disposed to the vanadyl bond V=O, viz. O3, O5, O4 and N, lie in plane 5. The pyridine and benzene rings are represented by planes 6 and 7 respectively. Inspection of Table 11 shows that the normal distances of the atoms from the planes selected are of the order of 0.01 to 0.1 Å.

The maximum deviation of the carbon atoms C16-C21 from plane 7 is 0.03 Å, so that the phenyl substituent may be regarded as planar, within the limits of error. In the case of plane 6, the maximum deviation from the plane is 0.05 Å, so that,

[53] *International Tables for X-Ray Crystallography* Vol. II p.43 (1952)

TABLE 11

Plane Number	Atoms involved in the Calculation of the best plane	D, the Perpendicular distance of the atom from the plane (Å)	Plane Number	Atoms involved in the Calculation of the best plane	D, the Perpendicular distance of the atom from the plane (Å)
1	V O2 O3	0.00 0.00 0.00	5	O4 O5 O3 N	-0.02 0.02 -0.01 0.01
2	O2 C1 C2 C3 C4 C5 O3	0.03 -0.04 0.02 -0.02 0.00 0.01 -0.01	6	N C11 C12 C13 C14 C15	0.01 0.00 -0.03 0.05 -0.05 0.02
3	V O4 O5	0.00 0.00 0.00	7	C16 C17 C18 C19 C20 C21	0.02 0.00 -0.01 0.00 0.02 -0.03
4	O4 C6 C7 C8 C9 C10 O5	-0.08 0.08 0.07 0.08 -0.06 -0.10 0.01	(D is positive if the atom is on the side of the plane opposite to that containing the origin.)		

within the limits of error, the pyridine ring may also be regarded as planar.

Angles between Planes

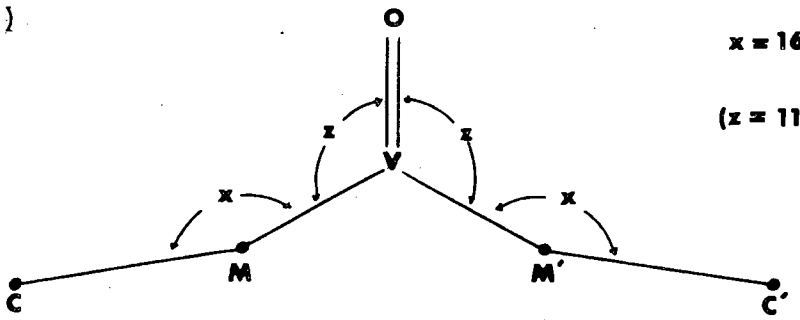
The calculation of interplanar angles is discussed in section 8.6.

The angle between the two planes constituting any one acetylacetonate ring is known[3,9,10] to vary with the nature of the coordination about the central vanadium atom. These differences in geometry can be understood by reference to fig. (xvi), in which M,M' are the midpoints between the dionato-oxygen atoms and C,C' the central carbon atoms of the dionato ligand.

The situation in $VO(ACA)_2$ and $VO(BZA)_2$ is shown in (i); (ii) shows the angles in $[VO(ACA)_2]_2$ (dioxan) and (iii), the situation in the adduct studied.

In (i) and (ii), the *trans*- arrangement of the chelate rings (symmetrical about V) results in the angle x being the same for both chelate rings. However, a *cis*- arrangement (iii) as found in the adduct studied, yields two angles x and y which are different by virtue of the asymmetry in the adduct. In the latter case, x and y are 179.0^0 and 161.5^0 respectively. The value of 179.0^0 for x implies that the chelate ring containing the six atoms V, O2, C1, C2, C3 and O3, is virtually planar. The 'flattening out' of this ring can be attributed to the presence of the bulky phenyl-pyridine ligand, whose approach in coordination with Vanadium, is at right angles to this ring. The second chelate ring

