A mixed valence heteropolyvanadate, $K_7Na[As^V_4V^V_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$

M. Ishaque Khan, Qin Chen, Jon Zubieta*
Department of Chemistry, Syracuse University, Syracuse, NY 13244 (USA)

David Goshorn and Robert C. Haushalter
Exxon Research and Engineering Company, Annandale, NJ 08801 (USA)

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Abstract

The reaction of $NaVO_3$ with As_2O_3, $Na_2C_6O_6$ and KSCN in water at pH 4.4 yields shiny black crystals of $K_7Na[As^V_4V^V_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$. The structure consists of an ϵ-Keggin core $\{AsV_{12}O_{40}\}$ with three [VO] vertices removed and capped by three [VO] and three [AsOH] units. Crystal data: monoclinic $C2/c$, $a=40.048(9)$, $b=13.326(1)$, $c=18.074(3)$ Å, $\beta=112.28(1)°$, $V=9005.9(14)$ Å^3, $D_{calc}=2.986$ g cm^{-3}, $Z=8$, $R=0.063$ for 5999 reflections.

Introduction

In addition to the two large V^V isopolyanions, $[V_{10}O_{28}]^{6-}$ [1] and $[V_{12}O_{32}]^{4-}$ [2], a number of V^{IV}-containing aggregates have been described [3–11]. Many of these latter complexes are hereroclusters containing arsenic [4, 7, 11] or phosphorus [12, 13] and displaying varying ratios of V^{IV} to V^V and unique structural types. As part of our investigations of the coordination chemistry of polyoxovanadates, we have isolated and structurally characterized the mixed valence heteropolyvanadate, $K_7Na[As^V_4V^V_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$. The potassium salt of the one-electron oxidized form of this anion $K_7[As^V_4V^V_8V^{IV}_4O_{43}H_3]\cdot 9H_2O$ is also known and has been cited in a recent review by Pope and Müller [14].

Experimental

Synthesis

The complex $K_7Na[As_4V_{12}O_{43}H_3]\cdot 7H_2O$ was initially synthesized by dissolving $NaVO_3$ (0.732 g; 6 mmol) and arsenic(III) oxide (0.198 g; 1 mmol) in water (50 ml) and heating to 80 °C. This solution was treated with the disodium salt of rhodizonic acid, $Na_2C_6O_6$ (0.214 g; 1 mmol) and after 10 min with KSCN (1.00 g; 10.3 mmol). The pH of the reaction was adjusted to 4.4 by dropwise addition of dilute sulfuric acid (0.5 N) to give a dark bluish-black solution. After heating at 80 °C for 16 h, the solution was allowed to cool to room temperature and maintained at ambient temperature for 36 h. The green crystalline material of cubic habit which deposited was filtered, and the bright green filtrate allowed to evaporate at room temperature to give shiny black crystals of $K_7Na[As^V_4V^V_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$.

Alternatively, the complex was isolated by adapting the above procedure with the addition of a large excess of KSCN (5.00 g; 51.5 mmol) and the exclusion of $Na_2C_6O_6$. The yield is significantly improved by the latter procedure to 40% (based on $NaVO_3$). The rhodizonic acid presumably functions as a reducing agent [15] and may be replaced by the mild reductant KSCN.

Crystals of $K_7Na[As_4V_{12}O_{43}H_3]\cdot 7H_2O$ are indefinitely stable in air. The complex is soluble in warm water to give a bluish-black solution and insoluble in all common organic solvents. Upon heating, the characteristic bluish-black color of aqueous solutions of the complex is discharged to give a mustard yellow solution. IR (KBr pellet, cm^{-1}): 3430(s), 1615(m), 972(s), 955(s), 897(s), 855(m), 835(s), 755(w), 719(w), 655(m), 577(w), 473(s). *Anal.* Calc. for $H_{17}O_{50}NaK_7V_{12}As_4$: K, 13.5; Na, 1.14. Found (atomic absorption): K, 13.6; Na, 1.14%. Thermogravimetric analysis was consistent with the presence of 7 water molecules of crystallization. Potentiometric titration revealed five V(IV) centers/formula unit.

