Inorganica Chimica Acta, *212* (1993) 199–206

Hydrothermal syntheses and structures of reduced and mixed valence polyoxovanadium clusters with capped cage cores: $K_3[H_{12}(AsO)_2(AsO_4)V_6^{IV}V_6^{V}O_{36}]\cdot 12H_2O$ and $Rb_5[(As_2O)_4(VO)_2V_{12}^{IV}O_{36}Cl]\cdot 2H_2O$

M. Ishaque Khan, Qin Chen and Jon Zubieta*

Department of Chemistry, Syracuse University, Syracuse, NY 13244 (USA)

(Received February 1, 1993)

Abstract

The reaction of $NaVO_3$, As_2O_3, KSCN, $H_2NC(CH_2OH)_3$, H_2SO_4 and H_2O yielded black crystals of $K_3[H_{12}(AsO)_2(AsO_4)V_{12}O_{36}]\cdot 12H_2O$ (**1**) The structure of **1** consists of a $\{(AsO_4)V_{12}O_{36}\}$ α-Keggin core capped on two tetragonal faces by {AsO} units. Crystal data for $H_{36}O_{54}K_3V_{12}As_3$: cubic space group $Pm3m$, $a = 10.583(2)$ Å, $V = 1185.3(9)$ Å^3, $Z = 1$, $D_{calc} = 2.664$ g cm^{-3}. Structure solution and refinement based on 193 reflections with $I_0 \geq 3\sigma(I_0)$ converged at a discrepancy value of 0.0628. The hydrothermal reaction of a mixture of V_2O_5, V_2O_3, V (−325 mesh), $H_5As_3O_{10}$, RbOH and H_2O in the mole ratio 5:5:5.3.6.4:333 for 60 h at 200 °C produced lustrous black crystals of $Rb_5[As_8V_{14}O_{42}Cl]\cdot 2H_2O$ (**2**). The structure of **2** is similar to those of the general class of 'reduced' or V(IV) clusters of the type $[V_{(18-p)}As_{2p}O_{42}(X)]^{m-}$, where $X = SO_3$, SO_4, H_2O and $p = 3$, 4, which are topologically related to the elongated square gyrobicupola and extended cage core of $[V_{18}O_{42}(X)]^{n-}$. Thus, the structure of **2** is constructed from the framework of 24 bridging oxo groups by the capping of four tetragonal faces by $\{As_2O\}$ groups and of fourteen faces by {VO} groups and by encapsulation of a Cl^- anion. Crystal data for $As_8ClH_4O_{44}Rb_5V_{14}$: monoclinic $P2_1$, $a = 13.141(2)$, $b = 13.525(2)$, $c = 13.412(2)$ Å, $\beta = 92\ 59(1)°$, $V = 2381.3(12)$ Å^3, $Z = 2$, $D_{calc} = 3\ 46$ g cm^{-3}. Structure solution and refinement based on 4518 reflections with $I_o \geq 3\sigma(I_o)$ converged at $R = 0.0623$.

Introduction

While the chemistry of the polyoxoanions in general is extensive [1], the structural chemistry of the larger polyoxovanadium anions has only recently witnessed significant expansion [2–31]. These polyanions are of continuing interest by virtue of their unique structural and topological properties [32, 33] and as a consequence of their inorganic host–guest characteristics [34].

While the earlier examples of polyoxovanadium clusters, such as $[PV_{14}O_{42}]^{9-}$ [2] and $[V_{18}O_{42}]^{12-}$ [3] adopt classical cage/cluster structures, recent investigations have expanded the structural chemistry to include not only novel types of cages but basket, ring, bowl and tire structures [33]. Many of these latter structural types reveal characteristics of inorganic host–guest chemistry, with the polyoxovanadium framework encapsulating anionic and even neutral organic substrates. Furthermore, the structures of many of these assemblies can only be explained if the host is constructed about the guest or captive entity in the condensation reaction in solution via a template effect [34].

A remarkably fertile area for the linking of fundamental inorganic units into molecular and supramolecular structures is the V/As/oxide system. Both mixed valence V(IV)/V(V) and reduced V(IV) polyoxoanion frameworks with encapsulated and/or capping As(V) or As(III) have been described, as well as several solid state phases related to the V/P/O system [35, 36]. During our investigations of the hydrothermal chemistry of vanadium oxides with As(V) and As(III) under reducing conditions, we isolated and characterized two new members of the V/As/O system of molecular anions, $K_3[H_{12}(AsO)_2(AsO_4)V_{12}O_{36}]\cdot 12H_2O$ (**1**) and $Rb_5[(As_2O)_4(VO)_2V_{12}O_{36}Cl]\cdot 2H_2O$ (**2**). The molecular anion of **1** exhibited an $\{(AsO_4)V_{12}O_{36}\}$ α-Keggin core capped by two {AsO} groups to give a structure reminiscent of that of the V(V) cluster $[(PO_4)(VO)_2V_{12}O_{36}]^{9-}$ [2]. Complex **2** is a member of the $[V_{18-p}As_{2p}O_{42}(X)]^{m-}$ class of reduced clusters [18] and displays a structure based on the elongated square gyrobicupola of the cage defined by 24 bridging oxygens

---

*Author to whom correspondence should be addressed

0020-1693/93/$6.00

with fourteen faces capped by {VO} centers and four faces capped by {As_2O} moieties.

Experimental

Reagent grade chemicals were used throughout; vanadium(III) oxide (Aldrich), vanadium(V) oxide (Aldrich), and vanadium metal (−325 mesh, Cerac).

Preparation of $K_3[H_{12}(AsO)_2(AsO_4)V_{12}O_{36}]\cdot 12H_2O$ (1)

Sodium metavanadate (10 mmol) and arsenic(III)oxide (2 mmol) were dissolved in water (50 ml) at 70 °C. To this solution, maintained at 70 °C, were added $H_2NC(CH_2OH)_3$ (3 mmol) and KSCN (20 mmol). The pH of the resulting light yellow solution was 8.0, which was adjusted to 4.6 by the addition of 2 M H_2SO_4. The dark green solution which was produced by this treatment was maintained at 70 °C for 22 h. The resulting mixture was filtered while hot, and the filtrate was allowed to stand for two weeks at room temperature, whereupon dark green cubic crystals of **1** were collected in 25% yield. *Anal.* Calc. for $H_{36}O_{54}K_3V_{12}As_3$: H, 1.94; K, 6.31. Found: H, 1.79; K, 6.92%. Thermogravimetric analysis shows a weight loss of *c.* 12% between 110 and 150 °C, while the theoretical weight loss for 12 H_2O molecules is 11.6%. Potentiometric titrations are consistent with the presence of six V(IV) sites. IR (KBr pellet, cm^{-1}): 960(vs), 831(s).