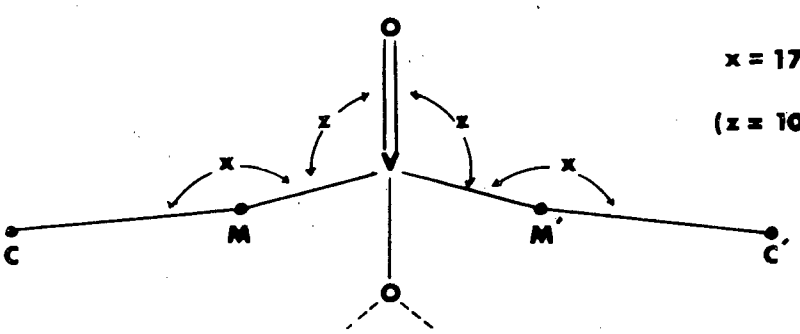
Fig. (xvi)



x = 169°

(z = 112°)

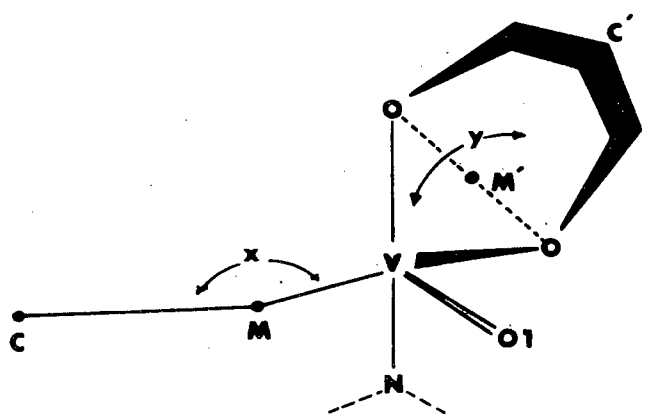
(i)



x = 179·5°

(z = 107·5°)

(ii)



x = 179·0°

y = 161·5°

(iii)

would not be expected to be affected in the same way, since it is further removed from the pyridine ligand. Hence the angle y (161.5^0) is considerably less than 179.0^0.

The pyridine ring and its phenyl substituent are almost coplanar, the calculated angle between these planes being 9.3^0. However, in addition to simple twisting about the bond C13-C16, there is a small amount of bending which accounts for the angle between the rings. This angle is therefore composite.

It is interesting to note that the angle between the plane containing atoms O3, O4, O5 and N and the plane through the pyridine ligand is 38.5^0; a three-dimensional model of the molecule shows this ligand orientation to be one which yields minimum repulsion between pyridine hydrogen atoms and the oxygen atoms O1, O2, O3 and O4. (See fig. (xvii) in which the dotted line represents the plane of the pyridine ring, approximately at right angles to the plane through O1, O2, O3 and O4. Angles are in degrees.) This feature can also be seen in the (100) projection of the structure. (See section on Intermolecular Structure.)

