

The Synthesis and Crystal Structures of the Tetraphenylarsonium Salts of $[V_2O_3(NO_3)_2X_4]^{2-}$, $X = Cl$ or NO_3

Stephen Arrowsmith,^a Michael F. A. Dove,^{*a} Martin N. Gibbons,^a Norman Logan^a and Andrei Batsanov^b

^a Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD

^b Department of Chemistry, University of Durham, Durham, UK DH1 3LE

The title compounds, $[Ph_4As]_2[V_2O_3(NO_3)_6]$ **1**, and $[Ph_4As]_2[V_2O_3Cl_4(NO_3)_2]$ **2**, crystallised from solution in the reaction of tetraphenylarsonium nitrate with $VO(NO_3)_3$ and $VOCl_3$, respectively, and the crystal structures of the dianions show that they are structurally related; the octahedral coordination of all vanadium atoms is achieved by two oxygens, a bidentate nitrate and two other monodentate groups, and an unusual feature of compound **2** is the presence of both chlorine and nitrate as ligands on vanadium(v).

The acetonitrile adduct of vanadium(v) oxotrinitrate¹ and the tetravanadium(v) crown anion, $[(VO_2(O_2CMe)_4(NO_3))^-]$,² are the only crystallographically characterised nitrates of vanadium(v) known. Vanadium in the oxide trinitrate has been shown to be seven-coordinate from the vibrational spectra,³ the dioxomononitrate has been poorly characterised⁴ and may not be stable at room temperature. Several other nitrate species have been identified by NMR spectroscopy in solution,⁵⁻⁷ only one of these, $V_2O_3(NO_3)_4$,⁷ is a binuclear species and is formally related to the two new dianions which have now been prepared and characterised for the first time.

The reaction of vanadium(v) oxide trinitrate and tetraphenylarsonium nitrate in dry acetonitrile produces an immediate colour change from yellow to orange. Reduction of the reaction solution to low volume followed by gradual addition of $CFCl_3$ by vapour phase diffusion yielded orange crystals of **1** in 75% yield. The orange crystals were found to be highly moisture-sensitive, turning black on exposure to air. Characterisation of **1** in the solid state by IR and Raman spectroscopy confirmed the presence of the Ph_4As^+ cation; in addition a band was observed at 960 cm^{-1} which was assigned to $\nu(V=O)$. A number of absorptions were observed in the high frequency region of the Raman spectrum associated with covalent nitrate coordination,⁸ too many, in fact, to accommodate just one mode of nitrate coordination; this was confirmed by single-crystal X-ray diffraction.† The structure of **1** comprises dimeric $[(NO_3)_3(O)VOV(O)(NO_3)_3]^{2-}$ anions, Fig. 1, possessing C_i crystallographic symmetry and tetrahedral Ph_4As^+ cations in general positions. The composition $[Ph_4As]_2[V_2O_3(NO_3)_6]$ is

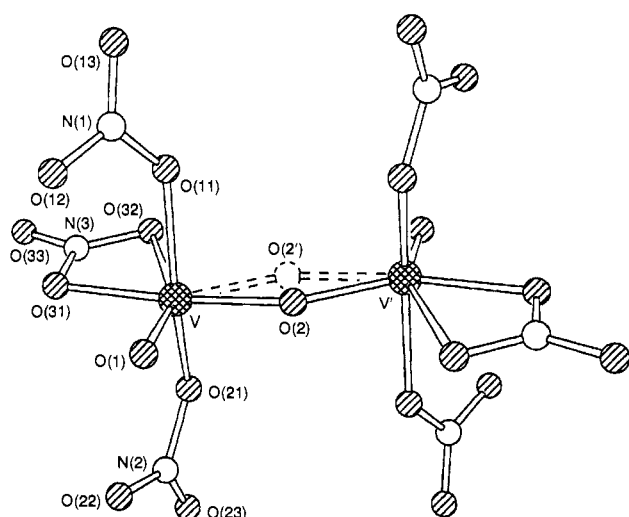


Fig. 1 The $[V_2O_3(NO_3)_6]^{2-}$ anion in the lattice of the tetraphenylarsonium salt **1**. Atoms symmetry related by the inversion centre are primed. Selected bond distances (Å): V–O(1) 1.555(6), V–O(31) 2.007(5), V–O(32) 2.360(6), V–O(2) 1.82(2), V–O(2') 1.78(2), V–O(11) 1.983(6), V–O(21) 1.915(5), N(3)–O(31) 1.279(7), N(3)–O(32) 1.235(8), N(3)–O(33) 1.223(8), N(1)–O(11) 1.275(8), N(1)–O(12) 1.222(9), N(1)–O(13) 1.162(9).