Preparation of $Rb_5[(As_2O)_4(VO)_2V_{12}O_{36}Cl]\cdot 2H_2O$ (2)

Method a: A mixture of V_2O_5, V_2O_3, NH_4VO_3, V (−325 mesh), $H_5As_3O_{10}$, NH_4Cl, RbCl and H_2O in the mole ratio 10:5:5:5:10:3:5:5:300 was heated for 60 h at 200 °C at autogenous pressure in a Parr acid digestion bomb. Brown crystals and a black amorphous powder were filtered from the yellow solution. The brown crystals were separated mechanically from the amorphous impurity and air dried. Yield based on V: 35%.

Method b: In a more straightforward synthesis, a mixture of V_2O_5, V_2O_3, V (−325 mesh), $H_5As_3O_{10}$, RbOH and H_2O in the mole ratio 5:5:5:3:6.4:333 was heated for 48 h at 200 °C. After cooling for 12 h at room temperature, lustrous dark crystals of **2** were collected in 40% yield.

Anal. Calc. for $H_4O_{44}ClV_{14}As_8Rb_5$: Cl, 1.43; As, 24.2. Found: Cl, 1.13; As, 23.9%. IR (KBr pellet, cm^{-1}): 977(vs), 794(sh), 761(s), 705(vs), 633(s), 550(m). UV–Vis (solid reflectance, nm): 260, 345, 560.

X-ray crystallographic studies

Compounds **1** and **2** were studied using a Rigaku AFC5S diffractometer. The crystal parameters and experimental conditions are summarized in Table 1. See also 'Supplementary material'.

TABLE 1 Summary of crystal data and experimental conditions for the structures of 1 and 2

	1	**2**
Formula	$H_{36}O_{54}K_3As_3V_{12}$	$H_4O_4ClAs_8V_{14}Rb_5$
Molecular weight	1901.6	2482.0
Space group	*Pm*3*m*	*P*2$_1$
a (Å)	10.583	13.141(2)
b (Å)		13.525(2)
c (Å)		13.412(2)
β (°)		92.59(1)
V ($Å^{-3}$)	1185.3(8)	2381.3(12)
Z	1	2
D_{calc} (g cm^{-3})	2.664	3.462
Crystal dimensions	0.25 × 0.21 × 0.22	0.31 × 0.33 × 0.42
Radiation	Mo Kα	Mo Kα
Absorption coefficient (cm^{-1})		133.7
2θ Range (°)	2 to 55	2 to 55
No. data, $I_o \geq 3\sigma(I_o)$	193	4518
R	0.0628	0.0623
R_w	0.0677	0.0729
Largest residual (e/$Å^3$)	0.43	0.73

In the case of **1**, the crystallographic symmetry associated with the space group *Pm*3*m* produces a disordered structure. However, attempts to refine the structure in the acentric alternative resulted in unsatisfactory temperature factors and higher residuals. Consequently, the centric but disordered model was chosen rather than the acentric, ordered model. As a result, structure **1** exhibits a number of partial occupancies. The As-bound oxygen O1, of the $V_3As(\mu_4\text{-}O)$ unit, is statistically disordered over eight sites and is assigned a site occupancy of 0.5. Similarly, the two face-capping As–O4 groups are disordered over the six tetragonal {V_4O_4} faces of the α-Keggin framework, resulting in a site occupancy of 0.333. No anomalies were encountered in the solution and refinement of structure **2**.

The structures were solved by direct methods and refined by full-matrix least-squares (see 'Supplementary material'). Tables 2 and 3 list atomic positional parameters for **1** and 2, respectively. Table 4 lists selected bond lengths and angles for **1** while Table 5 presents bond lengths for **2**.

Results and discussion

The reaction of $NaVO_3$, $H_2NC(CH_2OH)_3$ and KSCN for 22 h at 70 °C yields $K_3[H_{12}(AsO)_2(AsO_4)V_{12}O_{36}]\cdot 12H_2O$ (**1**) as lustrous dark green crystals. The IR spectrum of **1** exhibits a band at 960 cm^{-1} assigned to $\nu(V{=}O)$ and a feature at 831 cm^{-1} characteristic

