The Crystal and Molecular Structure of Bis-(2-methyl-8-quinolinolato)oxovanadium(IV)

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Summary The vanadium atom in bis-(2-methyl-8-quinolinolato)oxovanadium(IV) is five-co-ordinate and has a trigonal-bipyramidal co-ordination polyhedron in which the three oxygen atoms and the vanadium atom are in the equatorial plane and the two nitrogen donors occupy the apical positions.

THE molecular structures of all the monomeric five-co-ordinate oxovanadium(IV) complexes that are formed with multidentate ligands have several features in common.[1] The co-ordination polyhedron around the vanadium atom is an approximate square pyramid, the base of which is formed by the donor atoms of the multidentate ligands and the apex is occupied by the oxovanadium oxygen atom. The vanadium atom is displaced about 0·6 Å above the base of the pyramid towards the axial oxygen atom, and the vanadium–oxygen distance is in the range 1·57—1·63 Å. The square-pyramidal arrangement of the donor atoms leaves the sixth position vacant in the co-ordination sphere of vanadium. When these oxovanadium(IV) complexes are dissolved, this vacant position is usually filled by a solvent molecule and gives rise to solvent–complex interactions which result in changes in the spectral properties of the oxovanadium(IV) complex. A trigonal-bipyramidal geometry of the co-ordination polyhedron will hinder the addition of a solvent molecule to the co-ordination sphere around the vanadium atom. The structure and electronic spectrum of a trigonal-bipyramidal complex of oxovanadium(IV) formed with unidentate ligands has been described recently.[1] With the exception of the dimeric oxovanadium(IV) tartrate monohydrate in which the geometry of the co-ordination polyhedron is intermediate between that of a square pyramid and a trigonal bipyramid,[3] no other trigonal-bipyramidal oxovanadium(IV) complex has been reported. We report the first example of a trigonal-bipyramidal oxovanadium(IV) complex formed with the bidentate ligand, 2-methyl-8-quinolinol.

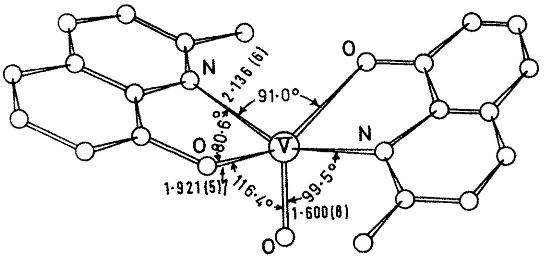

FIGURE 1. *A perspective view of the molecular structure of bis-(2-methyl-8-quinolinolato)oxovanadium*(IV) *with bond lengths* (*in Å*) *and angles* (*in degrees*). *The values in parentheses are the estimated standard deviations.*

Dark yellowish brown crystals of $VO(C_{10}H_8NO)_2$ are formed in the monoclinic space group $C2/c$ or Cc: $a = 17{\cdot}04 \pm 0{\cdot}006$, $b = 7{\cdot}843 \pm 0{\cdot}003$, $c = 13{\cdot}440 \pm 0{\cdot}006$ Å, $\beta = 105°14' \pm 1'$, $Z = 4$, $D_m = 1{\cdot}47$ g/cm^3, $U = 1733{\cdot}5$ Å^3. The intensities of 1155 reflexions were measured using Mo-K_α radiation (0·71069 Å) up to $2\theta = 45°$ on an automated Picker Nuclear FACS I diffractometer equipped with a graphite monochromator. A Wilson plot indicated that the space group was $C2/c$. The structure was solved by the usual Patterson and Fourier methods and refined in the space group $C2/c$ by a full-matrix least-squares method with anisotropic thermal parameters for all atoms. The final discrepancy factor R, was 6·2% for 873 independent non-zero reflexions.

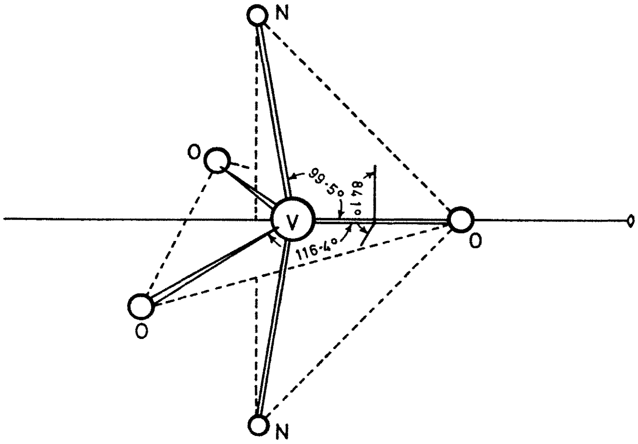

FIGURE 2. *The trigonal bipyramidal co-ordination polyhedron around the vanadium atom.*

A perspective view of the molecular structure is shown in Figure 1 and the co-ordination polyhedron around the vanadium atom is shown in Figure 2. The vanadium atom and the oxovanadium oxygen atom lie on a two-fold axis. Hence all three oxygen atoms and the vanadium atom are coplanar and these four atoms define the equatorial plane of the trigonal bipyramid. The plane defined by the two nitrogen atoms, the vanadium atom, and the oxovanadium oxygen atom, forms a dihedral angle of 84·1° with the equatorial plane. It is evident therefore, that the co-ordination polyhedron (Figure 2) is distorted and deviates significantly from C_{2v} symmetry. There are two vanadium–oxygen distances in the molecule (Figure 1). The short vanadium–oxygen distance is 1·60 Å, which is in the the range of the vanadium–oxovanadium oxygen distances (1·57—1·63 Å) found in the square pyramidal complexes.[1] The second V–O distance in the molecule is 1·92 Å which is just outside the range of the V–O distances (1·93—1·97 Å) that have been reported in other five-co-ordinate monomeric oxovanadium(IV) complexes. The V–N distances of 2·14 Å are slightly longer than the V–N distances (2·06—2·11 Å) found in the square-pyramidal oxovanadium complexes, although in the trigonal bipyramidal complex, bis(trimethylamine)oxovanadium(IV) dichloride, a much longer V–N distance of 2·18 Å has been reported.[2] It would be of interest to compare the structure of the oxovanadium(IV) complex formed with the unsubstituted ligand, 8-quinolinol, to determine whether the 2-methyl substituent has any effect on the molecular structure.[4]

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