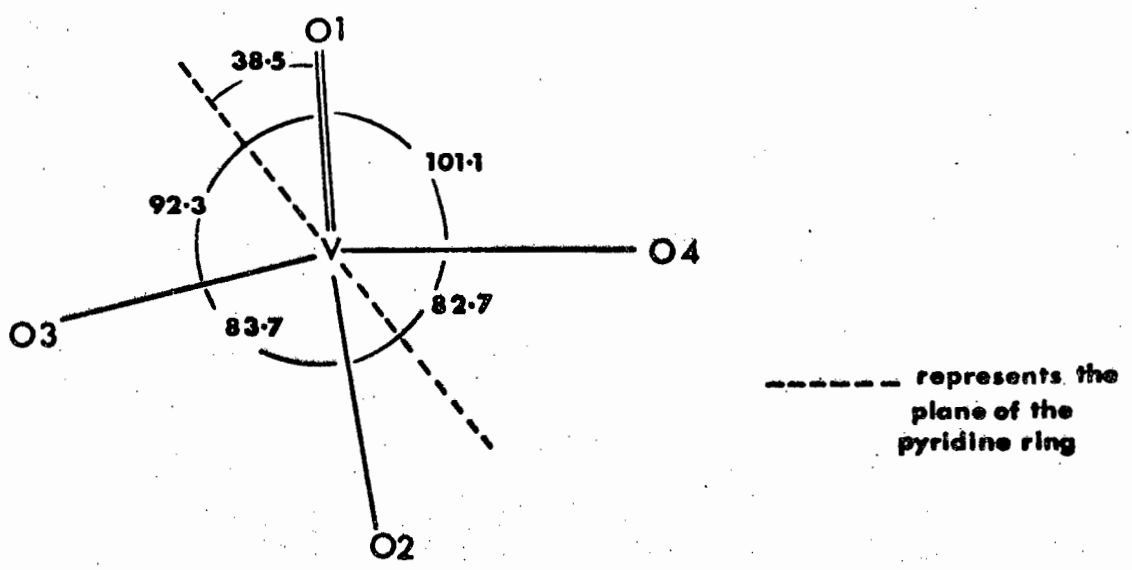


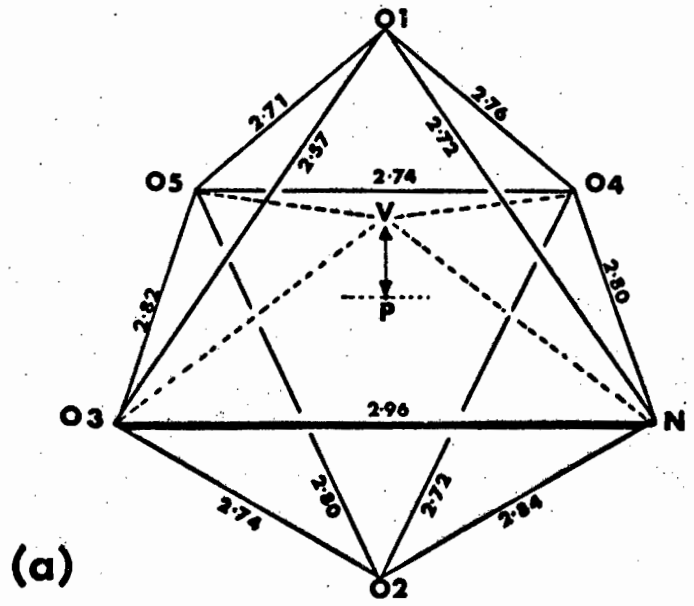
fig. (xvii)

The Environment about the Vanadium Atom

The "oxygen pyramid" referred to in the Introduction is a feature of both molecules $VO(ACA)_2$ and $VO(BZA)_2$, in which Vanadium has a coordination number of five. In the 4-phenylpyridine adduct, this feature is modified to what may be called an "oxygen-nitrogen bipyramid", since the vanadium is now octahedrally coordinated, the sixth ligand atom being nitrogen. The non-bonded distances (in Å) in this bipyramid are drawn in fig. (xviii)(a). These may be compared with the non-bonded distances in the oxygen pyramid in the molecule $VO(BZA)_2$ fig. (xviii)(b).

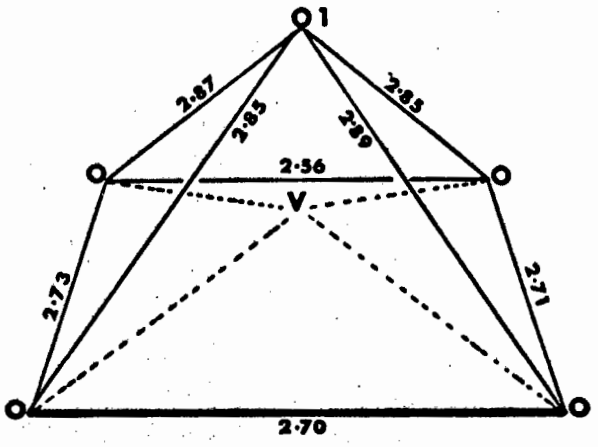
In this analysis, the atoms O3, O5, O4 and N have been shown to lie in a plane (see Table 11). The normal distance V-P of the Vanadium atom from this plane is 0.22 Å (see fig. (xviii)). The interatomic angles (in degrees) in, above and below this plane are drawn in fig. (xix), (a), (b) and (c) respectively. The significance of these results is that the Vanadium atom lies above the plane defined by the atoms O3, O5, O4 and N (see fig. (xviii)). Pure d^2sp^3 hybridisation would require all O-V-O and O-V-N bond angles to be 90^0. It has been found[54] that in vanadyl complexes thusfar investigated the vanadium atom never lies in the same plane as the four equatorial ligands (see e.g. fig. (xvi), angle z and fig. (xviii).) There is a defect therefore, in the theoretical models proposed thusfar concerning the actual geometries of the VO^{2+} complexes.