TABLE 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1**

	x	y	z	U_{eq}[a]
As(1)	0	0	0	21(1)
As(2)	3609(8)	0	0	46(2)
K	5000	5000	1418(14)	53(4)
V	2349(2)	0	2349(2)	32(1)
O(1)	919(12)	919(12)	919(12)	24(3)
O(2)	3416(6)	3416(6)	0	42(3)
O(3)	3031(9)	1228(7)	1228(7)	72(3)
O(4)	5000	2581(11)	2581(11)	75(5)
O(5)	5000	0	0	73(10)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}[a]
As(1)	221(2)	9378	4039(2)	10(1)
As(2)	258(2)	9094(3)	1619(2)	12(1)
As(3)	−246(2)	13471(3)	1054(2)	12(1)
As(4)	−256(2)	13771(3)	3467(2)	11(1)
As(5)	4894(2)	10454(3)	658(2)	11(1)
As(6)	4596(2)	12825(3)	319(2)	12(1)
As(7)	4608(2)	13391(2)	4769(2)	10(1)
As(8)	4859(2)	11019(2)	5112(2)	10(1)
V(1)	2614(3)	9397(4)	868(3)	12(1)
V(2)	2539(3)	8767(3)	3032(3)	10(1)
V(3)	2578(3)	9912(3)	4961(3)	9(1)
V(4)	2497(3)	12062(3)	5572(3)	10(1)
V(5)	2162(3)	12942(3)	4407(3)	9(1)
V(6)	1879(3)	14555(3)	2266(3)	11(1)
V(7)	2141(3)	13430(4)	343(3)	11(1)
V(8)	2511(3)	11303(4)	−257(3)	12(1)
V(9)	527(3)	11214(4)	479(3)	13(1)
V(10)	−404(3)	11384(4)	2546(3)	12(1)
V(11)	529(3)	11741(4)	4672(3)	9(1)
V(12)	4424(3)	9807(3)	2982(3)	9(1)
V(13)	5135(3)	11964(3)	2733(3)	10(1)
V(14)	3993(3)	13949(3)	2410(3)	10(1)
Rb(1)	7401(4)	9359(5)	1640(4)	75(2)
Rb(2)	3487(5)	6666(5)	1471(4)	83(2)
Rb(3)	3133(3)	9127(4)	−1992(3)	56(1)
Rb(4)	7590(3)	11978(4)	4745(3)	50(1)
Rb(5)	−449(3)	6504(4)	2426(3)	51(1)
Cl(1)	2311(16)	11614(19)	2622(16)	81(6)
O(1)	2734(14)	8479(16)	115(13)	19(4)
O(2)	3479(13)	9170(13)	2069(12)	13(3)
O(3)	3305(13)	12526(13)	126(13)	14(3)
O(4)	3574(12)	10409(13)	374(12)	12(3)
O(5)	1649(13)	10337(14)	313(13)	15(4)
O(6)	2661(14)	7625(15)	3200(14)	19(4)
O(7)	1557(12)	9272(12)	4007(12)	10(3)
O(8)	3466(12)	9490(13)	3952(12)	10(3)
O(9)	2685(13)	9175(14)	5905(13)	18(4)
O(10)	1613(13)	10943(14)	5231(13)	14(3)
O(11)	3532(12)	11028(13)	5288(12)	13(3)
O(12)	2430(15)	12290(15)	6722(14)	22(4)
O(13)	1437(12)	12813(13)	4899(12)	9(3)
O(14)	3319(12)	13110(12)	4978(12)	10(3)
O(15)	2069(14)	14849(14)	5189(13)	20(4)
O(16)	1030(12)	14114(13)	3366(12)	11(3)
O(17)	2935(12)	14298(12)	3296(12)	11(3)
O(18)	1051(12)	13795(13)	1228(12)	13(3)
O(19)	2911(12)	14084(14)	1364(12)	14(3)
O(20)	2029(14)	14125(15)	−615(13)	20(4)
O(21)	1427(13)	12198(14)	24(12)	14(3)
O(22)	1676(14)	15700(14)	2131(14)	19(4)
O(23)	−280(15)	11041(16)	−448(15)	26(4)
O(24)	1581(13)	9002(14)	1852(12)	25(5)
O(25)	99(12)	10395(13)	1622(12)	10(3)
O(26)	−133(13)	12197(14)	1390(13)	14(4)
O(27)	−1582(14)	11247(15)	2568(14)	22(4)
O(28)	−107(14)	12453(14)	3501(14)	17(4)
O(29)	117(13)	10646(13)	3726(12)	11(3)
O(30)	−291(13)	11806(14)	5499(13)	16(4)
O(31)	5383(13)	9075(14)	3146(12)	16(4)

(continued)

of ν(As=O). The hydrothermal reaction of V_2O_5, V_2O_3, vanadium metal, $H_5As_3O_{10}$, RbOH and H_2O for 60 h at 200 °C yields shiny black crystals of $Rb_5[(As_2O)_4(VO)_2V_{12}O_{36}Cl]\cdot 2H_2O$ (**2**). The IR spectrum of **2** exhibits bands at 977 and 633 cn^{-1} assigned to ν(V=O) and to ν(As–O), respectively.

The syntheses both exhibit a marked dependence of reducing conditions, such that the presence of KSCN in the case of **1** and of vanadium metal in the case of **2** are absolutely essential to product formation. The introduction of reduced metal centers into polyanion frameworks appears to expand dramatically the accessible structural chemistry of this class of clusters. This feature is particularly evident in the emerging class of reduced and mixed valence polyoxovanadium clusters described by Muller *et al.* [10–19]. Furthermore, many of these expanded cluster types retain structural motifs associated with classical polyanion prototypes, such as the Keggin core structure $\{M_{12}O_{36}\}$. While 'oxidized' Keggin clusters with all metal sites in the d^0 configuration generally exhibit unreactive oxo centers, reduction of the metal centers increases the basicity of the doubly-bridging oxo groups of the core and promotes both protonation of these sites and reactions with other electrophilic groups which 'cap' various faces of the parent core. Such structural expansion is apparent in the reduced and mixed valence polyoxomolybdenum clusters based on Keggin and Dawson cores, such as $[(C_5Me_5Rh)_8(Mo_{12}{}^{V}O_{36})(Mo^{VI}O_4)]^{2+}$ [37], $[H_{12}(Mo^{VI}O_3)_4(Mo_{12}{}^{V}O_{36})(NaO_4)]^{7-}$ [38], $[H_4As_2(Mo_8{}^{V}Mo_4{}^{VI}O_{36})(AsO_4)]^{1-}$ [39] and $[As_2\{(Mo_9O_{27})(AsO_4)\}_2]^{8-}$ [40], and in a number of polyoxovanadium clusters exhibiting Keggin or Keggin-derived cores [18].

The structure of the anion of **1** consists of the hypothetical $\{AsV_{12}O_{40}\}$ α-Keggin core capped on two of six tetragonal $\{V_4O_4\}$ faces by $\{AsO\}$ groups, as shown in Fig. 1. The structure is reminiscent of that of $[PV_{14}O_{42}]^{7-}$ which consists of the $\{PV_{12}O_{40}\}$ α-Keggin

TABLE 3. (*continued*)

	x	y	z	U_{eq}[a]
O(32)	4844(13)	10760(13)	1938(12)	12(3)
O(33)	4821(13)	10981(14)	3770(13)	17(4)
O(34)	6345(13)	12105(14)	2824(13)	18(4)
O(35)	4660(13)	12847(14)	1642(13)	15(4)
O(36)	4573(13)	13069(14)	3474(13)	16(4)
O(37)	4759(14)	14873(14)	2310(14)	20(4)
O(38)	−145(13)	8854(14)	2859(12)	15(3)
O(39)	−711(12)	13934(13)	2202(12)	13(3)
O(40)	5144(12)	11634(13)	167(12)	13(3)
O(41)	2514(12)	11102(15)	−1437(14)	23(4)
O(42)	5169(13)	12321(13)	5255(12)	14(4)
O(43)	5578(22)	7366(22)	1951(21)	53(7)
O(44)	2692(38)	6057(41)	−496(36)	120(16)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Selected bond lengths (Å) and angles (°) for **1**

