

## Synthesis of Tetranuclear and Pentanuclear Vanadium-Oxide-Carboxylate Aggregates

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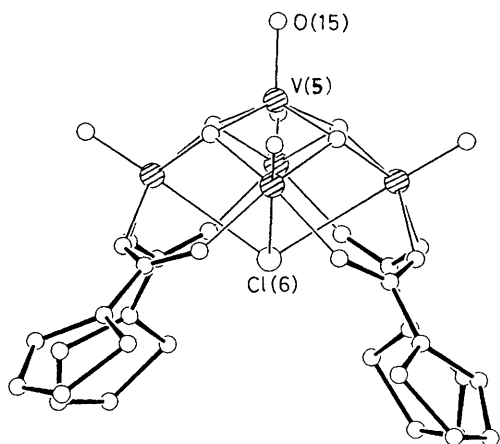
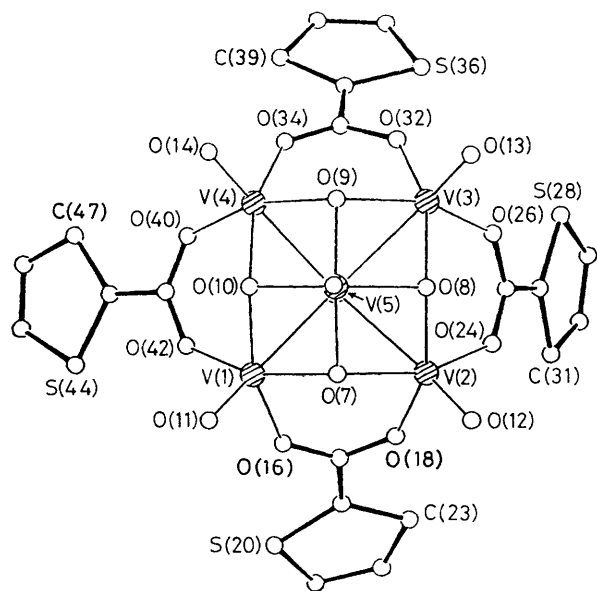
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Treatment of  $\text{VOCl}_4^{2-}$  with  $\text{tca}^-$  ( $\text{tca}^-$  = thiophene-2-carboxylate) under aerobic conditions leads to formation of  $[\text{V}_5\text{O}_9\text{Cl}(\text{tca})_4]^{2-}$ , whereas if  $\text{AgNO}_3$  is also present, the product is  $[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]^{2-}$ ; the two anions have been isolated as  $\text{NR}_4^+$  salts and their unusual structures elucidated by crystallographic methods.

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As part of our continuing interest in the structural and reactivity chemistry of vanadium with oxygen and/or sulphur ligands,<sup>1-4</sup> we have been exploring the chemistry of this metal with functionalized thiophene groups. In one such experiment, treatment of the hydrolytically-sensitive salt

$(\text{PhCH}_2\text{NEt}_3)_2[\text{VOCl}_4]$  with two equivalents of  $\text{Na}(\text{tca})$  ( $\text{tca}^-$  = thiophene-2-carboxylate) in MeCN under aerobic conditions led to formation of a deep green solution stable to prolonged exposure to air. A precipitate of NaCl was removed by filtration and the filtrate concentrated by slow evaporation



**Figure 1.** Top and side views of the anion of complex (1). Selected distances (Å) and angles (°) are: V(1)···V(2) 3.485(2), V(2)···V(3) 3.472(2), V(3)···V(4) 3.483(2), V(4)···V(1) 3.484(2), V(5)···V(1) 2.893(2), V(5)···V(2) 2.906(2), V(5)···V(3) 2.908(2), V(5)···V(4) 2.898(2), Cl(6)–V(1) 2.959(3), Cl(6)–V(2) 2.974(3), Cl(6)–V(3) 3.067(3), Cl(6)–V(4) 2.880(3), V(1)–O(11) 1.588(6), V(2)–O(12) 1.589(6), V(3)–O(13) 1.588(6), V(4)–O(14) 1.599(6), V(5)–O(15) 1.597(6), V(5)–O(7) 1.874(6), V(5)–O(8) 1.880(6), V(5)–O(9) 1.894(6), V(5)–O(10) 1.885(6), O(7)–V(1) 1.953(6), O(7)–V(2) 1.961(6), O(8)–V(2) 1.963(6), O(8)–V(3) 1.948(6), O(9)–V(3) 1.954(6), O(9)–V(4) 1.970(6), O(10)–V(4) 1.967(6), O(10)–V(1) 1.985(6), V(1,2,3,4)–O(16,18,24,26,32,34,40,42) 2.005(6)–2.033(6); V(1)–Cl(6)–V(2) 71.94(6); V(1)–Cl(6)–V(4) 73.24(6); V(2)–Cl(6)–V(3) 70.14(6) V(3)–Cl(6)–V(4) 71.61(6).