[54] Selbin, Maus and Johnson
J. Inorg. Nucl. Chem. 29 p.1735 (1967)
and references quoted therein.



VP=0·22 Å

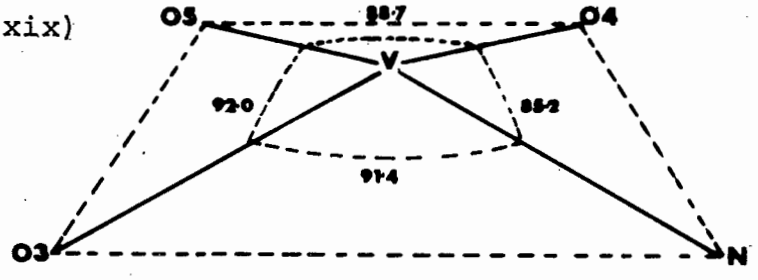
(a)



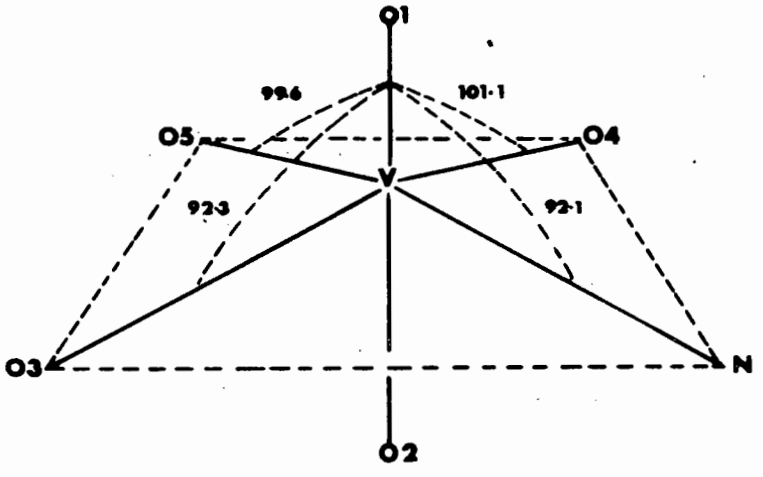
(b)

Fig. (xviii)

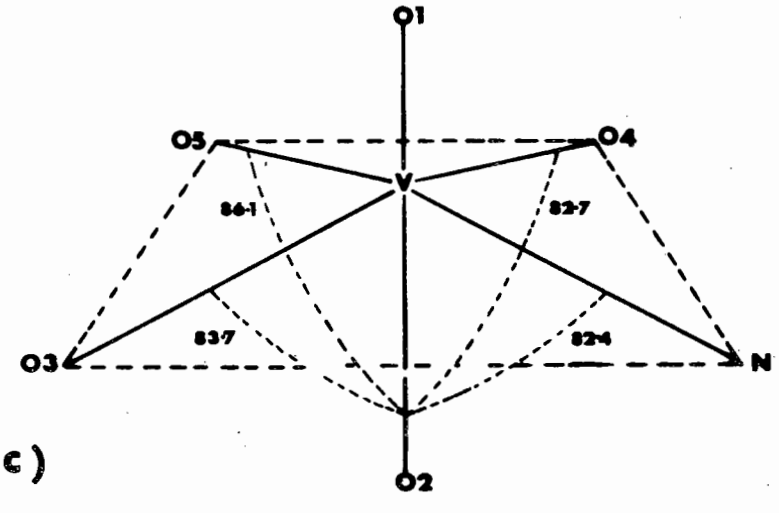
Fig. (xix)


