

Synthesis and Characterization of a Stable Hexa-amine Vanadium(IV) Cage Complex

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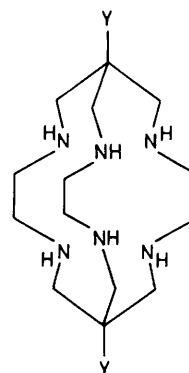
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The synthesis, structure, and preliminary aspects of electrochemical, magnetic, e.s.r., and electronic spectroscopic properties of a stable, near-trigonal-prismatic hexa-aminevanadium(IV) complex are reported.

The aqueous co-ordination chemistry of vanadium in the oxidation states IV and V is characteristically that of oxo species.¹ Square pyramidal and distorted octahedral species incorporating the 'vanadyl' ion, VO²⁺, are especially common for vanadium(IV) and they have been structurally and spectroscopically characterized.^{1,2} In contrast, only a few non-oxo species, such as those with dithiolene,³ catecholate,⁴ and acetylacetonate type ligands,⁵ are well characterized. In lower oxidation states, however, deprotonation of a ligand donor atom is less readily observed and simple octahedral complexes such as V^{III}(en)₃³⁺ and V^{III}(tn)₃³⁺ (en = ethane-1,2-diamine, tn = propane-1,3-diamine) are easily prepared and have been analysed spectroscopically.⁶ With cage-like hexa-amine ligands, such as sar and its derivatives it might therefore be expected that V^{III} complexes could be prepared and that, given the known properties of such encapsulating ligands with other metal ions, conversion of these V^{III} species into non-oxo V^{IV} and V^V compounds could be successful.

In an attempt to prepare directly the V^{III} complex of diamsar, V(acac)₃ (Hacac = pentane-2,4-dione) was treated with diamsar⁷ in aqueous ethanol under nitrogen. After 3 days at 40 °C, a deep red-brown colour had developed in the solution and this did not change on admission of air. Separation of the red-brown product from some VO²⁺ by

cation exchange chromatography (Dowex 50W-X2, H⁺ form) enabled a crystalline chloride salt to be isolated. This was converted into the dithionate salt, which was recrystallised from water to provide crystals of [V^{IV}{di(amH)sar -



sar: Y = H
 diamsar: Y = NH₂
 di(amH)sar: Y = NH₃⁺
 di(amH)sar-2H: Y = NH₃⁺, two co-ordinated
 NH groups deprotonated.

2H}(S₂O₆)₂·2H₂O suitable for X-ray structure determination.† The same material seemed to be obtained in a more rapid preparation starting with V^{IV} but in this case it was not the only product and the chemistry of this reaction is still under investigation.

The crystallographically characterised complex is stable in aqueous solution over a wide pH range (1 < pH < 10) under ambient conditions and does not appear to be appreciably

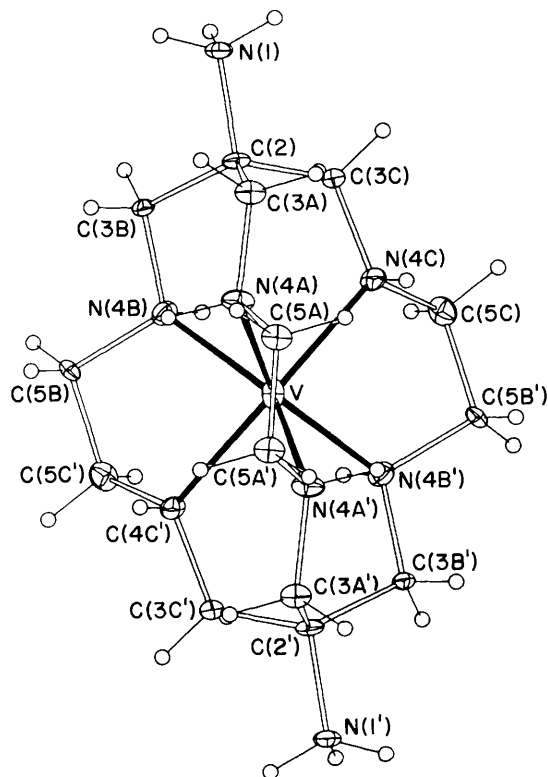


Figure 1. ORTEP diagram of the V^{IV}{di(amH)₂sar-2H}⁴⁺ ion with 20% thermal ellipsoids. Hydrogen atoms have an arbitrary radius of 0.1 Å. The dithionate dihydrate salt crystallizes in the orthorhombic space group C222₁ (*D*₂⁵, No. 20) with *a* = 10.432(3), *b* = 14.437(4), *c* = 18.204(6) Å, *U* = 2724(1) Å³, *D*_m = 1.74(1), *Z* = 4. X-Ray data (1386 reflections) were collected by diffractometer (Syntex P2₁ four-circle) with monochromatic Mo-*K*_α radiation. Anisotropic full-matrix least-squares refinement on |*F*| converged to a final *R* = 0.035. Bond lengths (Å) are: V-N(4A), 2.063(6); V-N(4B), 2.096(5); V-N(4C), 2.097(5); average N-C, 1.464; average C(2)-C(3), 1.533; N(1)-C(2), 1.499(7); average C(5)-C(5'), 1.49. Bond angles (°) are: N(4A)-V-N(4B), 85.4(2); N(4A)-V-N(4C), 85.3(2); N(4B)-V-N(4C), 85.4(2); N(4A)-V-N(4A'), 79.8(2); N(4A)-V-N(4B'), 147.5(2); N(4A)-V-N(4C'), 121.6(2); N(4B)-V-N(4A'), 147.5(2); N(4B)-V-N(4B'), 120.4(2); N(4B)-V-N(4C'), 78.1(2); N(4C)-V-N(4A'), 121.6(2); N(4C)-V-N(4B'), 78.1(2); N(4C)-V-N(4C'), 146.6(2); av. V-N(4)-C(3), 119.5; av. V-N(4)-C(5), 113.6; av. N(4)-C(3)-C(2), 111.4. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

