The 2:1 Vanadyl Acetylacetonate:1,4-Dioxan Complex. A Nuclear Magnetic Resonance and *X*-Ray Crystal Structure Study

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Summary Vanadyl acetylacetonate interacts with 1,4-dioxan in methylene dichloride solution, and a complex [VO(acac)$_2$]$_2$ (dioxan), $C_{24}H_{40}O_{12}V_2$, has been isolated; a dioxan molecule bridges two VO(acac)$_2$ groups by co-ordination to the sixth 'unoccupied' site of the vanadium atom.

THERE have been several studies of the reactions of vanadyl acetylacetonate, VO(acac)$_2$ with potential ligands.[1-5] Complexing with amines is strong[1,2] but there are conflicting reports concerning complexing with oxygen-containing ligands. Both acetone and 1,4-dioxan in particular are reported to give such small effects in the visible absorption spectrum that no association constant is measurable.[3] However, there is a substantial change in the V=O i.r. stretching frequency when 1,4-dioxan or tetrahydrofuran is added to VO(acac)$_2$ in chloroform.[4] Extensive spectroscopic and e.s.r. studies of the effect of 41 different solvents on VO(acac)$_2$ lead to the suggestion that oxygen-containing ligands interact *via* solvation of the vanadyl oxygen atom, whereas amine bases and dimethylsulphoxide co-ordinate directly to the vanadium atom.[5]

We report here definite n.m.r. evidence for the association of VO(acac)$_2$ with 1,4-dioxan in solution and the structure of the isolated complex as determined by *X*-ray analysis. The oxygen atoms of dioxan are co-ordinated directly to vanadium atoms.

The magnetic moment of VO(acac)$_2$ in CH_2Cl_2 solution, measured by the co-axial tube n.m.r. method[6] with cyclohexane as reference, was 1·76 B.M. On substituting dioxan for cyclohexane we observed an enhanced high-field shift of the reference line. The direction and magnitude of this shift [$+5.25 \times 10^{-2}$ p.p.m. for 1 : 1 dioxan–VO(acac)$_2$ ratio] is consistent with a dipolar, or pseudo-contact shift due to interaction between VO(acac)$_2$ and dioxan. The ^{1}H n.m.r. spectrum of VO(acac)$_2$ at 100 MHz was a single broad peak at δ 2·30 with a full width at half height of 54 Hz. This spectrum has previously been reported as unobservable.[7] It was unaffected by addition of dioxan to the sample, a result which would not be expected if (acac) were involved in equatorial–axial exchange as recently suggested for weak-base complexes.[8]

We isolated a dark green solid adduct, [VO(acac)$_2$]$_2$, dioxan, from CH_2Cl_2–dioxan solution by slow evaporation.

Crystals belong to the tetragonal system, a = 12·102(4), c = 9·987(4) Å. M 617·9. D_m = 1·41 g cm^{-3}, D_c (for two molecules of complex per cell) = 1·42 g cm^{-3}. Possible space groups $P\bar{4}2_1m$ and $P42_12$.

Intensity data were collected by automated four-circle diffractometer in θ–2θ scan mode using Cu-K_α radiation. Of the 825 non-equivalent reflections lying in the range of $0 < \sin\theta \leqslant 0{\cdot}92$, 806 were observable. Absorption corrections [μ (Cu-K_α) = 65·5 cm^{-1}] were applied to the data. The structure could not be solved in $P42_12$ but analysis was successful in $P\bar{4}2_1m$. Full-matrix least-squares refinement reached a conventional R factor of 0·065 with hydrogen atoms, as found from difference maps, included in F_c.

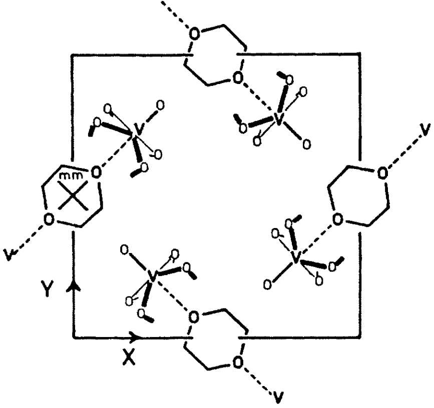

FIGURE 1

The four vanadium atoms per cell lie in special positions with z co-ordinates $\pm 0{\cdot}1853$ (see Figure 1). Two dioxan molecules lie between these pairs with their four oxygen atoms at $z = \pm\, 0{\cdot}1087$. Thus the dioxan molecules are centred at 0, $\frac{1}{2}$, 0·1087 and at $\frac{1}{2}$, 0, 0·8913 and are required to have symmetry *mm* as indicated in Figure 1. This is achieved by disordering of the four carbon atoms to give two possible and equal occupancies for the dioxan molecules. The mean plane of each such half molecule makes $12\frac{1}{2}$° with the *xy* basal plane.

Thus one co-ordination site of each vanadium atom is occupied by the dioxan oxygen. The V · · · O distance is 2·51 Å. The remaining five positions are occupied by the four oxygen atoms of (acac)$_2$ and the vanadyl oxygen atom with V · · · O distances of 1·99 and 1·62 Å, respectively. Since the vanadium atoms lie on mirror planes the two attached (acac) groups must either be related by the mirror plane or have the mirror plane running through their mid-lines. The latter is the case.

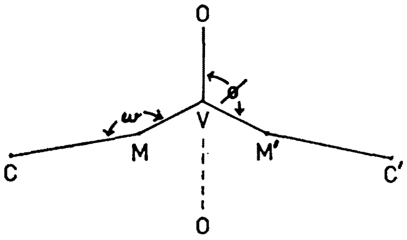

FIGURE 2

There are two other complexes of known crystal structure with which direct comparisons can be made. One (a) is VO(acac)$_2$ itself[2] and the other (b) is bis(phenyl-1,3-butanedionato)vanadyl.[9] The differences in geometry can be understood by reference to Figure 2, in which M,M′ are the midpoints between the dionato-oxygen atoms and C,C′ the central carbon atoms of the dionato-ligand. In complexes (a) and (b) all the positions indicated are closely coplanar (deviations all less than 0·1 Å); in the present complex (c) they are exactly coplanar because the plane of Figure 2 is a plane of symmetry. The geometric differences are between (a) and (b) on the one hand and (c) on the other. In (a) and (b) the angle ϕ is $112\frac{1}{2} \pm 1\frac{1}{2}$° whereas in (c) it is 107·2°. In (a) and (b) the angle ω is $169 \pm \frac{1}{2}$° whereas in (c) it is $179\frac{1}{2}$°. This latter effect, which may be due to intermolecular forces, has been noted in other (acac) complexes.[8]

No other bond lengths or angles deserve special comment. Details will be published in full elsewhere.

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