O5
88·7
O4
V
92·0
88·2
91·4
O3
N

(a)


O1
99·6
101·1
O5
O4
V
92·3
92·1
O3
N
O2

(b)


O1
O5
O4
V
86·1
82·7
83·7
82·4
O3
N
O2

(c)

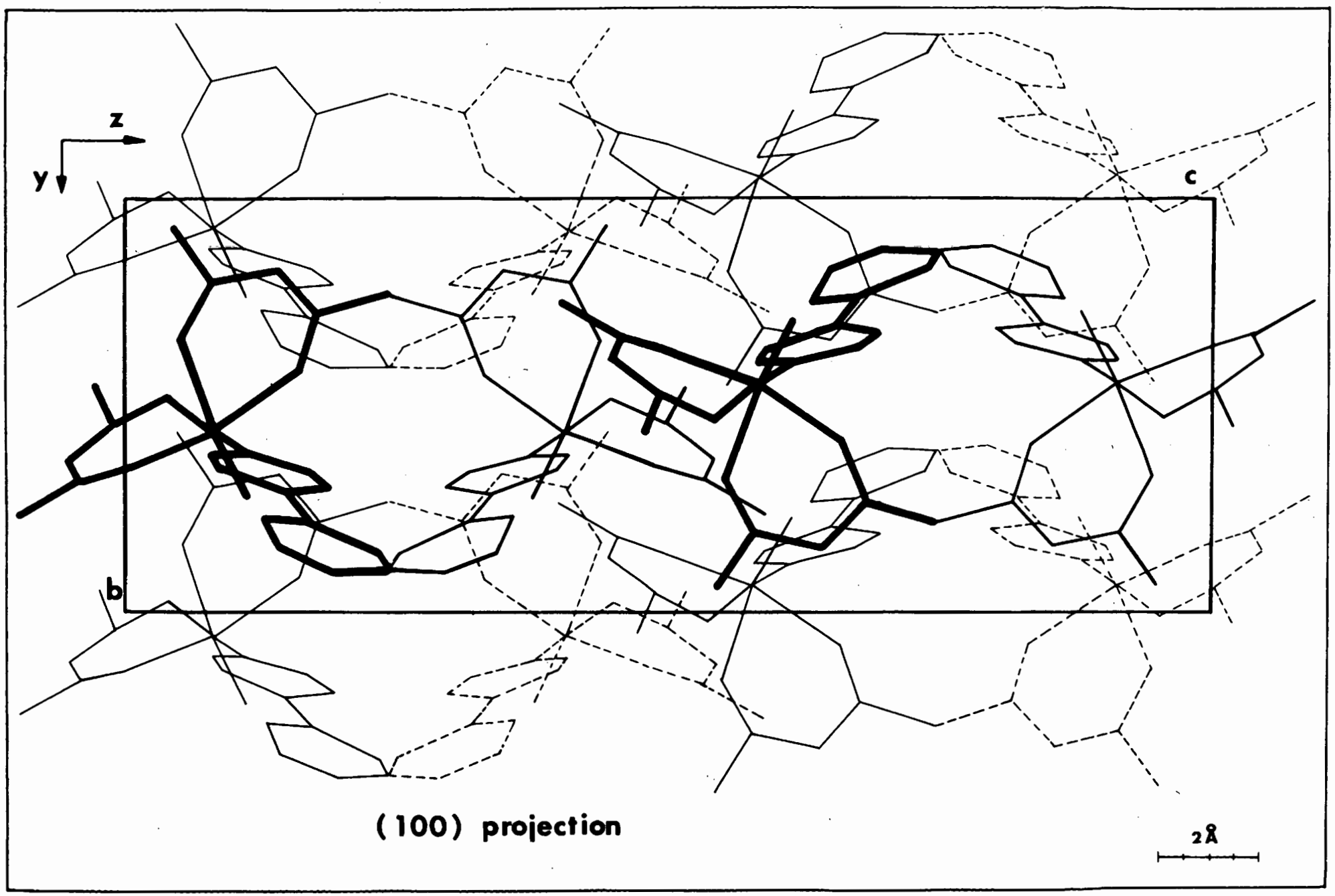
