Crystal Structure of the $[VO(C_2O_4)_2\ HO_2]^{2-}$ Ion; a *cis*-Oxalato Complex of Oxovanadium(IV)

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Summary Contrary to predictions based on spectroscopic evidence, the crystal structure of the $[VO(C_2O_4)_2H_2O]^{2-}$ anion has a distorted octahedral arrangement of oxygen atoms about vanadium with a *cis*-arranagement of oxalate groups and a co-ordinated water molecule.

PREVIOUS investigations of the structural chemistry of $(VO)^{2+}$ complexes have demonstrated the tendency of the ion to form square pyramidal five-co-ordinate configurations with bidentate ligands such as acetylacetonate[1,2] and tartrate[3,4] ions. In the isothiocyanate complex,[5] however, the co-ordination is increased to six by the inclusion of a water molecule *trans* to the oxo-oxygen.

The spectroscopy of the compound $(NH_4)_2[VO(C_2O_4)_2]$-$2H_2O$ has been previously reported.[6–8] The i.r.[6,7] spectrum gave no indication of co-ordinated water and the frequencies due to the oxalate groups indicated bidentate co-ordination consistent with an anion structure of C_{2v} symmetry. A square pyramidal structure was proposed which was analogous to the acetylacetonate complex. This structure has been supported by the electronic spectra[6,7] and the electron spin resonance spectrum of the compound.[8] The present *X*-ray investigation was carried out in order to provide further information about this complex.

The compound $(NH_4)_2[VO(C_2O_4)_2]\ 2H_2O$ was prepared by a method described by Palmer[9] and recrystallized from an aqueous propan-2-ol solution. The crystals are monoclinic with $a = 11{\cdot}10$, $b = 7{\cdot}92$, $c = 14{\cdot}34$ Å, $\beta = 117°$, $Z = 4$, $D_m = 1{\cdot}81$, $D_c = 1{\cdot}76$ g cm^{-3}, space group $P2_1/c$. The unit cell data agree with Hazell's[10] data. The intensities of 989 independent reflections were measured on an integrating microdensitometer using multiple film equi-inclination Weissenberg photographs recorded with Cu-K_α radiation. The structure was solved by conventional Patterson and Fourier methods. Positional and anisotropic thermal parameters of the eighteen non-hydrogen atoms have been refined by the method of least-squares to an R value of 0·12.

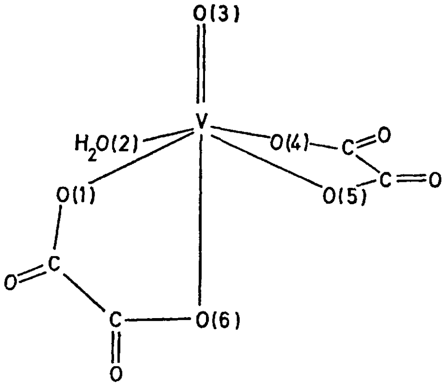

FIGURE.

As shown in the Figure, the vanadium atom is six-co-ordinate and not five-co-ordinate as was previously suggested. As in the isothiocyanate complex[5] the sixth co-ordination position is occupied by a water molecule. The ion differs from previously reported $(VO)^{2+}$ structures in that the oxalate groups are *cis* to one another rather than *trans*. However, the overall arrangement is remarkably similar to that recently reported[11] for the anion $[VO_2(C_2O_4)_2]^{3-}$ of the corresponding $(VO_2)^+$ complex.

In agreement with the low symmetry of the ion, there is a wide variation in the V–O distances in the present case. The shortest distance 1·61 (1) Å, is found for the bond V–O-(3) and implies substantial multiple bonding between these atoms. The longest distance, 2·18(1) Å, occurs for the bond V–O(6), which is *trans* to the oxo-oxgyen atom and provides another example of the *trans* effect in oxovanadium chemistry. The angle formed by these two oxygen atoms at the vanadium atom is 171°. The lengths of the four V–O equatorial bonds vary from 1·96(1) Å, for V–O(4) to, 2·04(1) Å, for V–O(2) and the angles, O–V–O, involving the equatorial oxygen atoms deviate only slightly from 90°. However, the angles formed at vanadium by O(3) and the equatorial oxygen atoms range from 96·0 to 106°. This significant deviation from 90° indicates a displacement of the vanadium atom from the centre of the octahedron in the direction of O(3); similar effects have been observed in other oxovanadium complexes.[1,4]

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