

(NEt₄)₃[V₆O₂S₄(edt)₆]: A Model for the Adsorption of Naked [VO]²⁺ Units on Vanadium Sulfide Surfaces

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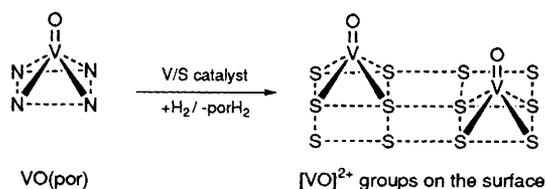
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(NEt₄)₃[V₆O₂S₄(edt)₆].EtCN **2** (edtH₂ = ethane-1,2-dithiol) has been obtained in small yield (5–10%) from (NEt₄)Na[VS(edt)₂]; complex **2** has a structure comprising two VO²⁺ units bound to a [V₄S₄] core and thus represents a model for the adsorption of [VO]²⁺ species on the surface of V sulfides during crude oil hydrotreating processes.

Our continuing interest in non-organometallic V sulfide chemistry derives from the desire to elucidate possible intermediates forming during the conversion of crude oil vanadyl porphyrin impurities into insoluble V sulfides during industrial hydrodesulfurization (HDS) and hydrodemetallation (HDM) processing of heavy crudes.¹ The formation of V sulfides (primarily V₂S₃ and V₃S₄) has deleterious consequences on the activity of the supported Mo HDS catalyst, although they are themselves good HDM catalysts, catalyzing the further conversion of vanadyl species into V sulfides.² The mechanism of this transformation is believed to involve initial Lewis acid–Lewis base interactions between the VO(por) (por = porphyrin) molecules and the V sulfide surface, followed by demetallation and subsequent reduction of the porphyrin ring to a chlorin.^{3–5} The liberated [VO]²⁺ entity becomes bound to surface S groups, as determined by EPR and EXAFS studies on used catalysts that indicate [VO]²⁺ groups in a VOS₄ first-coordination sphere.^{2,6,7} This is summarized in Scheme 1. The surface-bound [VO]²⁺ groups subsequently get sulfided and reduced to form another layer of the growing V sulfide crystalline phase. Thus, the crude oil V impurities catalyze their own removal (autocatalytic HDM activity).²

We have for a long time sought a molecular system to model the surface-bound [VO]²⁺ units *viz.* a complex containing [VO]²⁺ groups bound to a [V_xS_y] aggregate. Such a complex has, to-date, been unknown, but we herein report the attainment of such a species from the hydrolysis of the thiovanadyl complex (NEt₄)Na[VS(edt)₂] (**1**; edtH₂ = ethane-1,2-dithiol).⁸

Addition of 1 equiv. of HNEt₃Cl to a solution of complex **1** in EtCN led to a darkening of the solution colour from orange-brown to deep brown-black. The solution was maintained at room temp. overnight, NaCl removed by filtration, and the flask left undisturbed at room temp. for a further three days. A small quantity (5–10% yield) of black, diamond-shaped crystals of (NEt₄)₃[V₆O₂S₄(edt)₆].EtCN (**2**), were collected by filtration, washed with a little Et₂O, and dried *in vacuo*. We believe **2** is formed by attack on **1** by H₂O molecules in the HNEt₃Cl; complex **1** is extremely air sensitive.† Consideration of formal charges leads to a 3V^{III}, 3V^{IV} oxidation state description, suggesting that reducing equivalents are being provided from oxidation of edt²⁻ groups.



Scheme 1

† The yield of **2** is always low; we have been unable to increase the yield above 10%. The low solubility of **2** in EtCN is fortunate in allowing its separation from an undoubtedly complex reaction mixture.

