smaller *a* values for our L(*S*-aryl) compounds than for L(*S*-alkyl), which effectively happens (93×10^{-4} cm^{-1} for [(2etmp)$CuCl_2$]; 65.5×10^{-4} cm^{-1} for [(L3)$CuCl_2$]). The relatively high *a* values for the perchlorate complexes are attributed to oxygen coordination to Cu(II). A nonsplitting of the EPR signals by the pyridinic nitrogen atom is observed. This certainly implies a strong overlap of the metal $d_{x^2-y^2}$ orbital with the appropriate sulfur atomic orbital. Again these data are in agreement with the CV and visible spectra reported.

As a conclusion, the substitution of *S*-alkyl groups in 2,6-bis(thiomethyl)pyridine ligand derivatives by *S*-aryl groups markedly affects the physical and geometrical properties of the resulting copper complexes. Those L(*S*-aryl) ligands are softer and more π acidic than the L(*S*-alkyl) ones. Also, the incorporation of electron-withdrawing elements in the aromatic ring (Cl, COOR) of the *S*-aryl group does not significantly affect the behavior of the pure L(*S*-aryl) ligand. In a future work we will implement these materials as sensors in all-solid-state electrodes to find if these encountered structural and physical differences between L(*S*-alkyl) and L(*S*-aryl) find their counterparts in metal ion selectivity.

Acknowledgment. This work was partially supported by the "Comisión Interdepartamental de Ciencia y Tecnología" (CICYT) through Grant No. MAT88-0179 and the "Fundación Ramón Areces" of Spain.

Registry No. L1, 137058-21-0; L2, 137058-22-1; L3, 137058-23-2; [(L1)$CuCl_2$], 137058-24-3; [(L2)$CuCl_2$], 137058-25-4; [(L3)$CuCl_2$], 137091-67-9; [(L1)$Cu(ClO_4)_2$], 137058-26-5; [(L2)$Cu(ClO_4)_2$], 137058-27-6; [(L3)$Cu(ClO_4)_2$], 137058-28-7; [(L1)CuCN], 137058-29-8; [(L2)CuCN], 137058-30-1; [(2etmp)$CuCl_2$], 124406-33-3; [(MO1)$CuCl_2$), 132673-29-1; [(MO2)$CuCl_2$], 132673-34-8; Na, 7440-23-5; thiophenol, 108-98-5; 2,6-bis(bromomethyl)pyridine, 7703-74-4; thiosalicyl methyl ester, 119-36-8; 4-chlorothiophenol, 106-54-7.

Supplementary Material Available: Tables S1–S5, listing crystal data, anisotropic thermal parameters, hydrogen atomic coordinates and thermal parameters, full bond length and bond angle data, and least-squares planes (16 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Faculty of Chemistry,
University of Bielefeld, W-4800 Bielefeld 1, Germany

$[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ and Related Topological and/or Structural Aspects of Polyoxometalate Chemistry

A. Müller,* M. Penk, and J. Döring

Received April 5, 1991

On reduction of an aqueous solution of vanadate(V) with thiocyanide in the presence of As^V, the black-gray mixed-valence compound $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**) is formed. It crystallizes in the space group *C*2/*c* with *a* = 39.993 (15) Å, *b* = 13.467 (4) Å, *c* = 18.209 (6) Å, β = 111.52 (3)°, and *Z* = 8. Refinement of 686 variables with 8827 observed reflections yields *R* = 0.049 and R_w = 0.058. The compound contains an anion with approximate C_3 symmetry, which can be described as a fragment of a sphere capped with a potassium ion. The oxygen and/or metal atoms of polyoxometalates often span the vertices of topologically and/or geometrically interesting polyhedra. Related aspects of **1** are discussed.

Introduction

Close-packing effects of atoms as well as related geometrical and/or topological aspects play an important role in structural chemistry.[1] This is very typical for polyoxometalates of the d-group elements which represent one of the most versatile class of compounds if both structural *and* electronic properties are considered.[2] It is especially fascinating, as in most of the species only two or three different atoms are involved. These species also play a role in catalytic processes and many other applications.[2] A special type of chemistry seems to be related to reduced and/or mixed-valence V_xO_y clusters,[2] and in this paper we report the synthesis of a new high-nuclearity species of that type.

