The Preparation and Crystal Structure of a Salt with the $[\{VO_2(O_2CMe)\}_4(NO_3)]$ Monoanion

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Acetonitrile is oxidised to acetate by vanadium(v) oxide trinitrate in the presence of tetraphenylarsonium chloride and the crystal structure of the main reaction product, $(C_6H_5)_4As[V_4O_8(O_2CMe)_4(NO_3)]$ **1**, is solved; the anion consists of a tetravanadium(v) crown containing a guest nitrate group in a μ_4 mode.

On mixing a solution of vanadium(v) oxide trinitrate in dry acetonitrile, containing the yellow nitrile adduct,[1] with a colourless solution of tetraphenylarsonium chloride in acetonitrile at 20 °C there is a change of colour to red. Such a colour change is reminiscent of that observed when a solution of $VO(NO_3)_3$ in MeCN reacts with silver chloride.[1] When a concentrated equimolar mixture of $(C_6H_5)_4AsCl$ and $VO(NO_3)_3$ was treated gradually with $CFCl_3$ the solution formed some dark red block-like crystals as well as a small quantity of an off-white solid. Separation of the two types of crystals was effected by washing with acetonitrile which dissolved the off-white solid more rapidly. The off-white material was shown to be $(C_6H_5)_4AsNO_3$. Characterisation of the air-stable, red crystals by IR and Raman spectroscopy confirmed the presence of the $(C_6H_5)_4As^+$ cation and of a vanadyl (V^VO) group; in addition there were unexpected absorptions characteristic of coordinated acetate. The analytical data for vanadium and nitrogen were not consistent with a possible vanadium oxo nitrate anion salt and chloride was absent. A single-crystal X-ray diffraction study† demonstrated that the red solid is $(C_6H_5)_4As[\{VO_2(O_2CMe)\}_4(NO_3)]$ **1**, which composition is consistent with the elemental analyses; the product was obtained in 64% yield. The structure contains a tetrakis(μ-acetato μ-oxo oxovanadium) crown with all four vanadium(v) atoms linked to one oxygen of the nitrate anion, Fig. 1: this oxygen and the nitrogen atom lie on a twofold axis perpendicular to the V_4 plane. The V···O (nitrate) interactions [V(1)···O(9) 2.781(4) and V(2)···O(9) 2.566(4) Å] are *trans* to the V=O bonds thus creating a *pseudo*-octahedral environment around each vanadium. The attachment of O(9) of the nitrate group can thus be described as μ_4 (1L,4M).[2] Two crystallographically non-equivalent cations occupy $\bar{4}$ special positions thus giving the correct stoichiometry. The V–O distances and angles are very similar to those in the binuclear $[L_2V_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]I_2\cdot 2H_2O$, L = 1,4,7-trimethyl-1,4,7-triazacyclononane,[3] in which V^{III} is present.

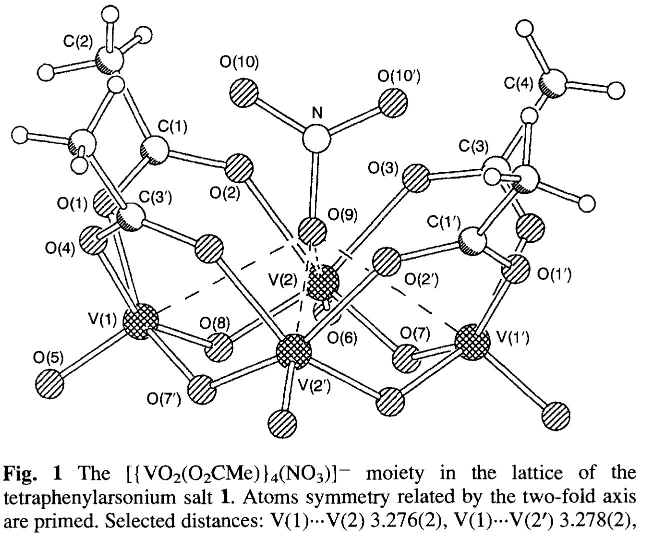

Fig. 1 The $[\{VO_2(O_2CMe)\}_4(NO_3)]^-$ moiety in the lattice of the tetraphenylarsonium salt **1**. Atoms symmetry related by the two-fold axis are primed. Selected distances: V(1)···V(2) 3.276(2), V(1)···V(2′) 3.278(2), V(1)···O(1) 1.991(4), V(1)···O(4) 1.998(4), V(1)···O(7′) 1.815(4), V(1)···O(8) 1.813(4), V(2)=O(2) 2.005(4), V(2)···O(3) 1.997(4), V(2)···O(7) 1.803(4), V(2)···O(8) 1.808(4), V(1)=O(5) and V(2)=O(6) 1.580(4), V(1)···O(9) 2.781(4), V(2)···O(9) 2.566(4), N–O(9) 1.345(7), N–O(10) 1.219(5) Å.

Compound **1** is the first example of a neutral polynuclear vanadium carboxylate to accommodate a guest anionic species inside the cavity. Work is in hand to determine the stability of the anionic aggregate in solution and to prepare related species containing other guest ions. Also of considerable interest is the neutral carboxylate species, a vanadyl acetate, $VO_2(O_2CMe)$, first obtained by Paul and Kumar[4] who described the compound as a yellow solid, readily hydrolysed by water. Preuss *et al.*[5] subsequently described this neutral compound as highly water-sensitive and also unstable in daylight. Compound **1** on the other hand undergoes very slow hydrolysis in both acidic and basic solution and is stable to both X-rays and to visible light. This contrasts with the properties of the complex formed by potassium 3,3-dimethylbutanoate with $[VO_2(O_2CH_2R)]_4$, R = Bu^t, in which potassium ion is the guest ion being coordinated by the eight carboxylate oxygens.[6] There is also a structure related to **1** in which the dianion consists of a tetravanadium($3V^VV^{IV}$) crown containing a guest nitrate group in a μ_4 mode.[7]

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Footnote

† *Crystal data* for: $C_{32}H_{32}AsNO_{19}V_4$, M = 1013.27, tetragonal, a = 15.988(2), c = 30.293(1) Å, U = 7743.6(7) Å^3, space group $I4_1/a$, Z = 8, $F(000)$ = 4064, Mo-Kα radiation, graphite monochromator, μ = 18.64 cm^{-1}, Siemens P4 diffractometer, room temperature, Wyckoff scan, $2\theta \leqslant 50°$, 3652 total data, 3393 unique, semi-empirical absorption correction (462 azimuthal scans of 40 reflections, T_{max} = 0.481, T_{min} = 0.327), 262 variables refined in full-matrix least squares against F^2 of 3392 data (SHELXL-93) to $wR(F^2)$ = 0.109; for 1509 data with $I > 2\sigma(I)$, $R(F)$ = 0.042, $\Delta\rho_{max}$ = 0.29 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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