to produce dark green crystals. These were collected by filtration, washed with tetrahydrofuran (THF) and ether and dried in air. The product was identified by analysis† and

crystallography‡ as  $(\text{PhCH}_2\text{NEt}_3)_2[\text{V}_5\text{O}_9\text{Cl}(\text{tca})_4]\cdot\text{MeCN}$  (1) in 75–80% yield. The structure of the anion is shown in Figure 1, and consists of a  $\text{V}_5$  square pyramid with a  $\mu_3\text{-O}^{2-}$  bridging each triangular face and a  $\mu\text{-tca}^-$  bridging each basal edge. Each V possesses a terminal, multiply-bonded oxide. The basal V atoms V(1–4) are additionally ligated to Cl(6), which is  $\mu_4$  and serves to cap the basal face of the  $\text{V}_5$  pyramid. Vanadium atoms V(1–4) are thus six co-ordinate in contrast to five co-ordinate V(5). The V–Cl(6) linkages are long (av. 2.970 Å) and *trans* to the terminal VO units; the complete anion has virtual  $C_{4v}$  symmetry, excluding thiophene rings.

The length of the V–Cl linkages suggested that (1) might be obtainable with Cl(6) absent. For this reason, essentially the identical reaction was carried out in the presence of 4 equiv. of  $\text{AgNO}_3$  to sequester all available  $\text{Cl}^-$  as  $\text{AgCl}$ .§ A much more intense dark green solution was now obtained which proved unstable to prolonged exposure to air. Exposure to  $\text{O}_2/\text{water}$  was thus carefully controlled,¶ and the dark green solution after filtration was found to produce essentially black crystals upon maintenance for several days under anaerobic conditions. The product was identified as  $(\text{NEt}_4)_2[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]\cdot\text{H}_2\text{O}$  (2) in 40% yield.† The structure of the anion‡ (Figure 2) can be considered as derived from that of (1) by removal of the apical V(5) leaving a square with  $\mu\text{-tca}^-$  and  $\mu\text{-O}^{2-}$  bridges on each edge. In addition, the  $\mu_4\text{-Cl}^-$  of (1) is replaced by a remarkable and unique example of a  $\eta^1, \mu_4\text{-NO}_3^-$  ( $\text{V}-\text{O}_{\text{av}} = 2.688$  Å). Prior examples of  $\mu_4\text{-NO}_3^-$  have

‡ Crystal data for (1):  $\text{C}_{48}\text{H}_{59}\text{N}_3\text{O}_{17}\text{S}_4\text{ClV}_5$ ,  $M = 1368.4$ , monoclinic,  $P2_1/c$ ,  $a = 20.607(4)$ ,  $b = 12.947(2)$ ,  $c = 22.523(4)$  Å,  $\beta = 101.59(1)^\circ$ ,  $U = 5886.62$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.544$  g cm<sup>-3</sup>,  $\lambda = 0.71069$  Å,  $T = -157^\circ\text{C}$ ,  $6^\circ \leq 2\theta \leq 45^\circ$ ,  $R(R_w) = 0.0843$  (0.0839) for 6036 unique reflections with  $F > 3.0\sigma(F)$ .