† A formally identical reaction in different media yields a stable spectroscopically distinctly different isomer of the complex described in this communication or a mixture of both species. Details of the synthesis, structure, and spectroscopy of the second species will be described elsewhere: P. Comba and L. L. Martin, unpublished results.

photosensitive. Outside the indicated pH range, decomposition occurs at elevated temperatures and the complex is also destroyed by oxidants such as I₂, KHSO₅, and HNO₃.

The results of the structure determination are consistent with the presence of complex cations, dithionate anions, and water molecules in 1:2:2 stoichiometry. The cation has crystallographically imposed two-fold symmetry. The precision of the determination allows meaningful refinement of hydrogen atom co-ordinates in association with the water molecule, the three terminal sites of the ligand (NH₃⁺), and the three sites associated with the three independent co-ordinated nitrogen atoms, as well as the methylene groups. Spectroscopic, magnetic, and e.s.r. studies are consistent with description of the metal centre as V^{IV}, requiring for a 4+ cation that two amine groups are deprotonated. The structural data, in connection with p*K*_a measurements and spectroscopy, are consistent with protonated apical NH₂ groups. However, which co-ordinated amines are deprotonated is not clear from the structure determination; the apparently saturated hydrogen atom distribution may be a consequence of disorder or of description of a 'lone pair' as a refined hydrogen atom. The cation symmetry is close to trigonal (*D*₃) and the co-ordination environment of the metal close to the trigonal prismatic, as shown by the twist angle $\phi = 18^\circ$ and the N-V-N angles: 2 × 147.5, 146.6° and 2 × 121.6, 120.4°,⁸ while the non-hydrogen angle sums at the co-ordinated nitrogen atoms are 347, 345, and 347°, indicative of considerably more trigonal-planar character than is observed in other transition metal complexes with sar-type ligands in which these sums are typically (333 ± 5)°.⁹ On the assumption of the latter value for a tetrahedral sar-type nitrogen and of disorder, a one-third population of the trigonal component might be expected to increase this angle to ~342°, not far removed from the observed value; it should be noted, however, that the thermal parameters of the co-ordinated nitrogen atoms are not excessively high and in keeping with those observed in other well behaved structure determinations of metal complexes of this ligand. The major perturbation from *D*₃ co-ordination symmetry is found in the pair of *cis* V-N(4A) distances, 2.063(6) Å [cf. V-N(4B,C), 2.096(5), 2.097(5) Å]; the associated C-N-N-C torsion angles are 44.1, 48.1, and 48.1° respectively. The 'hydrogen atoms' at all six co-ordinated nitrogen atoms are associated with plausible hydrogen-bonding interactions to dithionate oxygen atoms at 2.45(7), 2.44(7), and 2.36(6) Å, while the three at the terminal nitrogen have shorter contacts to the anion and water oxygen at 1.92(6), 2.03(7), and 1.95(7) Å.

In an acetate buffer (pH 4.05), two reduction waves are found at -0.42 and -0.69 V vs. saturated (KCl) Ag/AgCl electrode (cyclic voltammetry, hanging mercury drop electrode, 500 mV/s). Only one wave is seen upon reoxidation at -0.60 V. Controlled potential electrolysis at -0.54 V (neutral pH, *n* = 1.0) yields a pale brown solution of the d² V^{III} species. This solution is reoxidized in air to the original V^{IV} complex. Further electrochemical studies including the pH dependence and aprotic behaviour of V^{IV}{di(amH)₂sar-2H}⁴⁺ are continuing.

The vanadium(IV) complex has a room-temperature magnetic susceptibility of 1.80 μ_B, compared with the spin-only value for d¹ systems of 1.73 μ_B. The spin Hamiltonian parameters for e.s.r. studies are: ‡ *g*_x = 1.975, *g*_y = 1.970, *g*_z =

‡ A small deviation from pure axial symmetry is evident from a detailed e.s.r. study of the complex.¹⁰ It is clear that the geometry remains unchanged over a large temperature range and in solution over a large range of solvents.

1.992, $g_{\text{iso}} = 1.979$; $A_x = 92 \times 10^{-4}$, $A_y = 99 \times 10^{-4}$, $A_z = 16 \times 10^{-4}$, $A_{\text{iso}} = 68 \times 10^{-4} \text{ cm}^{-1}$, indicating a 2A_1 ground state. The aqueous solution electronic absorption spectra consists of transitions at 11 310, 20 750 (sh), 23 670, 30 170, and 36 300 cm^{-1} for the vanadium(IV) complex and 27 130 and 37 750 cm^{-1} for the electrochemically reduced vanadium(III) complex, respectively. Detailed analyses of the electronic structure of the complexes¹⁰ and of variable temperature magnetic studies¹¹ are in progress and will be published elsewhere.

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