X-ray crystallography

A crystal of the complex measuring 0.25×0.26×0.28 mm was mounted on a glass fiber and carefully centered at −40 °C on a Rigaku AFC5S diffractometer. Data

*Author to whom correspondence should be addressed.

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TABLE 1. Atomic positional parameters for $K_7Na[As^V_4V^V_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$

Atom	x	y	z
As(1)	0.37000(3)	0.68308(9)	0.40330(7)
As(2)	0.45590(3)	0.5535(1)	0.38540(8)
As(3)	0.31352(3)	0.4375(1)	0.30516(7)
As(4)	0.34653(4)	0.7871(1)	0.18504(8)
V(1)	0.34598(5)	0.6919(2)	0.5778(1)
V(2)	0.33897(5)	0.8969(2)	0.4839(1)
V(3)	0.41749(5)	0.8130(2)	0.5928(1)
V(4)	0.40472(6)	0.9315(2)	0.4258(1)
V(5)	0.41950(6)	0.5757(2)	0.5933(1)
V(6)	0.28176(5)	0.7122(2)	0.4031(1)
V(7)	0.33452(5)	0.4900(2)	0.4888(1)
V(8)	0.31134(6)	0.8798(2)	0.3011(1)
V(9)	0.46464(6)	0.7415(2)	0.5001(1)
V(10)	0.28494(5)	0.6660(2)	0.2249(1)
V(11)	0.43264(6)	0.7771(2)	0.3144(1)
V(12)	0.39563(6)	0.4191(2)	0.4342(1)
K(1)	0.37183(8)	0.5290(2)	0.2142(2)
K(2)	1/2	0.6045(5)	1/4
K(3)	0.24131(8)	0.9456(2)	0.4285(2)
K(4)	0.19068(9)	0.6630(3)	0.2916(2)
K(5)	1/2	0.3136(5)	1/4
K(6)	0.5409(1)	0.8278(4)	0.4523(3)
K(7)	0.1945(2)	0.7347(6)	0.0480(3)
K(8)	0.9309(3)	0.7767(8)	0.2987(5)
Na(1)	0.9451(1)	0.5826(5)	0.3244(4)
O(1)	0.3307(2)	0.6553(6)	0.6444(5)
O(2)	0.3204(2)	1.0022(6)	0.4874(5)
O(3)	0.4501(2)	0.8542(7)	0.6707(5)
O(4)	0.4141(2)	1.0483(6)	0.4415(6)
O(5)	0.4419(2)	0.5457(6)	0.6846(5)
O(6)	0.2462(2)	0.7307(6)	0.4222(5)
O(7)	0.3120(2)	0.4446(7)	0.5383(5)
O(8)	0.2941(2)	0.9890(6)	0.2853(5)
O(9)	0.5016(2)	0.7668(7)	0.5688(5)
O(10)	0.2491(2)	0.6361(6)	0.1522(5)
O(11)	0.4517(2)	0.8279(7)	0.2611(6)
O(12)	0.4145(2)	0.3123(7)	0.4461(5)
O(13)	0.4901(2)	0.4794(6)	0.3795(5)
O(14)	0.2852(2)	0.3440(7)	0.2512(5)
O(15)	0.3466(3)	0.8311(7)	0.0960(5)
O(16)	0.3272(2)	0.8162(6)	0.5527(5)
O(17)	0.3934(2)	0.7342(7)	0.6369(5)
O(18)	0.3872(2)	0.9163(7)	0.5608(6)
O(19)	0.4359(2)	0.8565(6)	0.5082(5)
O(20)	0.4141(2)	0.9022(7)	0.3457(5)
O(21)	0.4717(2)	0.7872(6)	0.4184(5)
O(22)	0.4486(2)	0.6347(6)	0.3114(5)
O(23)	0.3543(2)	0.3886(6)	0.3298(5)
O(24)	0.2995(2)	0.4594(6)	0.3809(5)
O(25)	0.3118(2)	0.6311(6)	0.4782(5)
O(26)	0.2986(2)	0.8364(6)	0.3923(5)
O(27)	0.3568(2)	0.9163(6)	0.3957(5)
O(28)	0.3717(2)	0.5630(6)	0.5737(5)
O(29)	0.4390(2)	0.6866(6)	0.5693(5)
O(30)	0.3689(2)	0.7456(6)	0.4841(5)
O(31)	0.4100(2)	0.7044(6)	0.3964(5)
O(32)	0.3367(2)	0.7228(6)	0.3219(5)
O(33)	0.3643(2)	0.5610(6)	0.4161(5)
O(34)	0.2677(2)	0.6531(6)	0.3140(5)
O(35)	0.2765(2)	0.8086(6)	0.2315(5)
O(36)	0.3384(2)	0.8889(6)	0.2296(5)
O(37)	0.4262(2)	0.4841(7)	0.5351(5)
O(38)	0.4735(2)	0.6017(6)	0.4781(5)
O(39)	0.3624(2)	0.3938(6)	0.4874(5)
O(40)	0.3870(2)	0.7359(6)	0.2292(5)
O(41)	0.3146(2)	0.6999(6)	0.1602(5)
O(42)	0.3090(2)	0.5327(6)	0.2430(5)
O(43)	0.4200(2)	0.4820(6)	0.3681(5)
O(51)	0.3740(3)	0.0684(8)	0.2169(7)
O(52)	0.2323(3)	0.523(1)	−0.0900(6)
O(53)	0.4132(3)	0.109(1)	0.6056(7)
O(54)	0.3470(4)	0.171(1)	0.3739(9)
O(55)	0.5508(5)	0.685(1)	0.366(1)
O(56)	1.0048(7)	0.491(2)	0.368(2)
O(57)	0.2382(6)	0.220(2)	0.501(2)
O(58)	1.0000	1/2	1/2