As(1)–O(1)	1.684(21)	As(2)–V	2.927(5)
As(2)–O(3)	1.914(11)	As(2)–O(5)	1.520(9)
K–O(2)	2.806(11)	K–O(4)	2.840(8)
V–O(1)	2.352(11)	V–O(3)	1.902(4)
V–O(2D)	1.596(10)		
O(1)–As(1)–O(1A)	180.0(1)	O(1)–As(1)–O(1B)	109.5(1)
O(1A)–As(1)–O(1B)	70.5(1)	O(3)–As(2)–O(5)	114.1(4)
O(3)–As(2)–O(3B)	80.4(3)	O(3A)–As(2)–O(3B)	131.7(7)
O(5)–As(2)–O(3C)	114.1(4)	O(2)–K–O(4)	72.1(3)
O(2)–K–O(2A)	115.3(6)	O(4)–K–O(2A)	140.4(1)
O(2)–K–O(2B)	73.4(3)	O(4)–K–O(2B)	72.1(3)
O(1)–V–O(2D)	155.6(4)	O(3)–V–O(2D)	100.0(3)
O(1)–V–O(3B)	97.2(4)	O(3)–V–O(3B)	86.2(6)
O(3B)–V–O(3D)	160.1(6)	O(1E)–V–O(3E)	63.9(4)
O(3B)–V–O(3E)	90.3(6)	As(1)–O(1)–V	120.3(4)
V–O(1)–VB	96.8(6)	As(2)–O(3)–V	96.7(3)

core bicapped by two {V–O} units. The As centers are all in the As(V) oxidation state. The As(1) site which is trapped within the $\{V_{12}O_{40}\}$ core is tetrahedrally coordinated at 1.68(2) Å to four oxygens which bridge to three vanadium sites. The As(2) sites exhibit square pyramidal geometry through coordination to a terminal apical oxygen and to four doubly-bridging oxo groups associated with the $\{V_4O_4\}$ tetragonal faces of the α-Keggin core. The vanadium centers are octahedrally coordinated in the usual fashion to a terminal oxo group, the μ_4-oxo groups bridging to the central As, and to four doubly-bridging oxo groups.

Valence sum calculations [41] provide an average oxidation state of 4.45 for the vanadium centers, suggesting that six of twelve vanadium sites have been reduced to V(IV). Potentiometric titrations are also consistent with six V(IV) sites per cluster. Given such an oxidation state assignment, the overall cluster charge for the anion $[(AsO)_2(AsO_4)V_{12}O_{36}]^{n-}$ is −15. Since there are three K^+ cations present, charge balance requires that 12 oxygen sites of the cluster be protonated. The V–O3 distances of 1.91(1) Å are significantly longer than the distance range of 1.80–1.85 Å generally observed for unperturbed V–O–V distances, indicating

TABLE 5. Selected bond lengths (Å) for **2**

As(1)–O(7)	1.765(16)	As(1)–O(29)	1.769(17)
As(1)–O(38)	1.781(17)	As(2)–O(24)	1.757(17)
As(2)–O(25)	1.772(18)	As(2)–O(38)	1.798(17)
As(3)–O(18)	1.766(16)	As(3)–O(26)	1.785(18)
As(3)–O(39)	1.795(16)	As(4)–O(16)	1.763(16)
As(4)–O(28)	1.794(19)	As(4)–O(39)	1.787(16)
As(5)–O(4)	1.760(16)	As(5)–O(32)	1.769(17)
As(5)–O(40)	1.762(18)	As(6)–O(3)	1.752(17)
As(6)–O(35)	1.773(17)	As(6)–O(40)	1.779(18)
As(7)–O(14)	1.770(16)	As(7)–O(36)	1.790(18)
As(7)–O(42)	1.738(18)	As(8)–O(11)	1.770(17)
As(8)–O(33)	1.799(18)	As(8)–O(42)	1.816(18)
V(1)–V(2)	3.030(5)	V(1)–V(8)	2.987(7)
V(1)–O(1)	1.613(20)	V(1)–O(2)	1.952(17)
V(1)–O(4)	1.994(18)	V(1)–O(5)	1.922(18)
V(1)–O(24)	2.008(17)	V(2)–V(3)	3.014(6)
V(2)–V(12)	2.853(6)	V(2)–O(2)	1.906(17)
V(2)–O(6)	1.568(20)	V(2)–O(7)	1.999(17)
V(2)–O(8)	1.957(16)	V(2)–O(24)	2.002(17)
V(3)–V(4)	3.025(7)	V(3)–O(7)	2.007(16)
V(3)–O(8)	1.914(16)	V(3)–O(9)	1.612(19)
V(3)–O(10)	1.930(18)	V(3)–O(11)	1.999(18)
V(4)–V(5)	3.007(6)	V(4)–V(11)	2.837(5)
V(4)–O(10)	1.949(18)	V(4)–O(11)	1.999(18)
V(4)–O(12)	1.579(20)	V(4)–O(13)	1.917(17)
V(4)–O(14)	1.972(17)	V(5)–V(6)	2.995(5)
V(5)–O(13)	1.933(18)	V(5)–O(14)	2.015(16)
V(5)–O(15)	1.622(19)	V(5)–O(16)	2.008(16)
V(5)–O(17)	1.902(16)	V(6)–V(7)	3.028(6)
V(6)–V(14)	2.894(6)	V(6)–O(16)	1.981(16)
V(6)–O(17)	1.943(16)	V(6)–O(18)	2.011(17)
V(6)–O(19)	1.964(17)	V(6)–O(22)	1.581(20)
V(7)–V(8)	3.032(7)	V(7)–O(3)	1.990(18)
V(7)–O(18)	1.964(17)	V(7)–O(19)	1.886(17)
V(7)–O(20)	1.593(19)	V(7)–O(21)	1.951(18)
V(8)–V(9)	2.833(6)	V(8)–O(3)	2.010(18)
V(8)–O(4)	2.006(17)	V(8)–O(5)	1.912(19)
V(8)–O(21)	1.920(18)	V(8)–O(41)	1.605(19)
V(9)–V(10)	3.088(6)	V(9)–O(5)	1.914(19)
V(9)–O(21)	1.899(18)	V(9)–O(23)	1.614(20)
V(9)–O(25)	1.992(17)	V(9)–O(26)	2.027(18)
V(10)–V(11)	3.090(5)	V(10)–O(25)	1.958(18)
V(10)–O(26)	1.948(18)	V(10)–O(27)	1.561(19)
V(10)–O(28)	1.960(19)	V(10)–O(29)	1.967(17)
V(11)–O(10)	1.913(18)	V(11)–O(13)	1.893(17)
V(11)–O(28)	1.993(18)	V(11)–O(29)	2.008(17)
V(11)–O(30)	1.583(18)	V(12)–V(13)	3.086(7)
V(12)–O(2)	1.910(17)	V(12)–O(8)	1.901(16)
V(12)–O(31)	1.610(18)	V(12)–O(32)	1.998(18)
V(12)–O(33)	1.965(19)	V(13)–V(14)	3.096(6)
V(13)–O(32)	1.975(18)	V(13)–O(33)	1.981(19)
V(13)–O(34)	1.600(18)	V(13)–O(35)	1.968(18)
V(13)–O(36)	1.957(19)	V(14)–O(17)	1.929(16)
V(14)–O(19)	1.960(16)	V(14)–O(35)	2.033(19)
V(14)–O(36)	1.984(18)	V(14)–O(37)	1.614(20)

