

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 $[(\text{acac})_4\text{V}_2(\mu\text{-OC}_6\text{H}_3(\text{OH})_2)_2]$ formed from $[\text{VO}(\text{acac})_2]$ and an excess of pyrogallol are described.

Vanadium is sequestered and stored as V^{III} (ref. 1) in certain species of tunicates at a level 10^6 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 tunichromes, was characterized as possessing pyrogallol and catechol moieties.^{3,4} E.p.r.⁴ and u.v.-visible absorption spectroscopy⁵ *in vitro* have shown that tunichrome reduces V^{V} to V^{IV} . Several descriptions of vanadium-catechol complexes have appeared in the literature. The reaction of $\text{VO}(\text{acac})_2$ with catechol under basic conditions, by use of the disodium salt of catechol or triethylamine, yields $[\text{V}^{\text{IV}}\text{O}(\text{3,5-dtbc})_2]^{2-}$ and $[\text{V}^{\text{IV}}(\text{3,5-dtbc})_3]^{2-}$ (3,5-dtbc = 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, $\text{V}(\text{3,5-dbsq})_3$;^{8a} this product is also obtained from the reaction of $\text{V}(\text{CO})_6$ 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.

In this paper we report the structure and spectral and magnetic properties of the product of reduction of V^{IV} by pyrogallol,[†] the pyrogallol-bridged V^{III} dimer, $[(\text{acac})_4\text{V}_2(\mu\text{-OC}_6\text{H}_3(\text{OH})_2)_2]$ (**1**) (Figure 1). The structure was solved by direct methods and refined to final residuals $R = 0.056$, $R_w = 0.075$.[‡] Without the solvent molecule (toluene) the compound has C_2 symmetry about the $\text{V} \cdots \text{V}$ axis. The $\text{V} \cdots \text{V}$ separation is 3.146 Å, which precludes $\text{V}-\text{V}$ bonding.¹³ The magnetic susceptibility, measured from 10 to 300 K, exhibited antiferromagnetically coupled dimer behaviour, first increasing and then decreasing with increasing temperature. The data fit the Hamiltonian (1),¹⁴ where $S_1 = S_2 = 1$ for V^{3+} , yielding

$$\mathbf{H} = -JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2 \quad (1)$$

$-J = 44.8 \text{ cm}^{-1}$ and $-j = 3.7 \text{ cm}^{-1}$. A temperature-

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 ($M + \text{H}$) 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.

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 $[\text{V}(\text{acac})_3]$.¹⁵⁻¹⁷ Whereas the methyl groups of $[\text{V}(\text{acac})_3]$ resonate at δ 45,¹⁶ 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'-methine protons exhibit shifts from δ 40.1 in $[\text{V}(\text{acac})_3]$ to δ 28.7. As suggested by Eaton,¹⁵ this arises from an increase in electron density at the methine position attributable to

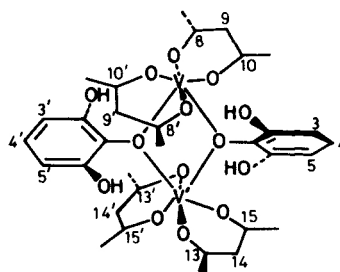
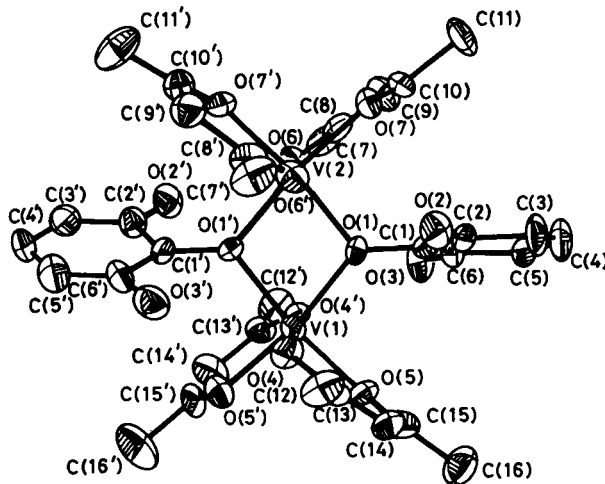


Figure 1. ORTEP structure of the complex (**1**).

[§] ^1H N.m.r. (250 MHz; CDCl_3 ; 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).

[†] The complex $[(\text{acac})_4\text{V}_2(\mu\text{-OC}_6\text{H}_3(\text{OH})_2)_2]$ (**1**) was prepared as follows. Pyrogallol (1.70 g, 13.5 mmol) was dissolved in THF (50 ml). $[\text{VO}(\text{acac})_2]$ ¹² (1.03 g, 3.9 mmol) was added and the mixture was stirred overnight. The solution was evaporated and the residue was treated with hot toluene (50 ml) and filtered. Cooling of the filtrate yielded dark crystals (0.281 g, 24%), suitable for *X*-ray diffraction. The solution was dark greenish brown (Found: C, 55.6; H, 5.7; V, 12.15. $\text{C}_{32}\text{H}_{38}\text{O}_{14}\text{V}_2 \cdot \text{C}_7\text{H}_8$ requires C, 55.7; H, 5.5; V, 12.1%).

[‡] Compound (**1**): $\text{C}_{32}\text{H}_{38}\text{O}_{14}\text{V}_2 \cdot \text{C}_7\text{H}_8$; M 840.68; crystal size, $0.30 \times 0.40 \times 0.50 \text{ mm}$; monoclinic; space group C_2 ; $a = 14.207(4)$, $b = 24.289(4)$, $c = 11.773(2)$ Å; $\beta = 96.27(2)^\circ$; $V = 4038(1)$ Å³; $Z = 4$; $D_c = 1.38 \text{ g cm}^{-3}$. Nicolet R3m diffractometer, $\text{Cu}(\lambda 1.54178 \text{ Å})$, 298 K; ω scan; $\sin\theta/\lambda$ limit 0.59 Å^{-1} ($2\theta_{\text{max}} 130^\circ$); 4269 reflections used; 454 parameters varied; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.056$, $R_w = 0.075$; $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.075$, $w = 1/[\sigma^2(F_o) + 0.00145(F_o)^2]$; bond absorption coefficient $\mu_{\text{calc}} = 46.9 \text{ cm}^{-1}$. 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.

ligand-to-metal α -spin transfer, which leaves a β -spin on the ligand. The *meta*-protons at positions 3, 3', 5, and 5' appeared as a singlet at δ 9.4. Upon deuteration of the phenolic groups (broad peaks at δ 11.5–10.2), the overlapping singlet at δ 11.0 integrated for 2 protons (H-4 and -4').

Overnight stirring of $[\text{VO}(\text{acac})_2]$ 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 V^{IV} under acidic conditions (HClO_4 in MeCN) has been reported to give V^{III} and V^{V} ,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 V^{III} *in vivo*.

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