collection was carried out as previously described [16]. Data was corrected for absorption using Ψ scans on 5 reflections with χ angles near 90 or 270°. The structure was solved by direct methods and refined using full matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all atoms with the exception of hydrogens and oxygens of the water molecules of crystallization. Crystal data: monoclinic space group $C2/c$, $a=40.408(9)$, $b=13.326(1)$, $c=18.074(3)$ Å, $\beta=112.28(1)°$, $V=9005.9(14)$ Å^3, $D_{calc}=2.986$ g cm^{-3}, $Z=8$. Structure solution and refinement based on 5999 reflections with $I_o \geq 6\sigma(I_o)$ (8343 collected; Mo Kα radiation, $\lambda=0.71073$ Å) converged at $R=0.063$, $R_w=0.069$. Atomic positional parameters are listed in Table 1, and selected bond lengths and angles are given in Table 2.

Results and discussion

The complex $K_7Na[As_4V_{12}O_{43}H_3]\cdot 7H_2O$ is synthesized from metavanadate and As_2O_3 by exploiting the weak reducing ability of rhodizonic acid and/or SCN^- in acidic media. Whereas under more reducing conditions V^{IV}/V^V clusters with high V^{IV}:V^V rations are isolated [14], these conditions favor the formation of

$$C_6O_6^{2-} \xrightarrow{[O]} 3C_2O_4^{2-}$$

$$2SCN^- \rightleftharpoons (CNS)_2 + 2e^-$$

species with fewer V^{IV} centers. The IR spectrum of the dark blue crystals of the cluster exhibits characteristic bands at 972 and 958 cm^{-1} assigned to $\nu(V{=}O_t)$ and a number of bands in the 750–900 cm^{-1} range associated with ν(V–O–V) and ν(V–O–As).