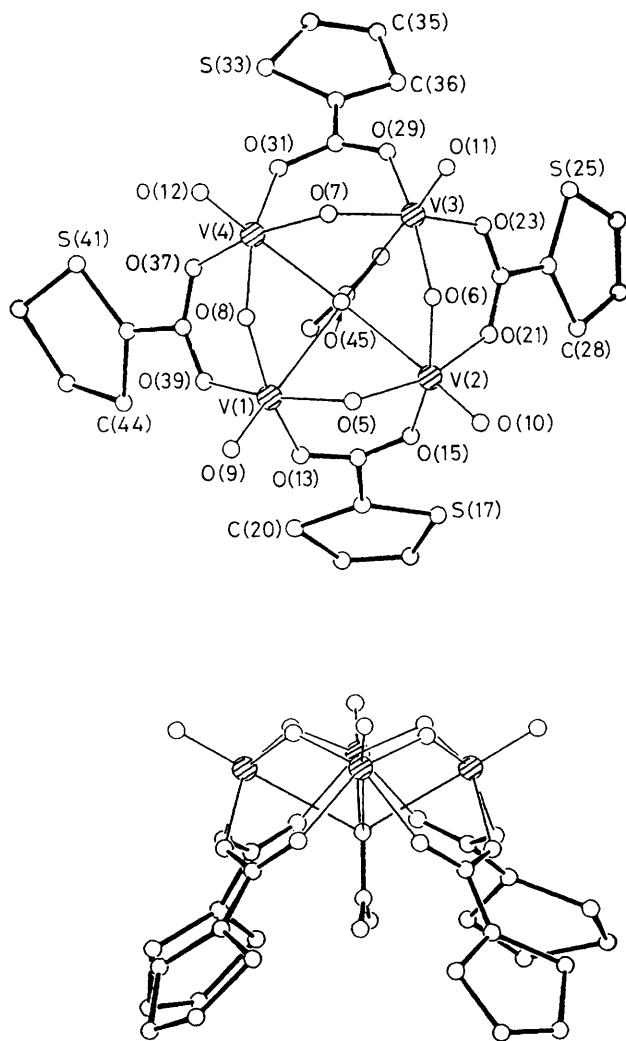
Crystal data for (2):  $\text{C}_{36}\text{H}_{54}\text{N}_3\text{O}_{20}\text{S}_4\text{V}_4$ ,  $M = 1180.8$ , orthorhombic,  $P2_12_12_1$ ,  $a = 18.638(3)$ ,  $b = 23.557(4)$ ,  $c = 12.731(2)$  Å,  $U = 5589.69$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.403$  g cm<sup>-3</sup>,  $\lambda = 0.71069$  Å,  $T = -139^\circ\text{C}$ ,  $6^\circ \leq 2\theta \leq 45^\circ$ ,  $R(R_w) = 0.0947$  (0.0953) for 2947 unique reflections with  $F > 3.0\sigma(F)$ . Both structures were solved by a combination of direct methods (MULTAN) and Fourier techniques, and refined by full-matrix least squares. For (1), the S and C atoms in the 3 position of the thiophene rings are disordered. Refinement of occupancies gave 70% occupancy of the positions shown in Figure 1. In addition, one of the two cations shows evidence of disorder. The type of disorder was not obvious, however, and no attempt was made to model it. The final difference Fourier showed five peaks in the 1–2  $e/\text{Å}^3$  range, all in the vicinity of the disordered cation. All other residual peaks were less than 1  $e/\text{Å}^3$ . For (2), disorder in the S/C positions was again observed in three of the rings, and refinement gave 45, 47 and 84% occupancies for S(17), S(25) and S(41), respectively, as shown in Figure 2. In contrast, S(33) refined with 100% occupancy but the C atoms in the 3 and 4 positions were not well-behaved and were best modelled with two positions for each atom with 50% occupancy. The solvate  $\text{H}_2\text{O}$  oxygen was found well separated from other peaks. The oxygen occupied two positions 1.8 Å apart and with an occupancy ratio of 75:25%. The final difference Fourier synthesis showed no peak greater than 0.6  $e/\text{Å}^3$ . The above disorder problems and the relatively poor data for (2) are the cause of the relatively high values of  $R(R_w)$  for the two complexes. The poor quality of the data for (2) also prevented determination of the absolute structure for the non-centrosymmetric space group.

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.

§ Treatment of (1) with  $\text{AgNO}_3$  yields a white precipitate of  $\text{AgCl}$ . However, we have been unable to-date to isolate a clean product from the resulting deep green filtrate.

¶ After preliminary experimentation, we have found that performing the reaction under anaerobic conditions but using solvents as received provides sufficient  $\text{H}_2\text{O}/\text{O}_2$  to facilitate formation of (2).

† The analytical data for complex (1) (C, H, N, S, Cl, V) and (2) (C, H, N, S, V) were satisfactory.