Experimental Section

Synthesis of $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (1). KVO_3 (1.66 g, 12 mmol) was dissolved with stirring in 50 mL of water at 90 °C (100-mL Erlenmeyer flask). After addition of $3As_2O_5\cdot 5H_2O$ (0.52 g, 4 mmol), the clear orange-red solution (pH 5) was stirred for 10 min at 90 °C and KSCN (8.70 g, 89.5 mmol) was added. A pH value of ca. 2 was adjusted by addition of 5 mL of 0.5 M H_2SO_4 (dark green solution). After 45 min at 90 °C (vessel covered with a watch glass), the color changed to deep black and the pH value increased to ca. 3. After cooling, the flask was stored at room temperature. The black-gray bladelike crystals thereby formed were filtered off after 1 day, washed with cold water, and dried in air. Yield: 0.7 g. Anal. Calcd (found): As, 14.0 (14.9); K, 13.1 (13.5); V, 29.8 (30.3). IR (KBr pellet; cm^{-1}): 3700–3200 (vs, br), ν(OH); 1605 (m), δ(HOH); 963 (s), ν(V=O); 898 (m), ν(As—O-(AsO_4^{3-})); 856 (s), 835 (s), 720 (m), 662 (m), ν_{as}(M—O—M (M = V, As)) and ν(As—O(H)).

Table I. Crystallographic Data for $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**)

formula	$As_4H_{19}K_7O_{51}V_{12}$	space group	*C*2/*c* (No. 15)
fw	2019.8	*T*, K	294
a, Å	39.993 (15)	λ, Å	0.71073
b, Å	13.467 (4)	ρ_{calc}, g·cm^{-3}	2.94
c, Å	18.209 (6)	μ, cm^{-1}	59.1
β, deg	111.52 (3)	R^a/R_w^b	0.049/0.058
V, Å^3	9124	no. of obsd reflns	8827 ($F_o > 4\sigma(F_o)$)
Z	8		

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$; $1/w = \sigma^2(F_o) + 0.0001F_o^2$.

Manganometric Titration. The V^{IV} content of **1** was determined by titration of a solution of 50 mg of **1** in dilute H_2SO_4 (10%) at 65 °C with 0.1 N $KMnO_4$. The redox reaction was potentiometrically followed with a Mettler instrument (Memo Titrator DL 40) using a Pt electrode against an SCE.

X-ray Structure Determination of 1. Data for **1** were measured at room temperature on a Siemens R3m/V four-circle diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections (ψ-scans) were applied, and the SHELXTL PLUS program package[3] was used for structure solution (direct methods) and refinement. The hydrogen positions of the anion in **1** were determined as stated in Table II. In the crystal lattice of **1**, some of the potassium ions and water molecules are disordered. K(7), K(7A), K(8),

---

(1) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984. Wells, A. F. *Three-Dimensional Nets and Polyhedra*; John Wiley & Sons: New York, 1977. The borderline between geometry and topology is indistinct (Flegg, H. G. *From Geometry to Topology*; The English Universities Press: London, 1974; cf. ref 6).

(2) (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49 (review). (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Inorganic Chemistry Concepts 8; Springer-Verlag: Berlin, 1983. (c) Müller, A.; Döring, J.; Bögge, H. *J. Chem. Soc., Chem. Commun.* **1991**, 273. (d) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533.

(3) SHELXTL PLUS, Release 4.2: Siemens Analytical X-Ray Instruments, 1990.

0020-1669/91/1330-4935$02.50/0 © 1991 American Chemical Society

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**)