consistent with elemental analyses. Each vanadium atom has a severely distorted octahedral coordination with two monodentate and one bidentate nitrate group, one terminal and one bridging oxo ligand. The latter, O(2), is disordered with equal probability over two positions related *via* the inversion centre. The presence of both monodentate and bidentate nitrate coordination modes is unusual within the realms of anhydrous metal nitrate chemistry.^{1,9} The bidentate nitrate groups coordinate in an unsymmetrical fashion,⁸ the difference between the distance of the metal atom and the two coordinated oxygen atoms of the nitrate group being 0.35 Å.

Compound **2** is produced as the minor product of the reaction of vanadium(v) oxide trichloride and tetraphenylarsonium nitrate in dry acetonitrile. The reaction solution, initially dark red due owing to the presence of the $VOCl_3 \cdot 2MeCN$ adduct,¹⁰ after removal of most of the solvent and slow addition of $CFCl_3$ by vapour phase diffusion, becomes nearly colourless. Crystals of two different colours were observed, the major component being yellow and the minor purple. The yellow crystals were characterised as $[Ph_4As][VO_2Cl_2]$, a species first isolated by Dehnicke.¹¹ Analysis of the minor component, **2**, by IR and Raman techniques revealed the presence of Ph_4As^+ cations, covalent nitrate bands and V–Cl stretches. A single-crystal X-ray diffraction study demonstrated the structure of **2** to be $[Ph_4As]_2[V_2O_3Cl_4(NO_3)_2]$, consistent with the elemental analyses.† The structure contains $[(NO_3)Cl_2(O)VOV(O)Cl_2(NO_3)]^{2-}$ anions, Fig. 2, possessing C_i crystallographic symmetry and tetrahedral Ph_4As^+ cations. The coordination sphere of each vanadium atom is severely distorted from octahedral, each being coordinated by two chlorines, one terminal and one bridging oxygen atom and one bidentate nitrate group. As in **1** the bidentate nitrate coordination is unsymmetrical and the bridging oxo ligand O(2) is disordered with equal probability over two positions related by the inversion centre. Compound **2** is the first example of a mixed halonitrate species of vanadium(v) to be isolated.

Grateful thanks are due to J. A. K. Howard for the use of the crystallographic data collection and computing facilities at the University of Durham and to C. H. Schwalbe for the

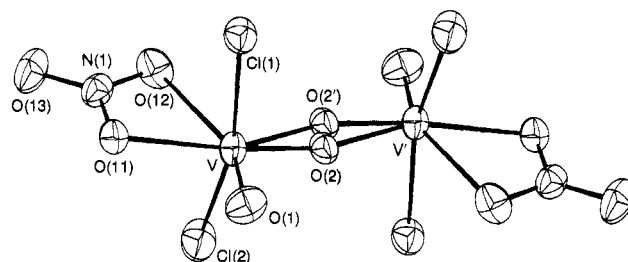


Fig. 2 The $[V_2O_3Cl_4(NO_3)_2]^{2-}$ anion in the lattice of the tetraphenylarsonium salt **2**. Atoms related by the inversion centre are primed. Selected atomic distances (Å): V–O(1) 1.566(4), V–Cl(1) 2.291(2), V–Cl(2) 2.272(2), V–O(2) 1.70(6), V–O(2') 1.83(5), V–O(12) 2.381(4), V–O(11) 2.063(3), N(1)–O(12) 1.240, N(1)–O(11) 1.300(5), N(1)–O(13) 1.197(5).

crystallographic data collected at the Joint Crystallography Unit of the Universities of Aston and Birmingham for compounds **1** and **2**, respectively.