TABLE 2. Selected bond lengths (Å) and angles (°) for $K_7Na[As^{V}_4V^{V}_7V^{IV}_5O_{43}H_3]\cdot 7H_2O$

Distances (Å)	
AS1–O30	1.696(9)
AS1–O31	1.690(9)
AS1–O32	1.660(7)
As1–O33	1.671(8)
AS2–O13	1.734(9)
AS2–O22	1.658(9)
AS2–O38	1.680(8)
AS2–O43	1.665(8)
V3–O29	2.011(9)
V3–O30	2.367(7)
V4–O4	1.601(9)
V4–O19	1.840(8)
V4–O20	1.68(1)
AS4–O15	1.71(1)
AS4–O36	1.672(9)
AS4–O40	1.670(8)
AS4–O41	1.668(8)
V1–O1	1.62(1)
V1–O16	1.807(8)
V1–O17	1.891(8)
V1–O25	1.979(7)
V1–O28	2.022(8)
V1–O30	2.33(1)
V2–O2	1.603(9)
V2–O30	2.351(8)
V2–O16	1.84(1)
V2–O18	1.934(8)
V2–O26	2.003(7)
V2–O27	2.00(1)
V3–O3	1.618(8)
V3–O17	1.81(1)
V3–O18	1.787(9)
V3–O19	2.02(1)
AS3–O14	1.724(8)
AS3–O23	1.668(8)
AS3–O24	1.69(1)
AS3–O42	1.658(9)
V4–O27	1.813(9)
V5–O5	1.603(8)
V5–O28	1.836(9)
V5–O29	1.803(9)
V5–O37	1.70(1)
V6–O6	1.62(1)
V6–O25	1.798(7)
V6–O26	1.827(8)
V6–O34	1.687(9)
V7–O7	1.62(1)
V7–O24	1.971(7)
V7–O25	2.069(8)
V7–O28	1.950(7)
V7–O33	2.29(1)
V7–O39	1.714(9)
V8–O8	1.592(9)
V8–O26	1.99(1)
V8–O27	2.039(7)
V8–O32	2.297(8)
V8–O35	1.768(7)
V8–O36	1.99(1)
V9–O9	1.576(8)
V9–O19	1.961(9)

(*continued*)

TABLE 2. (*continued*)

V9–O21	1.961(9)
V9–O29	1.72(1)
V9–O31	2.04(1)
V9–O38	2.345(7)
V10–O10	1.966(9)
V10–O32	1.593(7)
V10–O34	2.288(7)
V10–O35	1.99(1)
V10–O41	1.941(9)
V10–O42	2.02(1)
	1.991(9)
V11–O11	1.59(1)
V11–O20	1.99(1)
V11–O21	1.947(8)
V11–O22	2.011(9)
V11–O31	2.24(1)
V11–O40	1.981(8)
V12–O12	1.591(9)
V12–O23	2.031(7)
V12–O33	2.231(8)
V12–O37	1.974(8)
V12–O39	1.95(1)
V12–O43	2.00(1)
K1–O1	2.967(9)
K1–O28	2.82(1)
K1–O40	2.814(9)
K1–O42	2.78(1)
K1–O43	2.795(8)
K2–O5	2.967(9)
K2–O13	3.02(1)
K2–O22	2.73(1)
Angles (°)	
O30–AS1–O31	108.6(4)
O30–AS1–O32	109.2(4)
O30–AS1–O33	107.9(4)
O31–AS1–O32	111.0(4)
O31–AS1–O33	111.1(4)
O32–AS1–O33	109.0(4)
O13–AS2–O22	103.0(5)
O13–AS2–O38	103.4(4)
O13–AS2–O43	108.7(4)
O22–AS2–O38	115.7(4)
O22–AS2–O43	110.3(4)
O22–AS2–O43	114.6(5)
O14–AS3–O23	104.2(4)
O14–AS3–O24	103.2(4)
O14–AS3–O42	106.9(4)
O23–AS3–O24	116.8(4)
O23–AS3–O42	109.0(4)
O24–AS3–O42	115.5(4)
O15–AS4–O36	104.2(5)
O15–AS4–O40	103.8(5)
O15–AS4–O41	105.3(4)
O36–AS4–O40	115.9(4)
O36–AS4–O41	114.9(5)
O40–AS4–O41	111.2(4)
O1–V1–O16	102.6(5)
O1–V1–O17	105.0(4)
O1–V1–O25	102.8(4)
O1–V1–O28	96.8(4)
O1–V1–O30	178.9(3)
O16–V1–O17	96.1(4)