	x	*y*	*z*	*U*(eq)[a]
As(1)	1303 (1)	8194 (1)	984 (1)	20 (1)
As(2)	1529 (1)	7208 (1)	3160 (1)	26 (1)
As(3)	1871 (1)	10626 (1)	1937 (1)	24 (1)
As(4)	443 (1)	9499 (1)	1152 (1)	25 (1)
V(1)	1610 (1)	6048 (1)	203 (1)	26 (1)
V(2)	1548 (1)	8066 (1)	−742 (1)	25 (1)
V(3)	831 (1)	6890 (1)	−872 (1)	26 (1)
V(4)	2183 (1)	7869 (1)	978 (1)	24 (1)
V(5)	814 (1)	9246 (1)	−895 (1)	27 (1)
V(6)	952 (1)	5738 (1)	797 (1)	28 (1)
V(7)	1883 (1)	6249 (1)	2018 (1)	25 (1)
V(8)	1664 (1)	10081 (1)	127 (1)	25 (1)
V(9)	359 (1)	7622 (1)	41 (1)	26 (1)
V(10)	2151 (1)	8371 (1)	2740 (1)	25 (1)
V(11)	1052 (1)	10810 (1)	670 (1)	26 (1)
V(12)	671 (1)	7302 (1)	1876 (1)	27 (1)
O(1)	1792 (1)	5000 (3)	174 (3)	37 (2)
O(2)	1704 (1)	8403 (3)	−1404 (3)	34 (2)
O(3)	509 (1)	6471 (4)	−1628 (3)	39 (2)
O(4)	2535 (1)	7668 (3)	777 (3)	34 (2)
O(5)	595 (1)	9531 (3)	−1809 (3)	34 (2)
O(6)	851 (1)	4576 (3)	642 (3)	39 (2)
O(7)	2049 (1)	5159 (3)	2178 (3)	38 (2)
O(8)	1890 (1)	10502 (3)	−368 (3)	38 (2)
O(9)	−14 (1)	7383 (3)	−655 (3)	37 (2)
O(10)	2510 (1)	8670 (3)	3459 (3)	35 (2)
O(11)	864 (1)	11875 (3)	550 (3)	39 (2)
O(12)	474 (1)	6820 (4)	2410 (3)	45 (2)
O(13)	1742 (1)	6841 (3)	−475 (3)	36 (2)
O(14)	1076 (1)	7626 (4)	−1342 (3)	44 (2)
O(15)	1135 (1)	5847 (3)	−541 (3)	43 (2)
O(16)	2012 (1)	6649 (3)	1104 (3)	28 (1)
O(17)	1888 (1)	8679 (3)	236 (2)	28 (1)
O(18)	1295 (1)	9352 (3)	−714 (2)	28 (1)
O(19)	619 (1)	8137 (3)	−656 (3)	29 (1)
O(20)	645 (1)	6462 (3)	−26 (3)	29 (1)
O(21)	1428 (1)	5884 (3)	1081 (3)	29 (1)
O(22)	2227 (1)	6948 (3)	2682 (2)	27 (1)
O(23)	2326 (1)	8464 (3)	1857 (3)	30 (1)
O(24)	2010 (1)	10397 (3)	1183 (2)	28 (1)
O(25)	1385 (1)	11045 (3)	133 (2)	28 (1)
O(26)	745 (1)	10169 (3)	−342 (3)	32 (2)
O(27)	273 (1)	9011 (3)	233 (2)	28 (1)
O(28)	288 (1)	7194 (3)	856 (2)	28 (1)
O(29)	858 (1)	6055 (3)	1590 (3)	36 (2)
O(30)	1604 (1)	6188 (3)	2702 (3)	29 (1)
O(31)	1852 (1)	8060 (3)	3392 (3)	30 (1)
O(32)	1920 (1)	9696 (3)	2564 (3)	30 (1)
O(33)	1458 (1)	11105 (3)	1693 (2)	27 (1)
O(34)	803 (1)	10211 (3)	1332 (3)	32 (2)
O(35)	513 (1)	8703 (3)	1894 (2)	29 (1)
O(36)	1126 (1)	7715 (3)	2722 (3)	31 (2)
O(37)[c]	1541 (1)	6782 (4)	4054 (3)	39 (2)
O(38)[c]	2151 (1)	11565 (3)	2464 (3)	38 (2)
O(39)[c]	102 (1)	10244 (3)	1206 (3)	35 (2)
O(40)	1311 (1)	7546 (3)	187 (2)	24 (1)
O(41)	1638 (1)	7806 (3)	1793 (2)	26 (1)
O(42)	1360 (1)	9400 (3)	842 (2)	27 (1)
O(43)	903 (1)	7993 (3)	1059 (2)	26 (1)
K(1)	1283 (1)	9770 (1)	2860 (1)	39 (1)
K(2)	2418 (1)	537 (2)	4267 (1)	57 (1)
K(3)	1914 (1)	3365 (2)	2922 (1)	63 (1)
K(4)	416 (1)	13266 (1)	−399 (1)	54 (1)
K(5)	0	9066 (3)	2500	75 (1)
K(6)	561 (1)	4230 (3)	1880 (2)	55 (1)
K(7)[b]	1892 (2)	2832 (5)	552 (4)	65 (2)
K(7A)[b]	2002 (3)	2444 (6)	424 (5)	95 (4)
K(8)[b]	−42 (2)	1902 (3)	2715 (3)	91 (3)
O(44)	1509 (2)	3302 (6)	1303 (6)	126 (5)
O(45)	642 (3)	7790 (7)	−2941 (4)	106 (4)
O(46)	55 (2)	5059 (6)	−752 (8)	154 (6)
O(47)	523 (3)	8169 (6)	3675 (5)	104 (5)
O(48)	914 (2)	6002 (4)	3933 (3)	52 (2)
O(49)	1296 (2)	4390 (4)	2904 (4)	63 (3)
O(50)	2316 (2)	5197 (6)	4128 (4)	78 (3)
O(51)[b]	2410 (4)	12210 (12)	−27 (10)	81 (7)
O(52)	0	5202 (14)	2500	352 (31)
H(1)[c]	1337	6430	4030	
H(2)	2339	11540	2371	
H(3)	−100	10299	659	

