Vanadium Eight-co-ordination Shown in a Crystallographic Study of Tetrakis(dithiophenylacetato)vanadium(IV)

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Summary The crystal structure of tetrakis(dithiophenylacetato)vanadium(IV) shows a dodecahedral environment around the eight-co-ordinated vanadium.

RECENTLY the co-ordination of eight sulphur atoms to a central metal atom has been confirmed for the first time by an *X*-ray study by Brown *et al.*[1] of thorium(IV) tetrakis-(*NN*-diethyldithiocarbamate). Such co-ordination has since been found in the analogous neptunium[2] and titanium[3] complexes, and here crystallographic evidence is presented for an eight-co-ordinated vanadium(IV) complex. Spectrochemical work by Piovesana and Furlani[4] suggested that vanadium(IV) dithiocarboxylates contained octa-co-ordinated VS_8 chromophores, and the same feature was indicated in the tetrakis-*NN*-dialkyldithiocarbamates $V(S_2CNR_2)_4$ by the e.s.r. studies of Bradley *et al.*[5] and by the isomorphism of tetrakis-(*NN*-diethyldithiocarbamato)vanadium(IV) with the Ti analogue.[3] In collaboration with Furlani's group, we have undertaken the crystal structure analysis of tetrakis-(dithiophenylacetato)vanadium(IV) in order to confirm the existence of a VS_8 chromophore and to get details of its geometry and stereochemistry. The dark red crystals of $C_{32}H_{28}S_8V$ were found to be triclinic, $a = 9{\cdot}864$, $b = 11{\cdot}395$, $c = 16{\cdot}124$ Å, $\alpha = 77° 27'$, $\beta = 101°$, $\gamma = 106° 6'$; $Z = 2$; $U = 1683$ Å^3. Refinement of the structure indicated the space group to be $P\bar{1}$.

A total of 1881 independent non-zero structure amplitudes were obtained by visual estimation of Weissenberg photographs. The structure was solved by a direct phase-determining procedure, based on the iterative application of Sayre's equation, and refined by block-diagonal least-squares methods to a current *R*-value of 0·126 (with anisotropic temperature factors for V and S, and isotropic temperature factors for the carbon atoms).

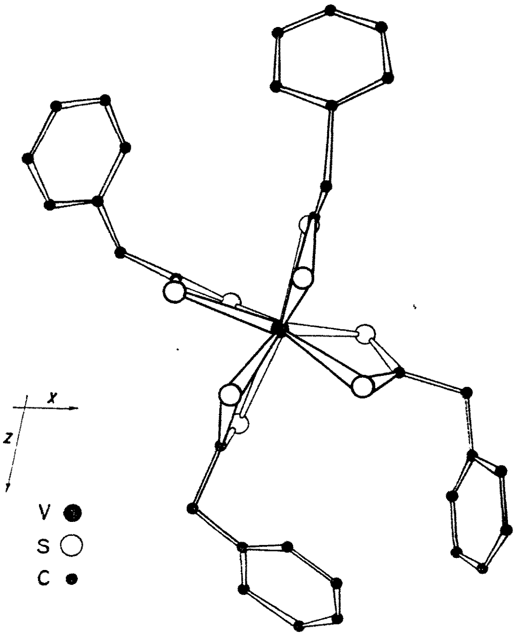

FIGURE. [010] *projection of the molecule.*

The vanadium atom was found to be co-ordinated to eight sulphur atoms, as shown in the Figure. The arrangement of these sulphur atoms around the vanadium is a good approximation to the ideal dodecahedral arrangement (according to Hoard and Silverton[6]). The shape of the dodecahedron is specified by the following parameters (mean values): $V{-}S_A = 2{\cdot}524 \pm 0{\cdot}007$, $V{-}S_B = 2{\cdot}470 \pm 0{\cdot}007$ Å, $\theta_A = 37{\cdot}6 \pm 0{\cdot}2$, $\theta_B = 76{\cdot}0 \pm 0{\cdot}2°$, $V{-}S_A/V{-}S_B$ 1·022, $a = 3{\cdot}078 \pm 0{\cdot}009$, $b = 3{\cdot}567 \pm 0{\cdot}01$, $g = 3{\cdot}197 \pm 0{\cdot}01$, $m = 2{\cdot}752 \pm 0{\cdot}01$ Å; the most favourable parameters for the dodecahedron[6] should be M–A/M–B 1·03, θ_A 35·2, θ_B 73·5°. The V–S bond lengths are slightly longer than values found in tris(diethyldithiophosphato)-vanadium(III) (2·435—2·473 Å).[7]

Co-ordination polyhedra previously found in complexes containing MS_8 chromophores can be classified (within the limits of more or less strong distortion) into the dodecahedral sub-classes I_da and II_da, following the notation of Hoard and Silverton[6] for the possible stereoisomers of $M(X_2)_4$ groups having four chemically symmetric bidentate ligands. Since the "bite" coincides with the edge "*m*," $Th(S_2CNEt_2)_4$ can be considered as belonging to a very distorted sub-class II_da; while $NEt_4[Np(S_2CNEt_2)_4]$ and $Ti(S_2CNEt_2)_4$, having the "bite" coincident with the edge "*g*," belong to the sub-class I_da. $V(S_2CH_2C_6H_5)_4$ also belongs to the latter sub-class, with D_{2d}-$\bar{4}2m$ symmetry nearly achieved in the VS_8 chromophore.

There is no apparent reason why a compound should be of one or the other group; however, it is interesting to note that the general shape of the molecule of the vanadium complex is very similar to that of the nickel(II) complex with the same ligand $Ni_2(S_2CH_2C_6H_5)_4$[8] (see Figure and also ref. 8). This may suggest that the steric properties of the ligand are important in the formation of eight-co-ordinated polyhedra.

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