Received, 7th June 1995; Com. 5/03671B

Footnote

† Crystal data for $C_{48}H_{40}As_2N_6O_{21}V_2$, $M = 1288.58$, triclinic, $a = 9.580(1)$, $b = 10.782(2)$, $c = 13.631(2)$ Å, $\alpha = 92.15(1)$, $\beta = 107.10(1)$, $\gamma = 96.97(1)^\circ$, $U = 1331.8(3)$ Å³, space group $P\bar{1}$, $Z = 1$, $F(000) = 650$, Mo-K α radiation, graphite monochromator, $\mu = 16.7$ cm⁻¹, Rigaku AFC6S 4-circle diffractometer, 293 K, Wyckoff scans, $2\theta \leq 50^\circ$, 5360 reflections, 4551 unique ($R_{int} = 0.017$), absorption correction ($T_{max} = 0.749$, $T_{min} = 0.611$),¹² the structure was solved by direct methods (SHELX),¹³ 361 variables being refined by full-matrix least squares against F^2 of all data with two-term Chebyshev weighting scheme (SHELXL-93)¹⁴ to $wR(F^2) = 0.129$ for all data, for 2752 data with $F^2 > 2\sigma(F^2)$, $R(F) = 0.059$, $\Delta\rho_{max} = 0.65$, $\Delta\rho_{min} = -0.43$ e Å⁻³.

For $C_{48}H_{40}As_2Cl_4N_2O_9V_2$, $M = 1182.39$, monoclinic, $a = 10.176(1)$, $b = 17.691(2)$, $c = 13.955(2)$ Å, $U = 2475$ Å³, space group $P2_1/c$, $Z = 2$, $F(000) = 1188$, Mo-K α radiation, graphite monochromator, $\mu = 19.6$ cm⁻¹, Enraf Nonius CAD4 4-circle diffractometer, 293 K, 5654 reflections, 3832 unique ($R_{int} = 0.031$). Absorption correction (DIFABS, $T_{min} = 0.859$, $T_{max} = 1.066$).¹⁵ The structure was solved by direct methods (SIR92)¹⁶ and 307 variables were refined by full-matrix least squares against F^2 (CRYSTALS)¹⁷ to $wR(F^2) = 0.070$ for all data, for 2730 data with $F^2 > 3\sigma(F^2)$, $R(F) = 0.034$, $\Delta\rho_{max} = 0.53$, $\Delta\rho_{min} = -0.37$ 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.

References

- 1 F. W. B. Einstein, E. Enwall, D. M. Morris, D. Sutton and C. C. Addison, *Inorg. Chem.*, 1971, **10**, 678.
- 2 S. Arrowsmith, M. F. A. Dove, N. Logan and M. Y. Antipin, *J. Chem. Soc., Chem. Commun.*, 1995, 627.
- 3 C. C. Addison, D. W. Amos, D. Sutton and W. H. H. Hoyle, *J. Chem. Soc. A*, 1967, 808.
- 4 J. A. Panontin, A. K. Fischer and E. A. Heintz, *J. Inorg. Nucl. Chem.*, 1960, **14**, 145.
- 5 R. C. Hibbert, *J. Chem. Soc., Chem. Commun.*, 1985, 317.
- 6 R. C. Hibbert, *J. Chem. Soc., Dalton Trans.*, 1986, 751.
- 7 R. C. Hibbert, N. Logan and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1986, 369.
- 8 C. C. Addison, N. Logan and S. C. Wallwork, *Chem. Soc. Quart. Rev.*, 1971, **25**, 289.
- 9 C. C. Addison, *Chem. Rev.* 1980, **80**, 21.
- 10 H. Funk, W. Weiss and M. Zeising, *Z. Anorg. Allg. Chem.*, 1958, **296**, 36.
- 11 D. Fenske, A. F. Shihada, H. Schwab and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1980, **471**, 140.
- 12 J. de Meulenaer and H. Tompa, *Acta Crystallogr., Sect. A*, 1965, **19**, 1014.
- 13 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 14 G. M. Sheldrick, SHELXL-93, Program for the refinement of Crystal Structures, Univ. of Göttingen, Germany, 1993.
- 15 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 16 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
- 17 D. J. Watkin, J. R. Carruthers and D. W. Betteridge, CRYSTALS User's Guide, Chemical Crystallography Laboratory, Oxford, England, 1985.