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupation factor: 0.5. [c] The valence sums[4] for O(37)–O(39) (1.07–1.12) clearly indicated that these atoms should be protonated. A high-angle refinement followed by a low-angle difference Fourier synthesis showed (among others) three maxima, which were assigned to H(1)–H(3) (not refined). These hydrogen atoms nicely complete the approximately tetrahedral surrounding of O(37)–O(39), which consists of one As, one H, and two K atoms.

and O(51) were refined with an occupancy factor (0.5) less than the normal occupancy because (a) K(7) has a distance of <1 Å to K(7A) and (b) K(8) and O(51) have distances of <1.1 Å to the symmetry-transformed atoms of K(8) and O(51), respectively. Crystallographic data and details of the crystal structure determination of **1** are summarized in Table I, and atomic coordinates are given in Table II.

Other Physical Measurements. Infrared spectra were obtained on a Mattson FT-IR spectrometer (Polaris) and susceptibility data with a Bruker electromagnet (BM-1) equipped with a Sartorius microbalance (4411). Diamagnetic corrections were performed for the determination of the magnetic moment.

Results and Discussion

Structure and Properties of 1. The anion $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ (**1a**; formally $[H_3KV^{IV}_4V^{V}_8As_3O_{39}(AsO_4)]^{6-}$) has approximate C_3 symmetry and interesting structural features and can be described as a fragment of a sphere capped by a potassium ion (see Figure 1). It is formally built of nine VO_6 octahedra, three VO_4 tetrahedra, and four AsO_4 tetrahedra, one of the latter being a central AsO_4^{3-} group. The terminal O atoms in each of the three peripheral AsO_4 groups are protonated. The number of the V^{IV} centers was determined by manganometric titration and is supported by valence-bond summations.[4]

In the crystal, the coordination sphere of the capping potassium ion is completed by oxygen atoms of another anion, which leads to a zigzag chain arrangement of linked anions (Figure 2). (In $[K_2Mo_8V_5O_{40}]^{5-}$, the capping of the two K^+ ions occurs by coordination to *terminal* O atoms.[5])

The bond lengths (Table III) and bond angles (ranges are given in Figure 1) are not discussed in detail, as we refer in this paper to geometrical and topological aspects. But all values are in the expected range.[2]

A complete assignment of the vibrational spectrum (IR) of **1** is difficult, but it is easy to assign the band at 898 cm^{-1} to the $\nu_{as}(AsO) = \nu_3(F_2)$ normal mode of the encapsulated AsO_4^{3-} ion, which leads to its identification. The bands in the $\nu(VO)$ stretching region (see Experimental Section) can easily be used as a very characteristic fingerprint for the identification of different polyoxometalates like **1a**. The total band structure is more typical for vanadates than for polymolybdates and tungstates, as the mechanical coupling is larger for the vanadates having the larger off-diagonal elements of the **G** matrix.

The μ_{eff} value (3.50 μ_B per cluster and 1.75 μ_B per V^{IV} center at room temperature) corresponds to four unpaired electrons in agreement with the results from manganometric titration. The Curie–Weiss law is fulfilled between 290 and 220 K. The negligible exchange interaction between the V^{IV} centers is expected from the rather long $V^{IV}\cdots V^{IV}$ distances of more than 5.649 Å between V(10), V(11), and V(12)[4] (Figure 1).

