

Investigations of the V/O/RAsO₃²⁻ System: Solvothermal Synthesis and Crystal and Molecular Structure of [(V₂O₃)(Ph₆As₆O₁₄)]

José Salta, Yuan-Da Chang and Jon Zubieta*

Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA

The reaction of PPh₄[VO₂Cl₂] with PhAsO₃H₂ in acetonitrile for 36 h at 100 °C and autogenous pressure yields [(V₂O₃)(Ph₆As₆O₁₄)], an unusual cluster with a {V₂O₃}⁴⁺ core straddled by the hexadentate ligand {Ph₆As₆O₁₄}⁴⁻ which forms *via* thermally induced condensation of PhAsO₃H₂ groups.

While the solid phases of the V/O/phosphate and V/O/arsenate systems have been extensively investigated,^{1,2} the corresponding systems incorporating organic substituents, V/O/RPO₃²⁻ and V/O/RAsO₃²⁻, remain relatively unexplored. Recent studies of the V/O/RPO₃²⁻ system have revealed a wealth of molecular clusters.³⁻⁹ In contrast, the chemistry of the V/O/RAsO₃²⁻ system is limited to two examples, the mixed-valence cluster [V₆O₁₀(PhAsO₃)₄(PhAsO₃H)₂]²⁻ and the vanadium(v) cluster [V₁₀O₂₄(RAsO₃)₃]⁴⁻.¹⁰ While the hexanuclear species forms exclusively in a variety of organic solvents under conventional conditions, we have found that the chemistry of the V/O/RAsO₃²⁻ system may be dramatically extended by exploiting the techniques of solvothermal synthesis,¹¹ which allow the isolation of metastable compositions not accessible through conventional or even hydrothermal techniques. The potential of this approach is demonstrated by the isolation of [(V₂O₃)(Ph₆As₆O₁₄)], an unusual vanadium(v) cluster incorporating a {V₂O₃}⁴⁺ unit coordinated to a {Ph₆As₆O₁₄}⁴⁻ ligand and resulting in an unusually large As : V ratio of 3 : 1.

The reaction of PPh₄[VO₂Cl₂] with PhAsO₃H₂ in a 1 : 2 molar ratio in acetonitrile for 36 h at 100 °C and autogenous pressure yields bright orange needles of [(V₂O₃)(Ph₆As₆O₁₄)] in 42% yield.† The infrared spectrum exhibits a medium intensity band at 907 cm⁻¹ assigned to ν(V=O) and a very strong broad band at 837 cm⁻¹, associated with ν(As–O–As) of the ligand and ν(V–O–As). While reaction of PhAsO₃H₂ alone under the conditions of this study yields no oligomeric species, solvothermal reaction of PhAsO₃H₂ in the presence of small amounts of vanadate produces a mixture of oligomeric materials, confirming that the polyarsenate unit {Ph₆As₆O₁₄}⁴⁻ is formed in a metal-mediated thermally induced process.

The X-ray crystallographic study of [(V₂O₃)(Ph₆As₆O₁₄)][‡] reveals that the structure consists of discrete neutral clusters, as illustrated in Fig. 1. The structure may be described as a {V₂O₃}⁴⁺ unit coordinated to six oxygen donors of the novel {Ph₆As₆O₁₄}⁴⁻ ligand and weakly associated with a seventh oxygen of this unit. The novel polyorganoarsenate moiety {Ph₆As₆O₁₄}⁴⁻ consists of a central {Ph₂As₂(μ-O)₂}⁴⁺ core, bonded to two symmetrically bridging (PhAsO₃)²⁻ groups and two unidentate (PhAsO₃)²⁻ units. Thus, the two central As sites, As(5) and As(6), are six-coordinate {PhAsO₅} centres, with relatively long As–O bond distances consistent with the higher coordination number. While six-coordinate As^V is relatively unusual, it has been documented in a variety of species, such as As₂O₅,¹³ [As₂F₁₀O]²⁻,¹⁴ and [As₂F₈O₂]²⁻.¹⁵

Alternatively, the structure may be viewed as a {V₂O₃}⁴⁺ unit and a {Ph₂As₂O₂}⁴⁺ group bridged by four (PhAsO₃)²⁻ groups. Each vanadium(v) site exhibits distorted octahedral geometry through coordination to a terminal oxo-group, a bridging oxo-group, three oxygen donors from each of three organoarsenate units, and weak interaction with the central oxo-group O(16) of the cluster, which assumes a quadruply bridging mode between the vanadium centres and As(5) and As(6). While the O(16)···V interaction contributes only 0.2 valence units to the oxygen bond valence,¹² this contribution to the total valence sum is significant and accounts for the lengthening of the As(5)–O(16) and As(6)–O(16) bond

lengths from the expected distances of *ca.* 1.79 Å to the observed 1.91 Å. Curiously, the {V₂O₃}⁴⁺ unit, while a common feature of V^V chemistry,¹⁷ is not observed in other V/O/RAsO₃²⁻ clusters reported to date.^{10,16}

The exploitation of solvothermal techniques has revealed a new member of the V/O/RAsO₃²⁻ system with an unexpected structure and incorporating a novel polyorganoarsenate unit. Modifications in reaction times, temperatures, fill volumes, templates, and vanadium precursors dramatically influence the product compositions obtained from the V/O/RAsO₃²⁻ system, leading to novel structural cores such as [V₁₂O₁₄(OH)₄(PhAsO₃)₁₀]⁴⁻ and [V₁₂O₁₄(H₂O)₂(PhAsO₃)₁₀(PhAsO₃H)₄]⁴⁻,¹⁶ and confirming that an extensive structural chemistry is accessible. The richness of the chemistry reflects not only the structural diversity inherent in the linking of vanadium square pyramids and octahedra with organoarsenate tetrahedra but the potential for the formation of polyorganoarsenate units to contribute to the closure of unusual V/O/As shells.

