A Trigonal Prismatic Vanadium(iv) Complex: Bis(acetylacetone benzoylhydrazonato)vandium(iv); *X*-Ray Crystal Structure

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Summary Reaction of benzoylhydrazine with bis(acetylacetonato)oxovanadium(iv) leads to polymeric vanadium(v) complexes as well as a monomeric bis(tridentate)-vanadium(iv) complex which has trigonal prismatic co-ordination and which does not contain an oxo-ligand.

Benzoylhydrazine and bis(acetylacetonato)oxovanadium(iv) react in methanol under dry N_2 to produce the intensely coloured [λ_{max} 330 (ϵ 1·11 × 10^4 mol dm^{-3} cm^{-1}) and 544 (1·93 × 10^3) nm] violet compound [V(aabh)$_2$], where (aabh) is the dianion of acetylacetone benzoylhydrazone, (PhCONNCMeCHCOMe)$^{2-}$. When the reaction is carried out in the presence of air a smaller yield of the violet complex is obtained together with two crystalline brown complexes formulated as [{V^VO(aabh)}$_2$O]$_2$ and [V^V(aabh)-OMe]$_n$ on the basis of analytical and spectroscopic evidence.

The air-stable, violet complex was believed to contain the known[1] tridentate ligand on the evidence of elemental analysis and i.r. (which shows no N–H or V=O groupings) and mass spectra {m/e = 483 (M^+) and an intense peak corresponding to [VO(aabh)]}. The complex is paramagnetic (μ_{eff}, by the Gouy method, is 1·87 B.M. at 298 °C) and in benzene solution has an e.s.r. spectrum which shows eight peaks due to hyperfine splitting with g = 1·9725 and a = 71·4 G. The pattern of linewidths is the same as observed in vanadyl complexes and the lines are approximately twice as broad as those in bis(acetylacetonato)oxovanadium(iv) under identical conditions.

The details of the structure of [V(aabh)$_2$] are shown in

Figures 1 and 2. The remarkable feature of the structure is the trigonal prismatic (TP) co-ordination of the d^1 V^{IV} ion. This geometry for transition metals is well known with bidentate dithiolene ligands[2] and rigid hexadentate ligands.[3] More recently Mo and W complexes with organometallic[4] and 1,2-quinone ligands[5] have been described with TP co-ordination. In several cases the geometry has been intermediate between TP and trigonal antiprismatic (TAP).[6]

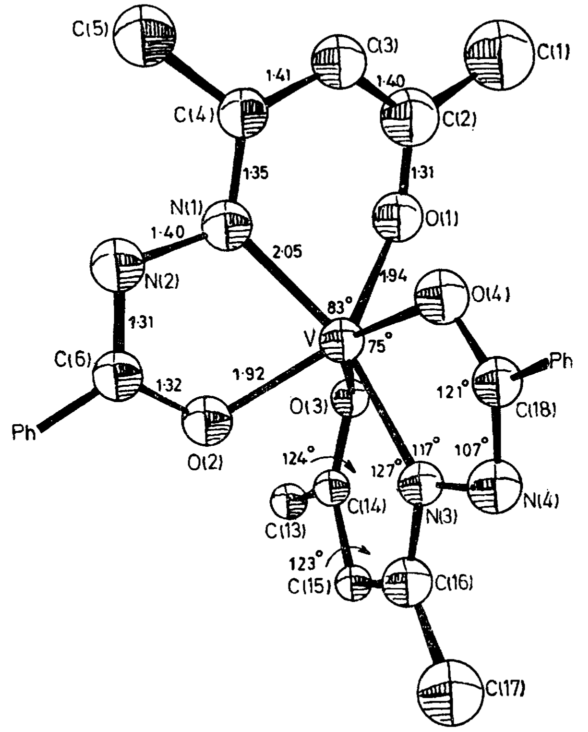

FIGURE 1. The structure of [V(aabh)$_2$].

The formal vanadium(IV) complex $(Me_4N)_2[V(S_2C_2(CN)_2)_3]$ is of this type[7] while the adduct $[VCl_4(NCH)_2]$ has an octahedral arrangement.[8] The co-ordination arrangement adopted is therefore determined to a considerable extent by the nature of the ligands. For tris(bidentate) complexes it has been shown that the smaller the bite of the bidentate (the distance between the chelate donor atoms) the greater is the distortion from the TAP towards the TP arrangement. Calculations show that this is the result of interdonor atom repulsion.[9,10] The (aabh) ligand forms both a 5-membered and a 6-membered chelate ring. The bite of the former ring (Figure 2) is the smallest of any 6-membered ring reported. It is approached by the value of 2·53 Å reported[11] for $[Fe^{III}(benzhydroxamato)_3]$. Similarly the bite of the 6-membered ring is as short as any tabulated[10] for tris-(acetylacetone) complexes (Co, 2·62; Al, 2·65 Å) which range up to 2·96 Å (Sc). The short bite is related to a very sharp angle in the 5-membered rings at N(2) and N(4) averaging only 107·5(5)° where angles nearer 120° would be expected. The 6-membered rings show a major distortion from the average ring planes. Thus O(1) and the vanadium are, respectively, 0·4 Å above and 0·4 Å below the tridentate-metal least-squares plane. This distortion can be seen in Figure 1 at the chemically identical O(3) atom and it enables the 6-membered ring to present a shorter bite than it would were the ring planar. The 5-membered ring is more closely planar enabling the lone pair of the donor nitrogen to point at the vanadium centre.

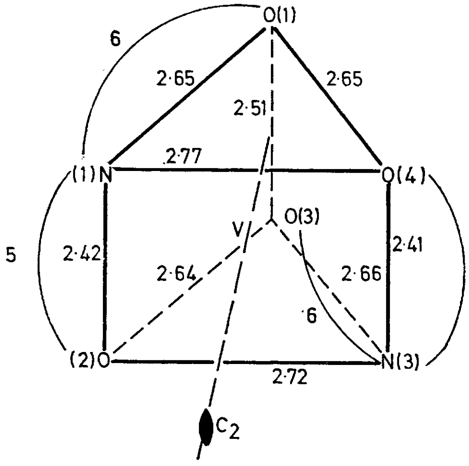

FIGURE 2.

The most probable alternative structure has planar ligands spanning the meridional sites of a distorted octahedron. Neglecting donor atom repulsions the application of crystal field theory indicates no co-ordination preference of TAP over TP co-ordination for d^0, d^1, and d^2 (low spin) metal ions.[3] However, a σ-bonding molecular orbital calculation which also considers the bonding orbitals shows a considerable preference for TP co-ordination with these d configurations and has been used to account for TP metal-sulphide structures of the early transition metals.[12]

Crystal Data: $C_{24}H_{24}N_4O_4V$, $M = 483·4$; monoclinic, space group $P2_1/c$; $a = 8·940(5)$, $b = 12·017(7)$, $c = 22.507(11)$ Å, $\beta = 97·8(1)°$; $U = 2396(5)$ Å^3, $D_m = 1·36$, $D_c = 1·34$ g cm^{-3}; $Z = 4$, Mo-K_α radiation, $\lambda = 0·7107$ Å, $\mu = 4·3$ cm^{-1}, $F(000) = 1004$ e.

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