The structure‡ of the anion of complex **2** is shown in Fig. 1. There is a central [V₄(μ₃-S)₄] core comprising a planar V₄ unit with μ₃-S²⁻ ions above and below this plane. Attached to the two ends of the core *via* atoms S(7) and S(10) are the two [VO]²⁺ units whose V atoms lie 0.98 Å above and below the V₄ plane. Peripheral ligation is provided by six edt²⁻ groups, four in a η¹:η²:μ mode and two in a η²:η²:μ mode. Two V

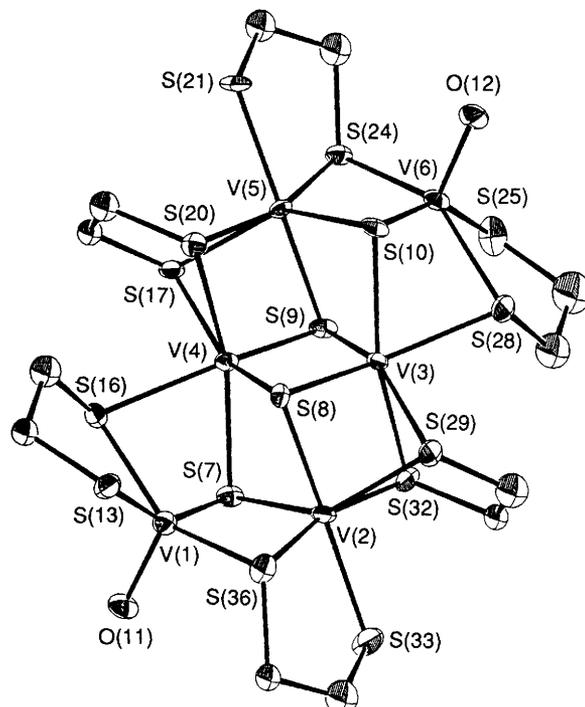


Fig. 1 ORTEP representation at the 50% probability level for the anion of complex **2**. Selected interatomic distances (Å): V(1)···V(2), 2.852(4); V(1)···V(4), 3.298(6); V(2)···V(3), 2.823(5); V(2)···V(4), 3.279(5); V(3)···V(4), 2.758(4); V(3)···V(5), 3.292(5); V(3)···V(6), 3.318(5); V(4)···V(5), 2.834(5); V(5)···V(6), 2.856(4); V(1)–O(11), 1.632(14); V(1)–S(7), 2.396(6); V(1)–S(13), 2.393(6); V(1)–S(16), 2.375(6); V(1)–S(36), 2.411(6); V(2)–S(7), 2.328(6); V(2)–S(8), 2.418(6); V(3)–S(9), 2.298(5); V(3)–S(10), 2.407(6); V(4)–S(7), 2.370(6); V(4)–S(8), 2.323(5); V(4)–S(9), 2.356(5); V(5)–S(9), 2.408(6); V(5)–S(10), 2.335(6); V(6)–O(12), 1.648(13); V(6)–S(10), 2.399(6); V(6)–S(24), 2.395(6); V(6)–S(25), 2.360(6); V(6)–S(28), 2.381(6).

‡ Crystal data: C₃₉H₈₉N₄O₂S₁₆V₆, *M* = 1464.95, monoclinic, *P*2₁, *a* = 12.477(2), *b* = 15.635(3), *c* = 16.536(3) Å, β = 108.40(1)°, *U* = 3060.96 Å³, *Z* = 2, *D*_c = 1.59 g cm⁻³, λ = 0.71069 Å, *T* = –173 °C, 6° ≤ 2θ ≤ 45°, *R*(*R*_w) = 0.0648 (0.0602) for 3289 unique reflections with *F* > 3σ(*F*). The structure was solved by MULTAN and refined by full-matrix least squares. The V, S and O atoms were refined anisotropically, the C atoms were refined isotropically, and the hydrogen atoms were introduced in fixed, idealized positions. The final difference Fourier map was essentially featureless, the largest residual peaks being about 1e Å⁻³ near one of the cations. Since this is an acentric space group, an attempt was made to assign the correct absolute structure; however, the difference in *R* values was insignificant. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