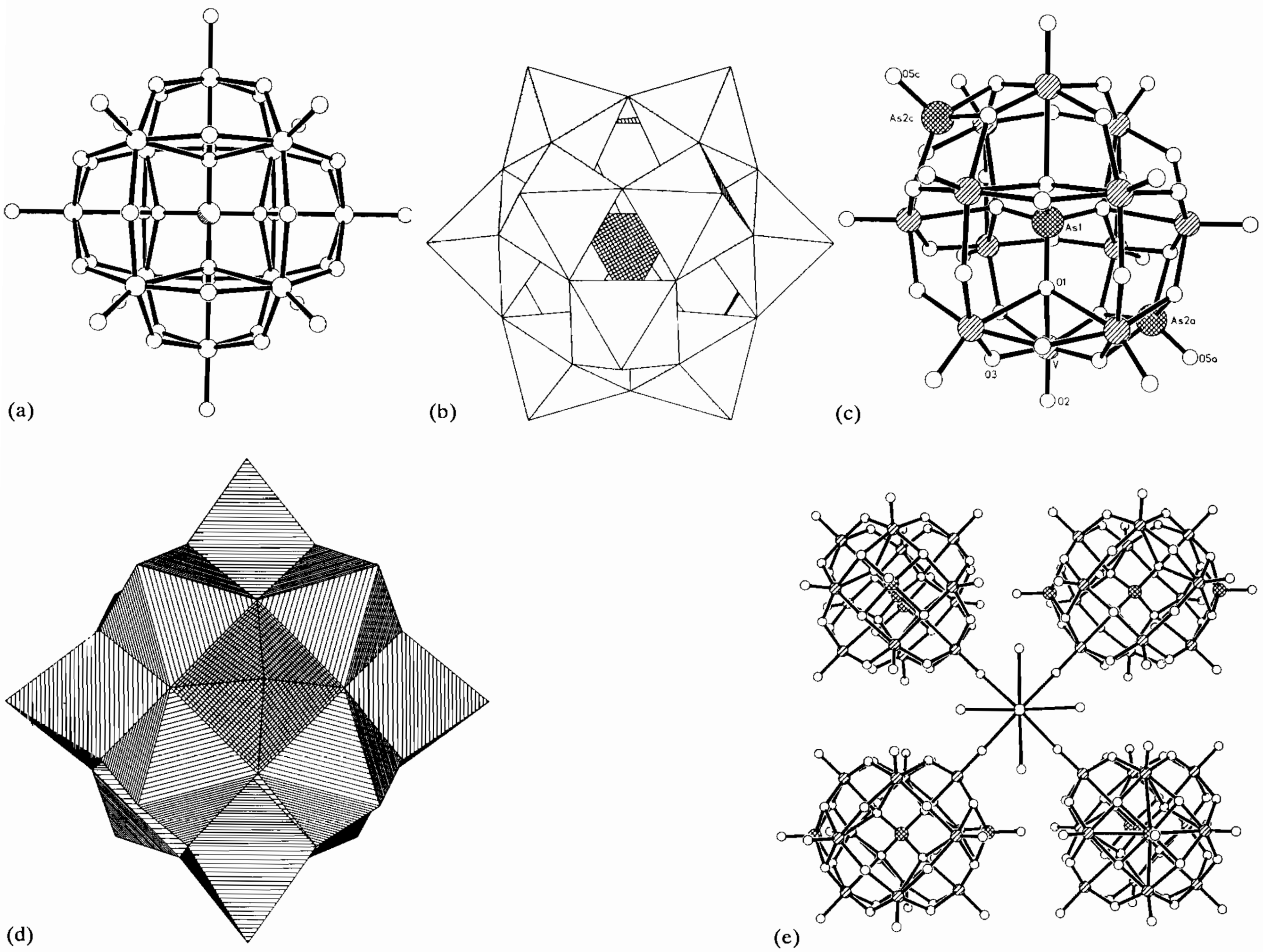

Fig. 1. (a) Ball and stick representation of the hypothetical $\{(AsO_4)(V_{12}O_{36})\}$ core with one of the tetragonal $\{V_4O_4\}$ faces projecting toward the reader. (b) Polyhedral representation of the $\{(AsO_4)(V_{12}O_{36})\}$ core viewed along a threefold axis (c) A perspective view of the structure of $[H_{12}(AsO)_2(AsO_4)(V_{12}O_{36})]^{3-}$ (**1**) showing the atom-labelling scheme. (d) A polyhedral representation of **1**. (e) The K^+ cation environment of **1**.

that these are likely protonation sites. The disorder of the As(2) and proton occupancies precludes further analysis of the protonation geometry.

The K^+ cation of **1** exhibits distorted square antiprismatic geometry through coordination to four water molecules at 2.84(1) Å and to O2 oxygens of four neighboring clusters with K–O2 distances of 2.81(1) Å, as shown in Fig. 1(e).

The structure of the anion of $Rb_5[(As_2O)_4(VO)_2V_{12}^{IV}O_{36}Cl]\cdot 2H_2O$ (**2**) is shown in Fig. 2. The structure belongs to the general class of reduced polyoxovanadium clusters $[V_{18-p}As_{2p}O_{42}X]^{m-}$, previously described by Müller and Doring for $X = SO_3$, SO_4 and H_2O and $p = 3$ and 4 [18]. The structure of the V(IV)/As(III)/O framework of **2** is essentially identical to those observed for this class, with the exception that the encapsulated species is chloride in this instance. The isolation of the chloride trapped species **2** emphasizes the dramatic versatility of the polyoxometalate cages in accommodating a variety of inorganic guest moieties and reinforces the importance of reaction conditions and cation identity in determining the ultimate cluster composition. It is noteworthy in this latter regard that the chloride derivative can only be isolated in the presence of Rb^+ cations, attempts at preparation with Na^+, K^+ and Cs^+ having failed. The crystallographically unique Rb^+ cations are bridged by oxo groups from neighboring anion clusters to form chains, shown in Fig. 2(d). These chains connect to form $\{Rb_8O_8\}$ rings, which in turn fuse to form the complex ring network illustrated in Fig. 2(f).

