Structure of [*NN*′-Ethylenebis-(1-acetonylethylideniminato)-*OO*′*NN*′]-oxovanadium(IV)

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Summary The molecular structure of *NN*′-ethylenebis-(1-acetonylethylideniminato)-oxovanadium(IV) is based on a five-co-ordinate vanadium atom with a square pyramidal arrangement of donors; an apical oxygen and two oxygen (*cis*) and two nitrogen (*cis*) atoms in the square base.

A characteristic of the five-co-ordinate complex bis(acetylacetonato)oxovanadium(IV), VO acac$_2$, is the interesting solvent dependence of its i.r., visible, and e.s.r. spectra.[1] A solvent–complex interaction involving the co-ordination of a donor molecule in the vacant axial position of the square pyramid gives rise to the change in the electronic structure of the metal.[2] Surprisingly the spectroscopy of some β-ketimine complexes is not markedly solvent dependent.[3] The striking difference in Lewis-acid behaviour of the vanadium atom when bound to β-diketone and β-ketimine may be related to a difference in molecular structure. While a square pyramidal geometry allows sterically unhindred ligation by a Lewis base,[4] trigonal bipyramidal,[5] dimeric (polymeric) or strongly solvated, six-co-ordinate structures would not show any solvent–complex interaction. We have determined the crystal structure of *NN*′-ethylenebis-(1-acetonylethylideniminato)-oxovanadium(IV), VO acen.

Crystals of VO acen, VO($C_{12}H_{18}N_2O_2$), form as greenish-black parallelepipeds in the monoclinic space group, $P2_1/a$: $a = 13{\cdot}687 \pm 0{\cdot}003$, $b = 11{\cdot}957 \pm 0{\cdot}002$, $c = 8{\cdot}140 \pm 0{\cdot}001$ Å $\beta = 93{\cdot}76 \pm 0{\cdot}02°$, $Z = 4$. Complete three-dimentional data were collected up to $2\theta = 42°$ using Mo-K_α radiation on an automated General Electric XRD 5 diffractometer. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The discrepancy index, R, is 9·2% for the 954 independent reflections above background.

The structure is depicted in the Figure. The oxovanadium(IV) oxygen atom and the two oxygen and nitrogen atoms of the β-ketimine ligand form an approximately square-pyramidal configuration around the central five-co-ordinate vanadium atom. Significantly, the angles around the central vanadium atom are very nearly equal to those found in the five-co-ordinate β-diketone complexes, VO acac$_2$ and *cis*-bis-(1-phenylbutane-1,3-dionato)oxovanadium(IV), VO bzac$_2$.[6] The four atoms of the chelating ketimine are approximately planar and the distances (Å) from the best least-squares plane through these four atoms are: O(2), 0·07; O(3), −0·06; N(1), 0·10; N(2), −0·10 with the vanadium atom displaced 0·58 Å above this plane toward the axial oxygen atom. The displacement of the vanadium atom is comparable to that found in VO acac$_2$, VO bzac$_2$ and in deoxophylloerythroetioporphyrinoxovanadium(IV), VO por.[7]

An oxovanadium(IV), vanadium–oxygen bond distance of 1·598(9) Å was found for this compound. This clearly falls in the middle of the 1·57 to 1·63 Å range determined previously for other oxovanadium complexes.[4] It appears that the vanadyl-oxygen bond-order is sufficiently high for this bond length to be relatively insensitive to in-plane bonding variations. The vanadium–oxygen [V–O(2) and V–O(3)] and vanadium–nitrogen [V–N(1) and V–N(2)] bonds appear to be among the shortest thus far determined for five-co-ordinate monomeric oxovanadium(IV) complexes. An average V–O distance of 1·951(4) Å was found here which can be contrasted with the average V–O distance of 1·969(4) Å found in VO acac$_2$. An average of 1·984(6) was also determined in VO bzac$_2$ for the two V–O distances on the side of the chelate rings to which the methyl groups are attached. Similarly the average V–N distance of 2·055(8) Å is shorter than the average of 2·113(12) Å found for three of the vanadium–nitrogen bonds in VO por. Although these trends are marginally significant (approximately 4—7σ) they are reasonable ones. The β-ketimine ligand itself has bond distances and angles comparable to those found in a similar copper(II) complex of this ligand.[8]

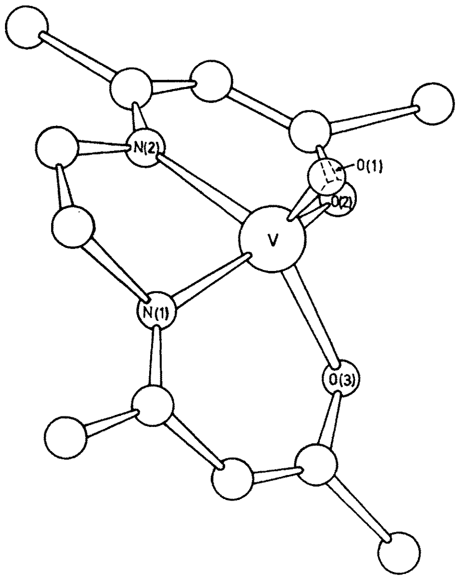

FIGURE. *The molecular structure of* VO acen *viewed down the crystal* c *axis.*

Since VO acen is five-co-ordinate and square pyramidal, there appears to be no structural reason why the vanadium atom should not become six-co-ordinate when dissolved in good donor solvents. The only apparent steric difference in the structure of VO acen and VO acac$_2$ is that the former complex has an ethylene group bridging the two chelate rings. Both of the ethylene carbon atoms are above the best plane of the donor atoms, toward the vanadium atom, and it adopts a gauche conformation. Models show that this cannot hinder addition of a donor molecule to the axial co-ordination position. Surprisingly a sterically similar complex, [*NN*′ethylenebis-(1-trifluoroacetonylethylideniminato)-*OO*′*NN*′]-oxovanadium(IV), VO tfen, shows a solvent dependence of its spectroscopy[9] that is comparable to that of VO acac$_2$. This suggests that donor solvent–complex interactions are occurring in VO tfen and that its molecular geometry is not much different from VO acac$_2$. Charge build-up on the vanadium by the strong in-plane donation of the β-ketimine ligand could prevent axial co-ordination if the axial oxygen–vanadium multiple bond is to be preserved. Axial ligation moves the vanadium closer to the plane of the base ligand, therefore increasing its σ-donation.[10] Trifluoromethyl substitutions on VO acen weaken the inplane donor and thus allow a substantial axial co-ordination which is observed for the weak donor β-diketones. The short bond distances for the vanadium to in-plane donor atoms in VO acen are consistent with the strong σ-donor properties of the β-ketimine.

(*Received, February* 10*th*, 1969; *Com.* 175.)

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