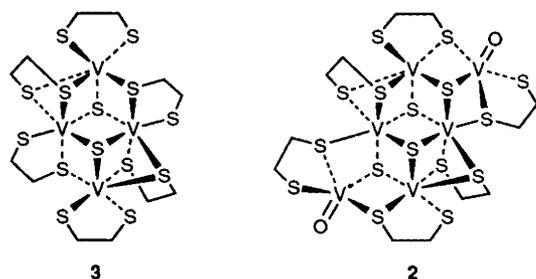
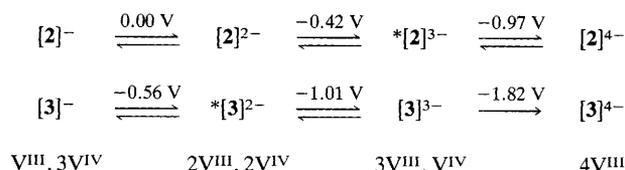


Fig. 2

atoms are thus in a VOS_4 environment, as suggested for surface-bound $[\text{VO}]^{2+}$ groups, and possess distorted square-pyramidal geometry. The VO bond lengths (1.63–1.65 Å) are slightly longer than normally observed (≤ 1.60 Å) but are similar to (but still longer than) previous values observed for $[\text{VO}]^{2+}$ units with four thiolate/sulfide ligands (1.62–1.63 Å).^{8,9}

The structure of complex **2** is related to that of previously-reported $(\text{NEt}_4)_2[\text{V}_4\text{S}_2(\text{edt})_6]$ (**3**).¹⁰ In fact, **2** may be considered as the anion of **3** with two $[\text{VO}]^{2+}$ and two S^{2-} groups added to the latter. This is shown in Fig. 2. Thus, conversion of **2** to **3** can be imagined by removal of two $[\text{VO}]^{2+}$ groups and S(7) and S(10), followed by S(13) and S(25) occupying the bridging positions of the latter. We have previously described how the structure of **3** can be considered a fragment of the CdI_2 -like, sheet structure of VS_2 ,¹⁰ emphasizing again the analogy of **2** to $[\text{VO}]^{2+}$ units bound on a V sulfide surface. Unlike complex **1**, which gives an EPR signal at $g \approx 2$ in fluid solution, with the eight-line hyperfine structure characteristic of coupling with the $I = 7/2$ ^{51}V nucleus,¹¹ complex **2** does not display a noticeable EPR signal even at liquid N_2 temperatures, suggesting the $[\text{VO}]^{2+}$ units are not electronically isolated; the six paramagnetic V centres in the anion are likely strongly interacting.

It should be pointed out that **3** formally possesses 2V^{III} , 2V^{IV} whereas **2** possesses 3V^{III} , 3V^{IV} . The $[\text{VO}]$ groups are undoubtedly V^{IV} {terminal $[\text{VO}]$ groups are unknown at the V^{III} level, and $[\text{VO}]^{3+}$ (*i.e.* V^{V}) would require the presence of V^{II} in the core, which seems very unlikely} and the V_4 core of **2** is thus 3V^{III} , V^{IV} . Examination of structural parameters reveals no good justification for a trapped-valence description, however, a conclusion already reached for **3**. The oxidation level of **3** is thus not exactly analogous to that of the core of **2**; note, however, that **3** displays reversible redox processes, and we have determined by cyclic voltammetry that the same is also true for **2** in MeCN. The redox processes for **2** and **3** are summarized in Scheme 2, with potentials vs. SCE and the oxidation level of the V_4 core indicated; the oxidation levels in the isolated complexes are indicated with an asterisk.



Scheme 2

We do not believe the $[\text{VO}]^{2+}$ groups are involved in the observed reduction or oxidation processes, for reasons stated earlier and because it seems highly unlikely that $[\text{VO}]^{2+}$ groups would be oxidized in preference to V^{III} centres.

The addition of the $[\text{VO}]^{2+}$ and extra S^{2-} units to the core of **3** thus results in the core being stabilized at a lower oxidation level (**2**) and all reductions becoming more facile (*i.e.* less negative potentials). This suggests that binding of $[\text{VO}]^{2+}$ units to the surface of the growing V sulfide phase during HDM may in fact assist in the reduction of the V ions to the level in the products, V_2S_3 and V_3S_4 .[§]

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