As previously discussed in some detail [18, 33], the structure of **2** is related to that of $[V_{18}O_{42}]^{12-}$ by the removal of four {VO} vertices and their replacement by $\{As_2O\}$ groups. The structure of **2** is thus related to the D_{4d} elongated square gyrobicupolar arrangement

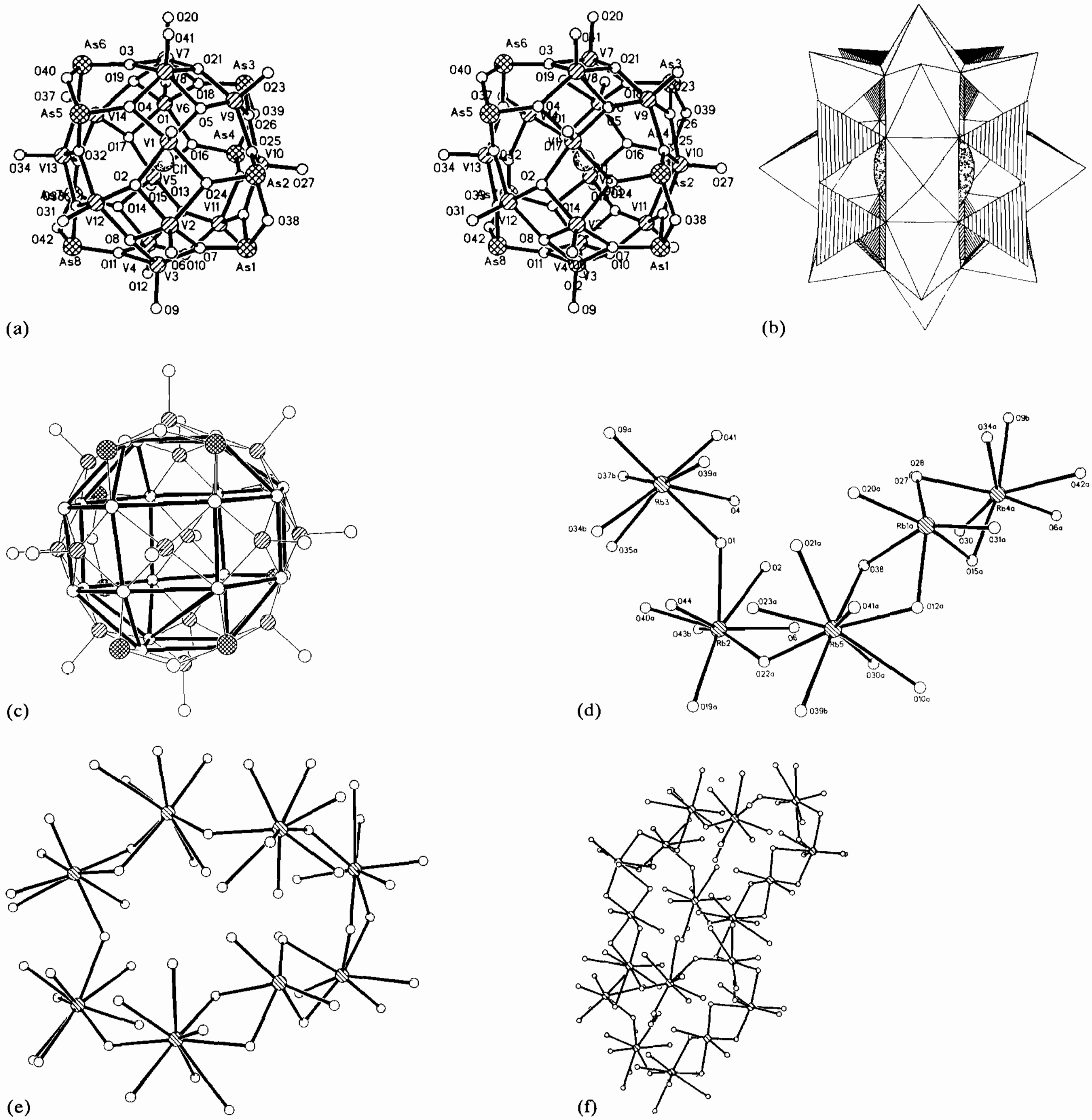

Fig. 2. (a) A stereo pair for the molecular anion of **2**, showing the atom-labelling scheme. (b) A polyhedral representation of the structure of **2**. (c) A view of the structure of the anion of **2**, showing the elongated square gyrobicupola of 24 oxygen atoms capped by 14 {VO} groups and 4 {ASO} groups. (d) The chain of Rb^+ cations formed through bridging oxo groups of adjacent anion clusters. (e) The linking of Rb^+ coordination spheres to form $\{Rb_8O_8\}$ rings (f) A view of the fusing of adjacent $\{Rb_8O_8\}$ rings.

of the 24 bridging oxo groups, capped on fourteen square faces by {VO} groups and on the remaining four square faces by $\{As_2O\}$ groups, as shown in Fig. 2(c).

The structure of **2** illustrates the recurrence of common structural themes in polyoxovanadium chemistry. Among these is the presence of square pyramidal $\{VO_5\}$ units sharing edges and aggregating to form spherical clusters and cluster topologies based on Platonic and Archimedean polyhedra [32]. Another feature common to a number of polyoxovanadium structures is the $\{V_8O_{24}\}$ belt, illustrated in Fig. 3, which is also found in $[V_{18}O_{42}]^{12-}$, the structurally related $[V_{18-2p}As_p\text{-}O_{42}X]^{n-}$ class, the $[CH_3CN(V_{12}O_{32})]^{4-}$ bowl, and the isolated ring cluster $[(VO)_8(OR)_{16}(C_2O_4)]^{2-}$. The emergence of the $\{V_8O_{24}\}$ unit as a common motif in