9.2(b) Intermolecular Structure

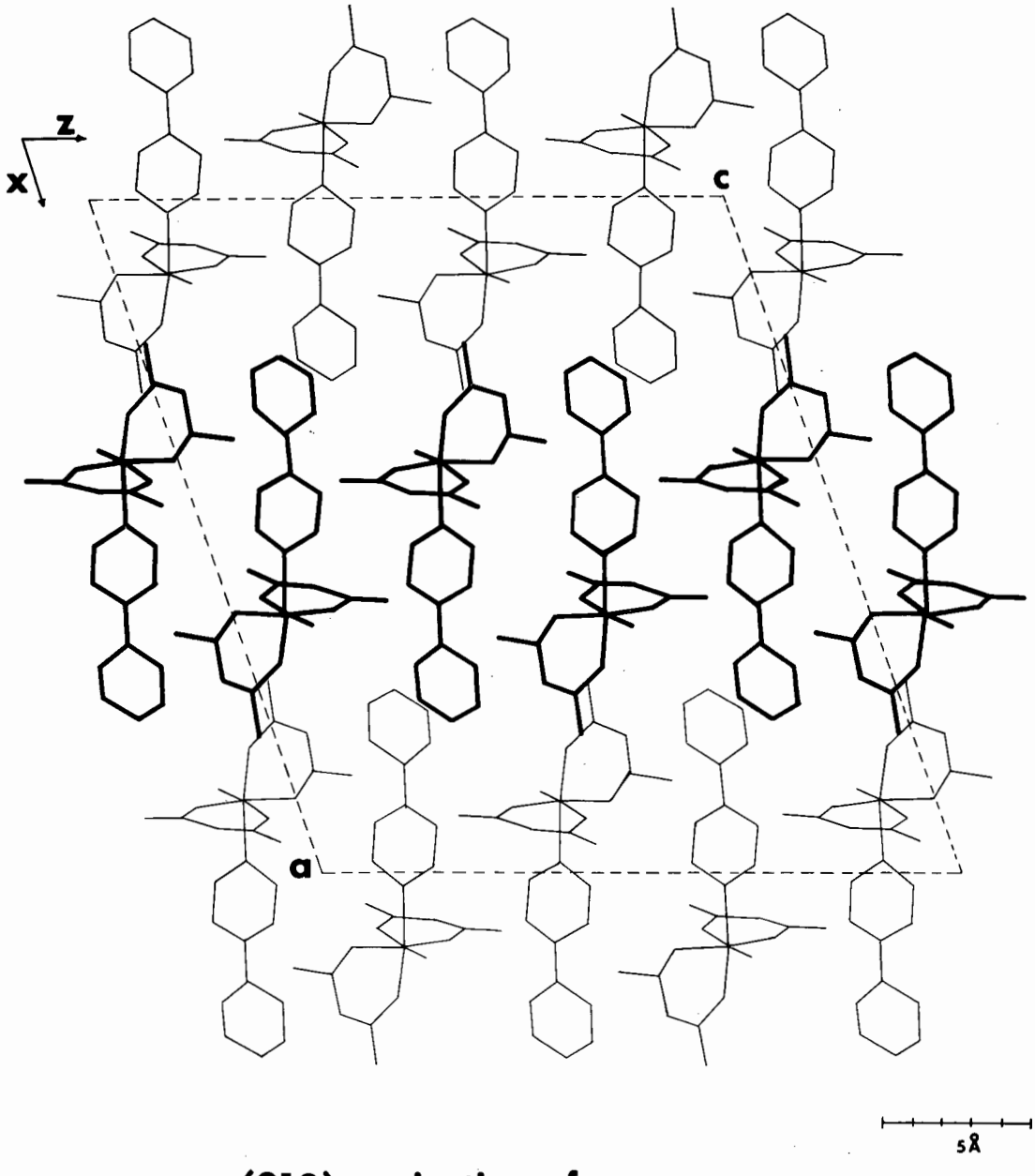
As hydrogen atoms were not placed during the analysis, intermolecular distances were not calculated.