(*continued*)

TABLE 2. (*continued*)

O16–V1–O25	93.7(3)
O16–V1–O28	160.4(4)
O16–V1–O30	77.3(4)
O17–V1–O25	147.5(4)
O17–V1–O28	81.4(4)
O17–V1–O30	73.9(4)
O25–V1–O28	79.0(3)
O25–V1–O30	78.2(3)
O28–V1–O30	83.3(3)
O2–V2–O16	104.0(5)
O2–V2–O18	102.3(4)
O2–V2–O26	97.9(4)
O2–V2–O27	103.5(5)
O2–V2–O30	177.1(3)
O16–V2–O18	92.3(4)
O16–V2–O26	89.1(3)
O16–V2–O27	151.5(4)
O16–V2–O30	76.2(4)
O18–V2–O26	158.7(4)
O18–V2–O27	89.2(4)
O18–V2–O30	74.7(3)
O26–V2–O27	79.6(4)
O26–V2–O30	85.0(3)
O27–V2–O30	76.8(3)
O3–V3–O17	102.2(5)
O3–V3–O18	104.6(4)
O3–V3–O19	98.5(4)
O3–V3–O29	101.1(4)
O3–V3–O30	176.4(4)
O17–V3–O18	99.9(5)
O17–V3–O19	156.0(4)
O17–V3–O29	87.4(4)
O17–V3–O30	74.3(3)
O18–V3–O19	86.5(5)
O18–V3–O29	151.0(4)
O18–V3–O30	76.8(3)
O19–V3–O29	76.7(4)
O19–V3–)30	84.8(3)
O29–V3–O30	78.2(3)
O4–V4–O19	109.9(4)
O4–V4–O20	105.3(5)
O4–V4–O27	108.4(4)
O19–V4–O20	105.2(4)
O19–V4–O27	120.5(4)
O20–V4–O27	106.3(4)
O5–V5–O28	108.6(5)
O5–V5–O29	108.9(4)
O5–V5–O37	107.3(4)
O28–V5–O29	123.5(4)
O28–V5–O37	102.5(4)
O29–V5–O37	104.7(5)
O6–V6–O25	109.3(4)
O6–V6–O26	106.3(4)
O6–V6–O34	105.7(4)
O25–V6–O26	116.9(3)
O25–V6–O34	109.1(4)
O26–V6–O34	108.9(4)
O7–V7–O24	97.3(4)
O7–V7–O25	94.0(4)
O7–V7–O28	100.3(4)
O7–V7–O33	177.0(4)
O7–V7–O39	103.8(5)

(*continued*)

TABLE 2. (*continued*)