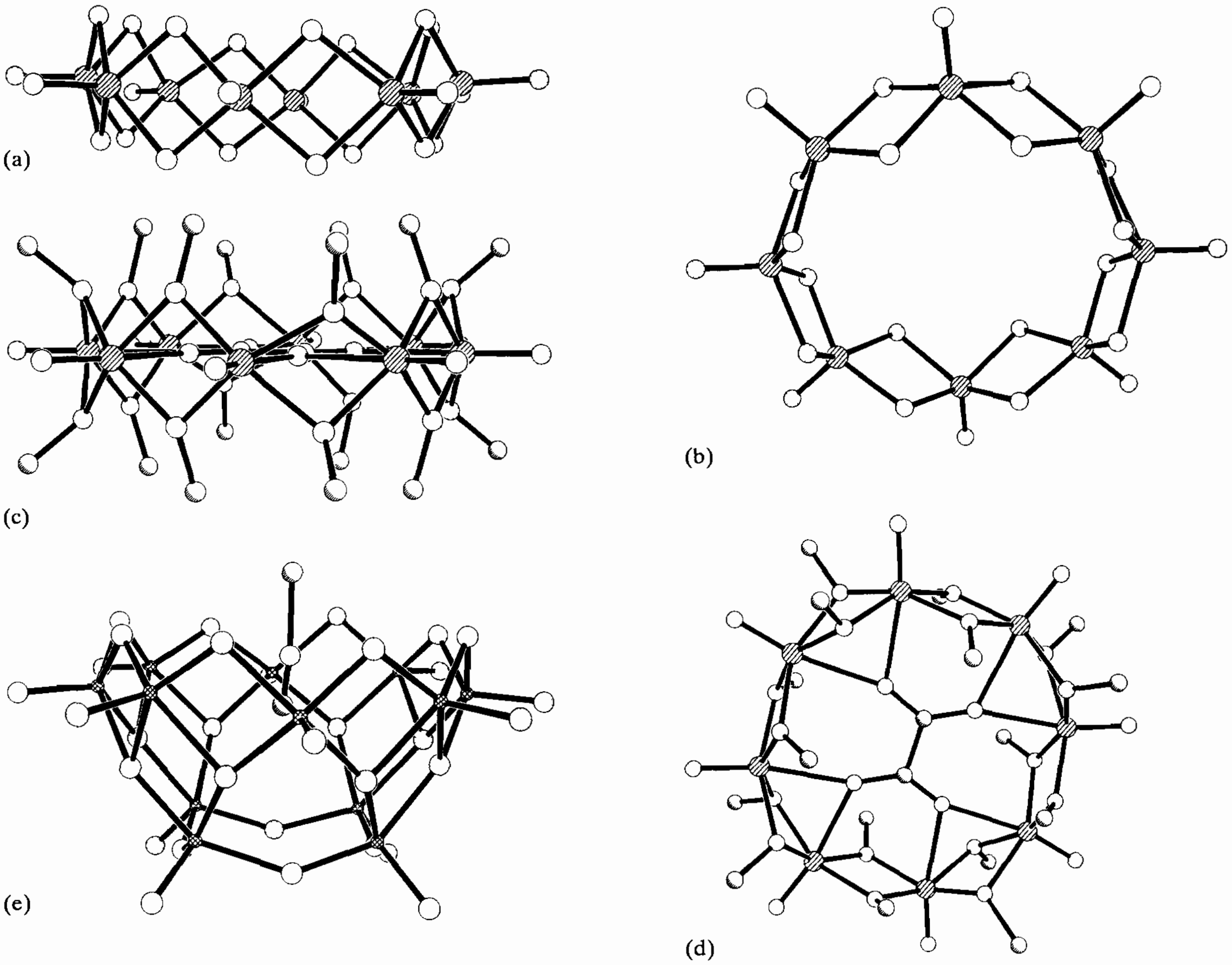

Fig. 3. (a) A view of the $\{V_8O_{24}\}$ ring of **2**, showing the tiara structure. (b) A view of the $\{V_8O_{24}\}$ belt normal to the perspective of 3(a). (c) A view of the structure of $[(VO)_8(OCH_3)_{16}(C_2O_4)]^{2-}$, illustrating the $\{V_8O_{24}\}$ tiara. (d) A view of the $[(VO)_8(OCH_3)_{16}(C_2O_4)]^{2-}$ ring. (e) A view of the $[(CH_3CN)V_{12}O_{32}]^{4-}$ bowl.

polyoxovanadium clusters requires the introduction of suitable templates, suggesting that the host cluster is built up around the guest substrate. Furthermore, the steric and bonding requirements of the guest should dictate whether the spherical, bowl or ring structure is achieved upon condensation of $\{VO_5\}$ units.

Supplementary material

A complete description of the crystallographic methods and details of structure solutions and refinements are available from the authors on request.

Acknowledgement

This work was supported by NSF Grant CHE 9119910.

References

1 M.T. Pope, *Heteropoly and Isopoly Oxometalates,* Springer, New York, 1983.

2 $(CH_3H_6)H[PV_{14}O_{42}]\cdot 2H_2O$: R. Kato, A. Kobayashi and Y. Sasaki, *Inorg. Chem., 21* (1982) 240, and refs. therein.

3 $K_{12}[V_{18}O_{42}]\cdot 16H_2O$: G.K. Johnson and E.O. Schlemper, *J. Am. Chem. Soc, 100* (1978) 3645.

4 $[V_{10}O_{28}]^{6-}$: H.T. Evans, *Inorg. Chem., 23* (1984) 501.

5 $[H_2V_{10}O_{28}]^{4-}$: M.V Capparelli, D.M.L. Goodgame, P.B. Hayman and A.C. Shapski, *J. Chem. Soc., Chem. Commun*, (1986) 776.

6 $[H_3V_{10}O_{28}]^{3+}$: V.W. Day, W.G. Klemperer and D.J. Maltbie, *J Am. Chem. Soc., 109* (1987) 2991.

7 $[(C_2H_5)_4N]_4[V_{10}O_{26}]$ H_2O: A. Bino, S. Cohen and C. Heitner-Wirguin, *Inorg Chem, 21* (1982) 429.

8 $(PPh_4)_4[MeCN(V_{12}O_{32})]$: V.W Day, W.G. Klemperer and O.M. Yaghi, *J Am. Chem. Soc., 111* (1989) 5959.

9 $(Bu_4N)_2[V_8O_8(OMe)_{16}(C_2O_4)]$: Q. Chen, S. Liu and J. Zubieta, *Inorg. Chem., 28* (1989) 4433.

10 $[V_{15}O_{36}(CO_3)]^{7-}$: A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer and J. Döring, *Angew. Chem., Int Ed. Engl., 29* (1990) 926.