The three figures which follow show the unit cell viewed along the three axes *a*, *b* and c respectively. The (100) projection has the plane-group symmetry *pgm*. In order of increasing elevation, the molecular skeletons are drawn in dashed, thin, heavy and very heavy lines. The same scheme applies to the other projections.

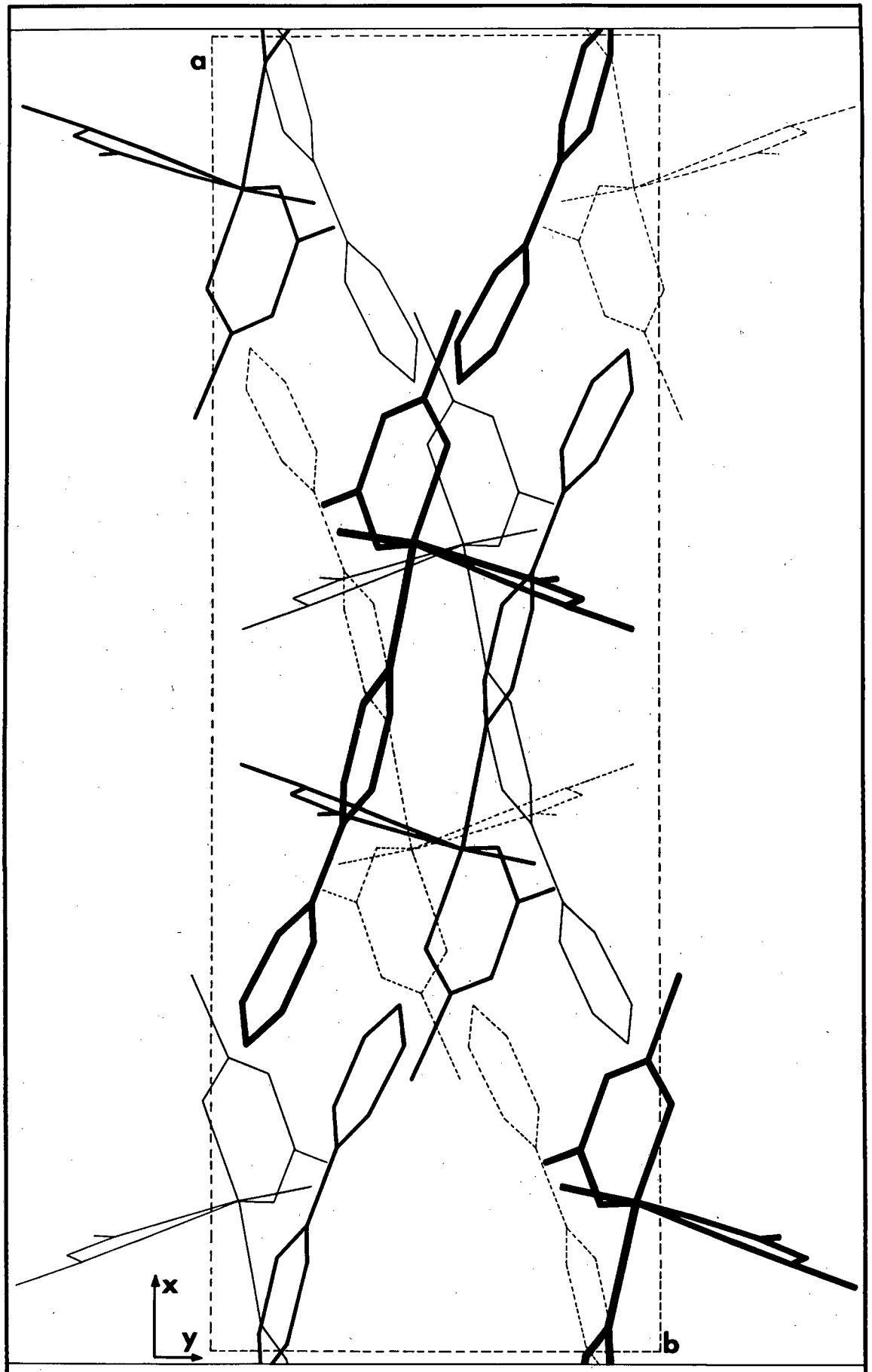
In the (010) projection, which has symmetry *p*2, the structure is viewed down the *b* axis of length 8.14 ± 0.02 Å. The two heavily-lined molecules occupying the centre of the cell are related by a centre of inversion and represent the two enantiomorphs of the adduct. Inspection of a three dimensional model of the structure shows that the only area of close intermolecular contact is that in which a carbon atom of the acetylacetonate ring of one molecule apparently overlaps with a methyl carbon of an adjacent molecule. This apparent overlap can be seen in the (010) projection.