---

(4) The sums of the bond valences for the V atoms $\sum_i(d(V\text{–}O_i)/1.78)^{-5.15}$ are in **1** 4.33–4.43 for three "symmetry-equivalent" V^{IV} atoms (V(10)–V(12); see Figure 2), 4.75–4.84 for three tetrahedrally coordinated V^{V} atoms (V(4)–V(6)), and 4.61–4.94 for the remaining V atoms (not localized V^{IV} (formally one) and V^{V} (formally five) centers): Brown, I. D.; Kang Kun Wu. *Acta Crystallogr.* **1976**, *B32*, 1957.

(5) Björnberg, A. *Acta Crystallogr.* **1980**, *B36*, 1530.

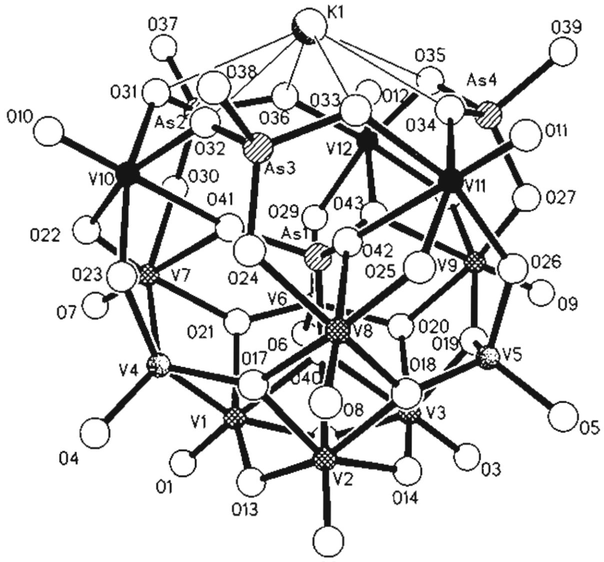

Figure 1. Structure of $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ in crystals of **1** (V^{IV} = black, V^{V} = dotted, and not localized V^{IV}/V^{V} = cross-hatched (see text); As = hatched, K = shaded, O = white; without H atoms). Ranges of bond angles (deg): O–As–O, 103.2 (2)–116.1 (2); O_t–V–O_b, 106.0 (2)–109.2 (2); O_b–V–O_b, 103.0 (2)–122.5 (2) (in VO_4 tetrahedra); O_t–V–O_b, 93.5 (2)–104.1 (3), 174.1 (2)–179.3 (2); O_b–V–O_b, 74.9 (2)–99.8 (3), 149.1 (2)–163.2 (2) (in VO_6 octahedra); As–(μ_2-O)–V, 120.9 (2)–136.3 (3); As–(μ_3-O)–V, 126.6 (2)–140.7 (2); As–(μ_4-O)–V, 126.9 (2)–129.1 (2); V–(μ_2-O)–V, 116.5 (2)–133.7 (2); V–O(As)–V, 85.7 (2)–87.9 (1); V–O(V)–V, 99.4 (2)–142.7 (3).

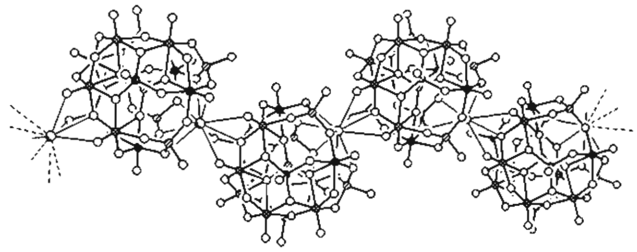

Figure 2. Zigzag chain arrangement of the linked anions in **1** viewed along the crystallographic *a* axis.