11 $[As_6V_{15}O_{42}(H_2O)_6]$: A. Muller and J. Doring, *Angew. Chem., Int. Ed. Engl, 27* (1988) 1721.

12 $[V_{15}O_{36}]^{5-}$· A. Muller, E. Krickemeyer, M Penk, H -J Walberg and H Bogge, *Angew Chem, Int Ed Engl, 26* (1987) 1045

13 $[V_{19}O_{41}(OH)_9]^{8-}$· A Muller, M. Penk, E Krickemeyer, H. Bogge and H.-J. Walberg, *Angew Chem, Int Ed Engl., 27* (1988) 1719

14 $[AsV_{14}O_{40}]^{7-}$: A Müller, J Doring, M.I Khan and V Wittneben, *Angew Chem, Int Ed Engl, 30* (1991) 210.

15 $[V_{18}O_{42}(SO_4)]^{8-}$ A Muller, J Doring and E Krickemeyer, *Chimica, 42* (1988) 300

16 $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ A Muller, J. Doring and H. Boggs, *J Chem Soc, Chem Commun*, (1991) 273.

17 $[HV_{22}O_{54}(ClO_4)]^{6-}$ and $[H_2V_{18}O_{44}(N_3)]^{5-}$. A. Muller, E. Krickemeyer, M Penk, R Rohlfing, A. Armatage and H Bogge, *Angew Chem, Int Ed Engl, 30* (1991) 1678

18 $[V_{18}O_{42}(X)]^{n-}$ ($X = SO_4$, VO_4) and $[V_{18-p}As_{2p}O_{42}(X))]^{m-}$ ($X = SO_3$, SO_4, H_2O; $p = 3$, 4). A Muller and J. Doring, *Z. Anorg Allg Chem, 595* (1991) 251

19 $[(NH_4)_2Cl_2V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}$: A. Muller, K Hovemeier and R Rohlfing, *Angew Chem, Int Ed Engl, 31* (1992) 1193.

20 $[As_8V_{14}O_{42}(0.5H_2O)]^{4-}$· G Huan, M.A Greaney and A.J Jacobson, *J. Chem Soc, Chem. Commun*, (1991) 260.

21 $[H_{12}(VO_2)_{12}(PhPO_3)_8]^{4-}$ G. Huan, V.W Day, A J Jacobson and D.P Goshorn, *J Am Chem Soc, 113* (1991) 3189.

22 $[H_6(VO_2)_{16}(PhPO_3)_8]^{8-}$: G. Huan, A J. Jacobson and V W. Day, *Angew Chem, Int Ed Engl, 30* (1991) 422

23 $(NEt_4)_2[V_4O_8(NO_3)(\text{thiophene-2-carboxylate})_4]\cdot H_2O$ and $(PhCH_2NEt_2)_2[V_5O_9Cl(\text{thiophene-2-carboxylate})_4]$ CH_3CN D D. Heinrich, K. Folting, W.E. Streim, J.C. Huffman and G Christou, *J Chem Soc, Chem Commun*, 1989) 1411.

24 $[K\{V_4O_4(\mu\text{-}O)_4(O_2CCH_2Bu)_4\}][O_2CCH_2Bu]\cdot 2BuCH_2COOH$· W. Priebsch, D. Rehder and M. von Oeynhausen, *Chem Ber., 124* (1991) 761.

25 $[V_6O_{10}(O_2CPh)_6]$· D Rehder, W. Priebsch and M von Oeynhausen, *Angew Chem, Int Ed Engl, 28* (1989) 1221

26 $[V_4O_8(C_2O_4)_4(H_2O)_2]^{4-}$. H Rirskamp, P Gietz and R Mattes, *Chem Ber, 109* (1976) 2090

27 $[V_9O_{16}$ (butanediaminetetraacetic acid)$_4]^{7-}$· J -P. Launay, Y. Jeannin and M Daoudi, *Inorg Chem, 24* (1985) 1052

28 $[V_6O_{13-n}(OH)_n\{RC(CH_2O)_3\}_2]^{2-}$ ($n = 2$, 4, 6) Q Chen, D P. Goshorn, C P Scholes, X -L. Tan and J Zubieta, *J Am Chem Soc, 114* (1992) 4667

29 $[V_6O_7(OH)_3\{RC(CH_2O)_3\}_3]^{1-}$ and $[V_6O_7\{RC(CH_2O)_3\}_4]^{2-}$: M I. Khan, Q Chen and J Zubieta, *Inorg Chem, 31* (1992) 1557.

30 $[V_{10}O_{16}\{RC(CH_2O)_3\}_4]^{4-}$ and $[V_{10}O_{13}\{RC(CH_2O)_3\}_5]^{1-}$. M I. Khan, Q. Chen, D.P. Goshorn, H Hope, S. Parkin and J. Zubieta, *J Am Chem Soc, 114* (1992) 3341

31 $[V_{13}O_{34}]^{3-}$ D Hou, K.S Hagen and C.L Hill, *J Am Chem Soc., 114* (1992) 5864.

32 M.T. Pope and A. Muller, *Angew Chem, Int Ed Engl, 30* (1991) 34

33 W G Klemperer, T A. Marquart and O.M. Yaghi, *Angew. Chem Int Ed. Engl, 31* (1991) 49.

34 H Reuter, *Angew Chem, Int Ed Engl., 31* (1992) 1185.

35 J W Johnson, D.C Johnson, A J. Jacobson and J.F. Brody, *J Am Chem Soc, 106* (1984) 8123, and refs. therein, G. Huan, J.W. Johnson, A J Jacobson, E.W Corcoran, Jr. and D.P. Goshorn, *J Solid State Chem., 93* (1991) 514, and refs. therein

36 S.L Wang, H Y Kang C.Y. Cheng and K.H. Lii, *Inorg Chem, 30* (1991) 3496, and refs therein.

37 H.K. Chae, W G. Klemperer, D E. Páez Loyo, V W. Day and T.A. Eberspacher, *Inorg. Chem, 31* (1992) 3187

38 M I. Khan, A Muller, S Dillinger, H. Bogge, A. Armatage, Q. Chen and J. Zubieta, *J. Am Chem Soc*, in press.

39 M I. Khan, Q. Chen and J. Zubieta, *Inorg. Chem.*, in press.

40 M I. Khan, Q. Chen and J. Zubieta, *J. Chem Soc, Chem Commun*, in press.

41 I.D. Brown, in M. O'Keefe and A. Navrotsky (eds), *Structure and bonding in Crystals,* Vol II, Academic Press, New York, 1981.