O24–V7–O25	88.2(3)
O24–V7–O28	158.7(4)
O24–V7–O33	81.6(3)
O24–V7–O39	93.5(4)
O25–V7–O28	78.6(3)
O25–V7–O33	83.2(3)
O25–V7–O39	161.7(4)
O28–V7–O33	80.2(3)
O28–V7–O39	94.0(3)
O33–V7–O39	79.0(4)
O8–V8–O26	100.4(5)
O8–V8–O27	97.3(4)
O8–V8–O32	178.9(5)
O8–V8–O35	100.8(4)
O8–V8–O36	98.0(5)
O26–V8–O27	79.0(4)
O26–V8–O32	80.7(3)
O26–V8–O35	92.7(4)
O26–V8–O36	159.2(3)
O27–V8–O32	82.9(3)
O27–V8–O35	161.2(4)
O27–V8–O36	89.3(4)
O32–V8–O35	79.2(3)
O32–V8–O36	80.9(4)
O35–V8–O36	93.2(4)
O9–V9–O19	100.7(4)
O9–V9–O21	100.6(5)
O9–V9–O29	98.3(5)
O9–V9–O31	179.1(5)
O9–V9–O38	99.8(4)
O19–V9–O21	94.7(4)
O19–V9–O29	77.4(4)
O19–V9–O31	79.6(3)
O19–V9–O38	156.1(4)
O21–V9–O29	160.5(3)
O21–V9–O31	78.5(3)
O21–V9–O38	93.4(4)
O29–V9–O31	82.6(3)
O29–V9–O38	87.7(4)
O31–V9–O38	80.1(3)
O10–V10–O32	174.3(4)
O10–V10–O34	99.1(4)
O10–V10–O35	99.8(4)
O10–V10–O41	97.6(4)
O10–V10–O42	98.4(4)
O32–V10–O34	84.6(3)
O32–V10–O35	76.1(3)
O32–V10–O41	78.4(3)
O32–V10–O42	85.6(3)
O34–V10–O35	84.9(4)
O34–V10–O41	162.9(3)
O34–V10–O42	95.1(4)
O35–V10–O41	88.5(4)
O35–V10–O42	161.6(3)
O41–V10–O42	86.3(4)
O11–V11–O20	97.8(5)
O11–V11–O21	98.9(4)
O11–V11–O22	98.7(5)
O11–V11–O31	175.8(3)
O11–V11–O40	99.6(4)
O20–V11–O21	85.6(4)
O20–V11–O22	162.7(4)

(*continued*)

TABLE 2. (*continued*)

O20–V11–O31	83.2(4)
O20–V11–O40	96.5(4)
O21–V11–O22	86.6(3)
O21–V11–O31	77.0(3)
O21–V11–O40	160.9(4)
O22–V11–O31	79.9(4)
O22–V11–O40	86.0(3)
O31–V11–O40	84.3(4)
O12–V12–O23	97.5(4)
O12–V12–O33	174.4(4)
O12–V12–O37	99.7(4)
O12–V12–O39	99.4(5)
O12–V12–O43	97.9(5)
O23–V12–O33	79.2(3)
O23–V12–O37	162.3(4)
O23–V12–O39	87.0(4)
O23–V12–O43	86.9(3)
O33–V12–O37	83.4(3)
O33–V12–O39	76.1(3)
O33–V12–O43	86.4(4)
O37–V12–O39	85.8(4)
O37–V12–O43	95.2(4)
O39–V12–O43	162.3(3)

The structure of the complex is shown in Fig. 1. The overall structure may be viewed in terms of the hypothetical $\{AsV_{12}O_{40}\}$ ϵ-Keggin structure with three [VO] vertices removed and capped by three [VO] and three [AsOH] units. The 'open' pole of the $[As_4V_{12}O_{43}H_3]^{8-}$ cluster is capped by a potassium cation and two cluster units are bridged by a second potassium cation, as shown in Fig. 2. There are four distinct V environments: the tetrahedral centers (V4, V5 and V6), the pseudo-octahedral sites which participate in long range bonding to the quadruply bridging oxo group of the central $[AsO_4]$ group (V1, V2 and V3), the octahedral sites which participate in three V–O–As interactions (V10, V11 and V12), and the octahedral sites which exhibit two V–O–As interactions (V7, V8 and V9).

