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-O₃C₆H₃(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. 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. The structure, n.m.r. spectrum, and magnetic properties of the product of reduction of VIV by pyrogallol,† the pyrogallol-bridged VIII dimer, [(acac)4V2(μ-O₃C₆H₃(OH)₂)₂] (I) (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 $V \cdots V$ axis. The crystal structure has been identified on the basis of data from potentiometry, polarography, and u.v. spectroscopy, 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 IV by pyrogallol,† the pyrogallol-bridged IV dimer, [(acac)₂V₂(μ-O₃C₆H₃(OH)₂)₂] (I) (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 $V \cdots V$ axis. The crystal structure has been identified on the basis of data from potentiometry, polarography, and u.v. spectroscopy, but as yet no X-ray crystallographic structure has been reported.

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The structure, n.m.r. spectrum, and magnetic properties of the vanadium(III) dimer [(acac)₄V₂(μ-O₃C₆H₃(OH)₂)₂] formed from [VO(acac)₂] and an excess of pyrogallol are described.

† The complex [(acac)₂V₂(μ-O₃C₆H₃(OH)₂)₂] (I) was prepared as follows. Pyrogallol (1.70 g, 13.5 mmol) was dissolved in THF (50 ml). [VO(acac)₂] (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. C₁₉₂H₇₈O₄₄V₂C₆H₁₂ requires C, 55.7; H, 5.5; V, 12.1%).

‡ Compound (1): C₂₀H₁₆O₄V₂C₂H₂O₇ 940.68; crystal size, 0.30 × 0.40 × 0.50 mm; monoclinic; space group $C_1$: $a = 14.207(4)$, $b = 24.289(4)$, $c = 11.773(2)$; $β = 96.27(2)^\circ$; $V = 4038(1)$ Å³; $Z = 4$; $D_\text{c} = 1.38$ g cm⁻³. Nicolet R3m diffractometer, CuKα (λ = 1.54178 Å), 298 K; ω scan; $\sin2θ/λ$ limit 0.9 Å⁻¹ (2θmax = 130°); 4269 reflections used, 454 parameters varied, $R = \Sigma|F_{o}|-|F_{c}|\Sigma|F_{c}|= 0.056$, $R_w = \Sigma|w(F_{o})^-w(F_{c})|^2\Sigma|w(F_{c})|^2 = 0.075$, $w = 1/[σ(F_{o})^2+0.00135σ(F_{o})^2]$, absorption coefficient $\mu_{\text{calc}} = 46.9$ 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.

§ δH 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 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 [VO(acac)] and 2 equiv. of pyrogallol in THF with neither heat nor catalyst produced a mixture of products containing the complex (I), as evidenced by n.m.r. Although disproportionation of V(V) under acidic conditions (HClO in MeCN) has been reported to give V(III) and V(V), 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 might reduce V(V) to V(III) in vivo.

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References


