Preparation, Crystal Structure, and Physical Properties of a Pyrogallol-bridged Vanadium(III) Complex

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The structure, n.m.r. spectrum, and magnetic properties of the vanadium(III) dimer [(acac)4V2(μ-OC6H3(OH)2)2] formed from [VO(acac)2] and an excess of pyrogallol are described.

Vanadium is sequestered and stored as VIII (ref. 1) in certain species of tunicates at a level 106 times that present in sea water. 2 Although this subject has been studied extensively by chemists and biologists, many questions remain. Several years ago, a class of low molecular weight blood pigments, the tunicromes, was characterized as possessing pyrogallol and catechol moieties. 3-4 E.p.r. 4 and u.v.-visible absorption spectroscopy 5 in vitro have shown that tunicochrome reduces V(V) to V(IV). Several descriptions of vanadium–catechol complexes have appeared in the literature. The reaction of VO(acac)2 with catechol under basic conditions, by use of the disodium salt of catechol or triethylamine, yields [V2O(3,5-dtbch)2]2- and [V2O(3,5-dtbch)2]2- (3,5-dtbch = 3,5-di-t-butylcatechol), respectively. 6,7 In contrast, the product formed in the absence of base displayed an e.p.r. spectrum assignable to a V(III)-semiquinone complex, V(III)-3,5-dbsq, 8 this product is also identified on the basis of data from potentiometry, 9 polarography, 10 and u.v. spectroscopy, 11 but as yet no X-ray crystallographic structure has been reported.

In this paper we report the structure and spectral and magnetic properties of the product of reduction of V(IV) by pyrogallol, 1 the pyrogallol-bridged V(IV) dimer, [(acac)4V2(μ-OC6H3(OH)2)2] (1) (Figure 1). The structure was solved by direct methods and refined to final residuals R = 0.056, R = 0.075. 12 Without the solvent molecule (toluene) the compound has C2 symmetry about the V . . . V axis. The V . . . V separation is 3.146 Å, which precludes V-V bonding. 13 The magnetic susceptibility, measured from 10 to 300 K, exhibited magnetic properties of the product of reduction of V(IV) by pyrogallol matrices, together with magnetic moment data, supports the presence of two V(III) atoms in the molecule.

Since electron relaxation of V(III) is rapid, complexes of this oxidation state are detectable by n.m.r. The n.m.r. spectrum of the complex (1) has been compared with that of [V2O(acac)4] 15,16-17 whereas the methyl groups of [V2O(acac)4] resonate at δ 45.46, those in the complex (1) resonate at 47.9 and 39.4 (1:1); the 10-, 10'-, 15-, and 15'-methyl groups are shielded by the aromatic rings (Figure 1) and exhibit the expected upfield shift to δ 39.4. The 9-, 9'-, 14- and 14'-methylene protons exhibit shifts from δ 40.1 in [V2O(acac)4] to δ 28.7. As suggested by Eaton, 15 this arises from an increase in electron density at the methine position attributable to independent paramagnetic term and a small (3%) paramagnetic impurity contribution were also included. Attempts to fit the data by assuming two antiferromagnetically coupled S = 1/2 spins were not successful. The molecular ion (M + H) at 749 (fast atom bombardment mass spectrometry; ethylene glycol matrix), together with magnetic moment data, supports the presence of two V(III) atoms in the molecule.

The solution was dark greenish brown (Found: C, 55.6; H, 5.7; V, 12.1%). Pyrogallol complexes of vanadium have been obtained from the reaction of V(CO)6 with 3,5-di-t-butyl-1,2- benzoquinone. 8 Pyrogallol complexes of vanadium have been identified on the basis of data from potentiometry, 9 polarography, 10 and u.v. spectroscopy, 11 but as yet no X-ray crystallographic structure has been reported.

Preparation of the Complex (1): C20H20O14V2·2H2O 840.68; crystal size, 0.30 x 0.40 x 0.50 mm; monoclinic; space group C2; a = 14.207(4), b = 24.289(4), c = 11.773(2) Å; β = 96.27(2); V = 4038(1) Å3; Z = 4; Dc = 1.38 g cm-3. Nicolet R3m diffractometer, CuKα (1.54178 Å), 298 K; ω scan; sinθ/λ limit 0.5 Å-1 (2θmax 130°); 4269 reflections used, 454 parameters varied; R = Σ|Fo| - |Fc|)/Σ|Fo| = 0.056, R = [Σw(|Fo| - |Fc|)2)/Σw|Fo|2]1/2 = 0.075, w = 1/[σ2(IFo) + 0.00145(IFc)]; absorption coefficient μ = 46.9 cm-1. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 1. ORTEP structure of the complex (1).

§ 1H N.m.r. (250 MHz; CDCl3; 20°C) δ 47.9 (s, 12H), 39.4 (s, 12H), 28.7 (s, 4H); 11.0 (br, s, >4H), and 9.4 (s, 4H).
ligand-to-metal $\alpha$-spin transfer, which leaves a $\beta$-spin on the ligand. The $meta$-protons at positions 3, 3’, 5, and 5’ appeared as a singlet at $\delta$ 9.4. Upon deuteration of the phenolic groups (broad peaks at $\delta$ 11.5—10.2), the overlapping singlet at $\delta$ 11.0 integrated for 2 protons (H-4 and -4’).

Overnight stirring of [VO(acac)$_2$] and 2 equiv. of pyrogallol in THF with neither heat nor catalyst produced a mixture of products containing the complex (1), as evidenced by n.m.r. Although disproportionation of VI$^V$ under acidic conditions (HClO$_4$ in MeCN) has been reported to give VIII and VV,$^{18}$ this is not occurring here because no acid was employed. The results support the idea that the large amount of tunichrome present in A. nigra blood$^{3,4}$ might reduce V$^V$ to VIII in vivo.

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References