Solid-state magnetic susceptibility studies on $K_7Na[As_4V_{12}O_{43}H_3]\cdot 7H_2O$ gave an effective magnetic moment of 3.59 μ_B, which corresponds to 1.61 μ_B per V^{IV} center. Thus, the five V^{IV} d^1 centers are practically uncoupled, an observation consistent with the relatively small number of spins, which are effectively trapped as far apart as possible to give rise to approximately spin-only values for μ_{eff} per V^{IV}. The one-electron oxidized form of the cluster $[As_4V_{12}O_{43}H_3]^{7-}$ [14] has been reported to possess four V^{IV} centers with an effective moment of 1.75 μ_B per V^{IV}. Other examples of trapped V^{IV} sites in polyvanadate clusters include $[V_{14}AsO_{40}]^{7-}$ [17] and $[V_{12}As_8O_{40}(HCO)_2]^{3-}$ [18]. As demonstrated most elegantly by the recent work of Müller *et al.* [18], antiferromagnetically coupled systems are observed when the V^{IV}/V^V ratio is greater than

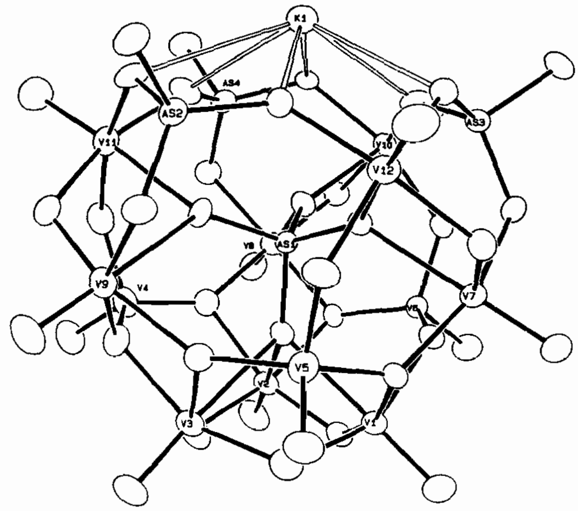

Fig. 1. ORTEP view of the structure of $[KAs_4V_{12}O_{43}H_3]^{7-}$, showing the capping of the $[As_4V_{12}O_{43}H_3]^{8-}$ anion by K1.

0.5, resulting in complicated magnetic behavior arising from both trapped and delocalized V^{IV} centers.

Valence sum calculations [19] suggest that three spins are trapped on the V10, V11 and V12 centers, while two spins are delocalized in the cluster. The oxidized species $[As_4V_{12}O_{43}H_3]^{7-}$ exhibits a pattern of three trapped spins and one delocalized. The isolation of the $[As_4V_{12}O_{43}H_3]^{8-}$ mixed valence cluster demonstrates that the aggregates of the family of arseno-vanadates exist with different electron populations and that subtle variations in reaction conditions allow isolation of species in different overall cluster oxidation states.

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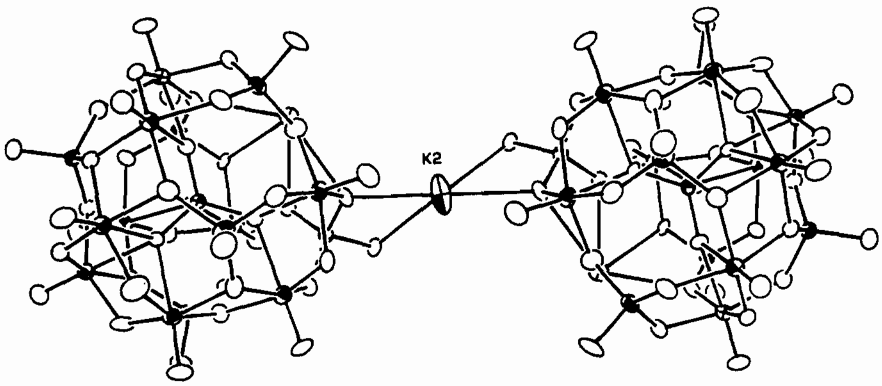

Fig. 2. Perspective view of two $[KAs_4V_{12}O_{43}H_3]^{7-}$ units bridged by a potassium cation (K2) located on a crystallographic two-fold axis.

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