This work was supported by NSF Grant 9119910.

Received, 21st September 1993; Com. 3/056751

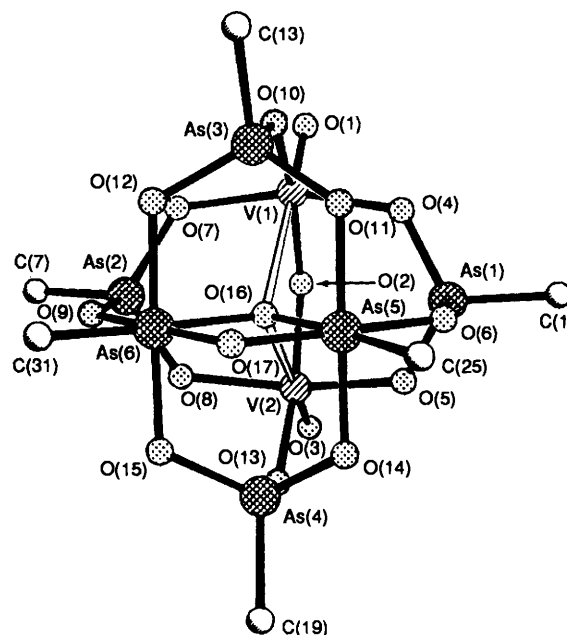


Fig. 1 A view of the structure of [(V₂O₃)(Ph₆As₆O₁₄)], showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.581(10), V(1)–O(2) 1.813(9), V(1)–O(As) 1.885(9), 1.917(9), 1.873(9), V(1)–O(16) 2.95(1), V(2)–O(3) 1.568(10), V(2)–O(2) 1.790(9), V(2)–O(As) 1.922(9), 1.912(9), 1.936(9); V(2)–O(16) 2.97(1), As(5)–O(16) 1.904(9), As(6)–O(16) 1.909(8), As(5)–O(17) 1.792(8), As(6)–O(17) 1.791(9), As(5)–O(11) 1.894(9), As(5)–O(14) 1.894(9), As(5)–O(6) 1.855(9), As(6)–O(9) 1.845(9), As(6)–O(12) 1.902(9), As(6)–O(15) 1.910(9), As(1)–O (av.) 1.70(1), As(2)–O (av.) 1.70(1), As(3)–O (av.) 1.69(1), As(4)–O (av.) 1.68(1), O(1)–V(1)–O(16) 176.0(5), O(3)–V(2)–O(16) 175.6(5).

Footnotes

† Satisfactory elemental analyses

‡ X-ray data for $[(V_2O_3)(Ph_6As_6O_{14})]$: monoclinic, space group $P2_1/c$, $a = 10.963(2)$, $b = 10.664(2)$, $c = 35.931(6)$ Å, $\beta = 96.15(2)^\circ$, $V = 4177(2)$ Å³, $Z = 4$, $D_c = 2.045$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 52.39$ cm⁻¹; structure solution and refinement based on 3351 reflections with $2\theta \leq 45^\circ$ and $I_0 \geq 3\sigma(I_0)$ converged at $R = 0.0499$.

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 See for example: V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1596 and references cited therein; H.-Y. Kang, S.-L. Wang, P.-P. Tsai and K.-H. Lii, *J. Chem. Soc., Dalton Trans.*, 1993, 1525 and references cited therein; G. Villeneuve, K. S. Suh, P. Amoros, N. Casan-Pastor and D. Beltran-Porter, *Chem. Mater.*, 1992, **4**, 108 and references cited therein.
- 2 See for example: M. A. G. Aranda, J. P. Attfield, S. Bruque and M. Martinez-Lara, *Inorg. Chem.*, 1992, **31**, 1045; P. Amoros, A. Beltran-Porter; G. Villeneuve and D. Beltran-Porter, *Eur. J. Solid State Chem.*, 1992, **29**, 257.
- 3 Q. Chen, J. Salta and J. Zubieta, *Inorg. Chem.* 1993, **32**, 4485.
- 4 Q. Chen and J. Zubieta, *Angew. Chem., Int. Ed. Engl.* 1993, **32**, 261.
- 5 Y. Chang, J. Salta and J. Zubieta, *Angew. Chem.*, 1994, **106**, 347.
- 6 J. Salta, Y. Chang, Q. Chen and J. Zubieta, *Angew. Chem.*, in the press.
- 7 G. H. Huan, A. J. Jacobson and V. W. Day, *Angew. Chem.*, 1991, **103**, 426.
- 8 G. Huan, V. W. Day, A. J. Jacobson and D. P. Goshorn, *J. Am. Chem. Soc.*, 1991, **113**, 3188.
- 9 A. Müller, K. Hovemeier and R. Rohlfing, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1192.
- 10 M. I. Khan, Y. Chang, Q. Chen, H. Hope, S. Parkin, D. P. Goshorn and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1197.
- 11 M. Figlarz, *Chim. Scr.*, 1988, **28**, 3.
- 12 I. D. Brown and D. Alternatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
- 13 M. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 214.
- 14 W. Haase, *Acta Crystallogr., Sect. B.*, 1974, **30**, 1722.
- 15 W. Haase, *Chem. Ber.*, 1974, **107**, 1009.
- 16 M. I. Khan, Q. Chen, J. Zubieta, manuscript in preparation.
- 17 L. V. Boas and J. C. Pessoa, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, p. 453.