The (001) projection is rectangular and has the plane-group symmetry *cmm*.


z
y
c
b
(100) projection
2Å



(010) projection of structure



(001) projection

APPENDIX

OBSERVED AND CALCULATED STRUCTURE FACTORS

h	ℓ	F_o	F_c	h	ℓ	F_o	F_c	h	ℓ	F_o	F_c
k=0											
0	4	1288	-1338	4	10	180	- 190	12	4	875	- 910
0	6	1288	-1117	4	12	890	- 880	12	8	160	- 152
0	8	641	- 554	4	16	474	588	12	10	243	- 264
0	12	1246	1211	4	18	227	- 206	12	12	743	- 612
0	14	313	- 283	4	22	298	- 300	12	14	637	- 562
0	20	185	247	4	24	423	- 499	12	16	389	373
0	22	326	317	6	0	3195	-2726	12	18	413	370
0	24	270	405	6	2	1737	1673	12	20	301	246
2	- 4	295	- 171	6	6	929	- 847	12	26	275	- 318
2	- 8	1242	-1142	6	8	1177	-1159	14	-14	377	- 503
2	-12	505	644	6	10	1059	-1011	14	-12	477	- 528
2	-14	285	323	6	12	1078	-1037	14	- 8	283	- 286
2	-16	314	286	6	16	741	943	14	- 6	230	213
2	-20	383	- 441	6	18	571	568	14	- 2	524	- 422
2	-22	395	- 378	6	20	751	- 727	14	0	631	- 544
4	- 2	1317	1293	8	-12	605	622	14	2	683	542
4	- 4	1849	1905	8	- 2	1367	-1468	14	4	985	997
4	- 6	317	421	8	0	769	819	14	6	216	194
4	- 8	520	400	8	2	1823	1846	14	8	176	- 214
4	-10	949	-1077	8	4	958	- 805	14	10	587	- 393
4	-12	1379	-1315	8	6	1023	1025	14	12	789	- 776
4	-16	205	272	8	8	271	226	14	16	401	400
4	-18	301	348	8	10	135	106	14	22	330	- 307
4	-22	225	- 276	8	12	1560	1581	14	24	336	- 340
6	- 4	280	- 337	8	14	754	700	16	-10	604	685
6	- 6	718	640	8	16	295	- 306	16	- 6	405	- 421
6	- 8	1159	1188	8	20	750	- 712	16	- 4	683	- 708
6	-10	642	653	8	22	300	- 245	16	- 2	520	- 479
6	-12	804	- 903	8	24	553	548	16	2	864	782
6	-14	790	- 905	10	-14	299	383	16	6	508	- 524
8	- 4	1338	-1270	10	- 6	744	- 718	16	8	670	- 703
8	- 6	966	- 997	10	- 4	360	- 360	16	10	491	- 509
8	- 8	679	685	10	- 2	1774	1603	16	14	1064	1019
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