Table III. Bond Lengths and Selected K–O Distances for $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (**1**)

As(1)–O(40)	1.703 (4)	As(1)–O(41)	1.672 (3)
As(1)–O(42)	1.673 (4)	As(1)–O(43)	1.676 (4)
As(2)–O(30)	1.689 (5)	As(2)–O(31)	1.662 (4)
As(2)–O(36)	1.663 (4)	As(2)–O(37)	1.713 (5)
As(3)–O(24)	1.687 (5)	As(3)–O(32)	1.657 (4)
As(3)–O(33)	1.673 (4)	As(3)–O(38)	1.727 (4)
As(4)–O(27)	1.692 (4)	As(4)–O(34)	1.659 (4)
As(4)–O(35)	1.667 (4)	As(4)–O(39)	1.725 (5)
V(1)–V(7)	3.089 (1)	V(1)–O(1)	1.598 (5)
V(1)–O(13)	1.849 (6)	V(1)–O(15)	1.907 (4)
V(1)–O(16)	1.999 (4)	V(1)–O(21)	1.997 (5)
V(1)–O(40)	2.340 (4)	V(2)–V(8)	3.090 (1)
V(2)–O(2)	1.611 (6)	V(2)–O(13)	1.810 (5)
V(2)–O(14)	1.897 (4)	V(2)–O(17)	1.982 (4)
V(2)–O(18)	2.019 (4)	V(2)–O(40)	2.332 (5)
V(3)–V(9)	3.099 (2)	V(3)–O(3)	1.604 (4)
V(3)–O(14)	1.814 (6)	V(3)–O(15)	1.809 (5)
V(3)–O(19)	1.986 (5)	V(3)–O(20)	2.024 (5)
V(3)–O(40)	2.337 (3)	V(4)–O(4)	1.603 (5)
V(4)–O(16)	1.825 (4)	V(4)–O(17)	1.799 (4)
V(4)–O(23)	1.692 (4)	V(5)–O(5)	1.616 (4)
V(5)–O(18)	1.833 (5)	V(5)–O(19)	1.811 (5)
V(5)–O(26)	1.684 (5)	V(6)–O(6)	1.616 (5)
V(6)–O(20)	1.832 (4)	V(6)–O(21)	1.790 (4)
V(6)–O(29)	1.677 (6)	V(7)–O(7)	1.594 (5)
V(7)–O(16)	1.990 (5)	V(7)–O(21)	2.047 (4)
V(7)–O(22)	1.738 (4)	V(7)–O(30)	1.953 (5)
V(7)–O(41)	2.286 (4)	V(8)–V(11)	3.116 (2)
V(8)–O(8)	1.597 (6)	V(8)–O(17)	2.069 (4)
V(8)–O(18)	1.956 (4)	V(8)–O(24)	1.961 (4)
V(8)–O(25)	1.713 (4)	V(8)–O(42)	2.275 (5)
V(9)–O(9)	1.598 (4)	V(9)–O(19)	2.034 (5)
V(9)–O(20)	1.966 (5)	V(9)–O(27)	1.955 (4)
V(9)–O(28)	1.711 (5)	V(9)–O(43)	2.337 (3)
V(10)–O(10)	1.601 (4)	V(10)–O(22)	1.949 (4)
V(10)–O(23)	1.980 (5)	V(10)–O(31)	2.011 (5)
V(10)–O(32)	1.980 (4)	V(10)–O(41)	2.271 (4)
V(11)–O(11)	1.596 (5)	V(11)–O(25)	1.949 (5)
V(11)–O(26)	1.998 (4)	V(11)–O(33)	2.012 (4)
V(11)–O(34)	1.991 (5)	V(11)–O(42)	2.223 (4)
V(12)–O(12)	1.597 (6)	V(12)–O(28)	1.932 (4)
V(12)–O(29)	1.982 (5)	V(12)–O(35)	1.994 (4)
V(12)–O(36)	1.983 (4)	V(12)–O(43)	2.225 (5)
O(31)–K(1)	3.131 (4)	O(32)–K(1)	2.794 (5)
O(33)–K(1)	3.057 (5)	O(34)–K(1)	2.804 (4)
O(35)–K(1)	3.265 (4)	O(36)–K(1)	2.827 (5)
O(2a)–K(1)[a]	3.006 (5)	O(5a)–K(1)	3.168 (5)
O(8a)–K(1)	3.269 (4)	O(18a)–K(1)	2.838 (5)

[a] Symmetry transformation: $x, -y, 0.5 + z$.

