Synthesis of Tetranuclear and Pentanuclear Vanadium-Oxide-Carboxylate Aggregates

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Treatment of $\text{VOCl}_4^{2-}$ with $\text{tca}^- \ (\text{tca}^- = \text{thiophene-2-carboxylate})$ 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 $[\text{V}_4\text{O}_6(\text{NO}_3)(\text{tca})_4]^{2-}$; the two anions have been isolated as $\text{NR}_4^+$ salts and their unusual structures elucidated by crystallographic methods.

As part of our continuing interest in the structural and reactivity chemistry of vanadium with oxygen and/or sulphur ligands, 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 $\text{Na(tca)}$ ($\text{tca}^- = \text{thiophene-2-carboxylate}$) 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.
dried in air. The product was identified by analysis and filtration, washed with tetrahydrofuran (THF) and ether to produce dark green crystals. These were collected by crystallization and then treated with a suitable solvent to obtain the final product.

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(5) 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(16) 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) - O(12) 1.618, V(1) - O(13) 1.624, V(2) - O(14) 1.618, V(2) - O(15) 1.624, V(3) - O(16) 1.618, V(3) - O(17) 1.624, V(4) - O(18) 1.618, V(4) - O(19) 1.624.

To produce dark green crystals, these were collected by filtration, washed with tetrahydrofuran (THF) and then dried in air. The product was identified by analysis and filtration, washed with tetrahydrofuran (THF) and ether to produce dark green crystals. These were collected by crystallization and then treated with a suitable solvent to obtain the final product.

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

‡ Crystal data for (1): C6H26N2O5S2Cl2V2, M = 1263.4, monoclinic, P21/c, a = 20.670(4), b = 12.947(2), c = 22.532(4) Å, β = 101.59(1)°, U = 5886.62 Å³, Z = 4, D = 1.54 g cm⁻³, λ = 0.71069 Å, T = −157°C, 6θ ≤ 20°, R(R,) = 0.0843 (0.0839) for 6036 unique reflections with F > 3σ(F).

Crystal data for (2): C6H26N2O5S2V2, M = 1180.8, orthorhombic, P221/21, a = 18.638(3), b = 23.557(4), c = 12.731(2) Å, U = 5389.69 Å³, Z = 4, D = 1.403 g cm⁻³, λ = 0.71069 Å, T = −139°C, 6θ ≤ 20°, R(R,) = 0.0947 (0.0953) for 2947 unique reflections with F > 3σ(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 Å⁻³ range, all in the vicinity of the disordered cation. All other residual peaks were less than 1 e 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 H₂O 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 Å⁻³. The above disorder problems and the relatively poor data for (2) are the cause of the relatively high values of R(R,) 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 AgNO₃ yields a white precipitate of AgCl. However, we have been unable to date to isolate a clean product from the reaction mixture.
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/ferricyanide) are summarized in equation (1). In contrast, complex (2) shows only very broad, grossly irreversible and ill-defined CV features.

\[
\text{V}_5\text{O}_9\text{Cl(tca)}_4^{2-} + 0.67\text{V} \rightarrow \text{V}_5\text{O}_9\text{Cl(tca)}_4^{3-} + 0.28\text{V}
\]

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 V/O/RCO$_2^-$ aggregates, akin to the iso- and heteropolyvanadates. 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 PV$_{14}$O$_{42}$$^{9-}$, V$_3$Mo$_{20}$$^{6-}$ and V$_{18}$O$_{42}$$^{12-}$. Detailed structural comparisons (not possible here) show that the carboxylates in (1) and (2) lie at positions occupied by [VO$_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.

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References

The quoted potentials are DPP peak potentials. For the reversible process, $\Delta E = 0.53 V$.