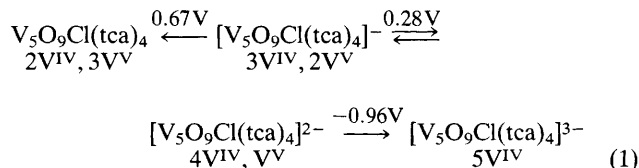


**Figure 2.** Top and side views of the anion of complex (2). Selected distances (Å) and angles (°) are: V(1) ··· V(2) 3.287(5), V(2) ··· V(3) 3.288(5), V(3) ··· V(4) 3.268(5), V(4) ··· V(1) 3.292(5), O(45)–V(1) 2.793(14), O(45)–V(2) 2.680(13), O(45)–V(3) 2.716(13), O(45)–V(4) 2.564(13), O(5)–V(1) 1.783(12), O(5)–V(2) 1.851(12), O(6)–V(2) 1.792(11), O(6)–V(3) 1.803(11), O(7)–V(3) 1.821(13), O(7)–V(4) 1.799(12), O(8)–V(4) 1.780(12), O(8)–V(1) 1.808(11), V(1,2,3,4)–O(13,15,21,23,29,31,37,39) 1.961(14)–2.073(13); V(1)–O(45)–V(2) 73.8(3), V(1)–O(45)–V(4) 75.7(4), V(2)–O(45)–V(3) 75.1(3), V(3)–O(45)–V(4) 76.4(3).

always involved  $\eta^2$  or  $\eta^3$  ligation modes. The most related previous example is the  $\eta^1, \mu_3\text{-NO}_3^-$  in  $\text{Cu}_4(\text{NO}_3)_2(\text{OH})_6$ .<sup>5</sup> The complete anion in complex (2) has virtual  $C_{2v}$  symmetry, excluding thiophene rings.

In both complexes (1) and (2) it is obvious that, relative to the  $\text{VOCl}_4^{2-}$  starting material, both additional oxide incorporation and metal oxidation have occurred. Charge considerations necessitate a mixed-valence description for (1) and (2) of  $(4\text{V}^{\text{IV}}, \text{V}^{\text{V}})$  and  $(\text{V}^{\text{IV}}, 3\text{V}^{\text{V}})$ , respectively. The unique metal V(5) is assigned as the  $\text{V}^{\text{V}}$  centre in (1) but there is no clear justification for a trapped-valence description of (2). Previous examples of  $\text{V/O/RCO}_2^-$  species are few, being the trinuclear  $[\text{V}_3\text{O}]$ -containing complexes possessing the commonly encountered 'basic carboxylate' structure.<sup>6,7</sup> These possess metal oxidation states of  $\text{V}^{\text{III}}$  and/or  $\text{V}^{\text{IV}}$ , although examples of  $\text{V}^{\text{II}}$ ,  $2\text{V}^{\text{III}}$  are also known, namely  $\text{V}_3\text{O}(\text{O}_2\text{CR})_6(\text{L})_3$  (R = Me,  $\text{CF}_3$ ; L = pyridine, THF).<sup>7</sup>

The redox properties of both complexes in MeCN have been investigated by the cyclic voltammetric (CV) and differential pulse polarography (DPP) techniques. Complex (1) displays one irreversible reduction and two oxidations, the first of which is reversible. These processes and their potentials (vs. ferrocene/ferricinium)<sup>||</sup> are summarized in equation (1). In contrast, complex (2) shows only very broad, grossly irreversible and ill-defined CV features.



Finally, it is interesting to note that complexes (1) and (2) represent the first two members of what may well prove to be a large new class of higher oxidation state  $\text{V/O/RCO}_2^-$  aggregates, akin to the iso- and heteropolyvanadates.<sup>8–11</sup> Indeed, (1) and (2) are structurally related to some of these polyvanadates, for they possess units which are recognizable sub-structures of aggregates such as  $\text{PV}_{14}\text{O}_{42}^{9-}$ ,  $\text{V}_3\text{Mo}_{10}^{6-}$  and  $\text{V}_{18}\text{O}_{42}^{12-}$ . Detailed structural comparisons (not possible here) show that the carboxylates in (1) and (2) lie at positions occupied by  $[\text{VO}_4]$  groups in the polyvanadates and thus terminate higher oligomer formation.

We are currently investigating the reactivity chemistry of (1) and (2) and seeking access to additional structural types. This work and the results of e.s.r. and magnetochemical studies will be reported in due course.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

Received, 2nd May 1989; Com. 9/01845J

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<sup>||</sup> The quoted potentials are DPP peak potentials. For the reversible process,  $i_{a/c} \approx 1$  and  $E_a - E_c = 80$  mV at 100 mV/s in the CV. The oxidation potential calculated from the CV was 0.26 V.