Geometrical and Topological Aspects of Keggin Isomers and Derived Structures like That of 1a and 2a.[6] The Keggin structure can be viewed as a *basic type in polyoxometalate chemistry*, since many polyanions adopt this structure or a variety of structures derived from its fragments.[2a,b] The 24 bridging O atoms of the α isomer span a rhombicuboctahedron (Table IV) with three different sets of faces. Several polyoxovanadate structures can be described by capping the square faces with different fragments, for example V=O_t or As_2O groups.[2a] The O_{24} polyhedra of these structures are regarded as topologically equivalent, since their structural distortions or the kind of atoms and the structure of

---

(6) Basic background features of general interest for understanding are as follows. In the broadest sense, *structure* is the arrangement or interrelation of parts as dominated by the general character of the whole. The structure of a molecule can contain interesting metric and nonmetric features. *Geometry* deals with metric properties such as the congruence of angles and line segments, and *topology*, with those properties which remain invariant under one-to-one and continuous mappings. A typical example for such a topological relation is the connectivity of the atoms in a molecule, expressed by a mathematical graph consisting of knots and edges representing atoms and bonds. Stability parameters can be derived from this graph and compared to certain properties of the molecule (King, R. B., Rouvray, D. H., Eds. *Graph Theory and Topology in Chemistry*; Elsevier: Amsterdam, 1987. Merrifield, R. E.; Simmons, H. E. *Topological Methods in Chemistry*; Wiley: New York, 1989). This has been tried for polyoxometalates before (Nomiya, K.; Miwa, M. *Polyhedron* **1984**, *3*, 341; **1985**, *4*, 89, 675, 1407), but the limitation for an application is demonstrated by the fact that the derived stability index has the same value for all five different Keggin isomers. Comparing different molecules or anions with reference to their connectivities can show unexpected relations; furthermore, it can provide a tool for predicting possible structures, e.g. after substituting building moieties by others with different structures. Cluster shells like those of the polyoxometalates can be treated topologically as covering or "tiling" a sphere with polygons. This tiling can be described by the so-called Delaney symbol, based on a barycentric subdivision of the polygons into triangles (Dress, A. W. M.; Huson, D. *Geometriae Dedicata* **1987**, *24*, 295. Delaney, M. S. *MATCH* **1980**, *9*, 73). This symbol is related to the numbers of possible symmetry elements and to the curvature of the tiling, which can be demonstrated by analyzing the polyhedra of Table IV. Convex polyhedra with idealized edges of equal length are very important for the description of polyoxometalates, since their vertices can be spanned by oxygen and/or metal atoms (see Table IV). They may be *regular* (Platonic) with all vertices equivalent and all faces of the same type, *semiregular* (Archimedean), where only the first condition is fulfilled, or *nonuniform* with at least two different types of vertices (Wenninger, M. J. *Polyhedron Models*; Cambridge University Press: Cambridge, U. K., 1971). (A polyhedron is *convex*, if the sum of the angles around each vertex is less than 360°[7]). It is no simple matter to establish the exact number of the nonuniform polyhedra, but it appears that there are just 92 such solids.[7] These nonuniform solids, especially the ones with more than 12 vertices, have been considered only little in chemistry (Reference 1. Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305. Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959) with the discovery of the 14th Archimedean solid in a polyoxometalate.

(7) Johnson, N. W. *Can. J. Math.* **1966**, *18*, 169.

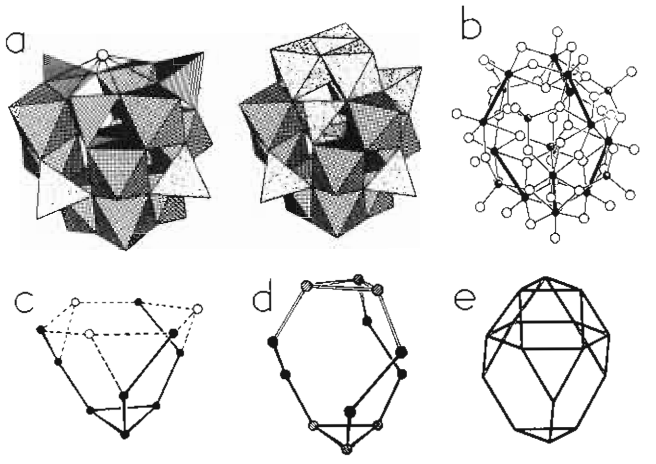

Figure 3. Demonstration of geometrical aspects of $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ (**1a**) and $[H_9V_{18}O_{46}(VO_4)]^{8-}$ (**2a**). (a) Polyhedral representation of **1a** (left) and **2a** (right). The nine VO_6 octahedra that build a fragment of the ϵ Keggin ion in both polyanions are drawn with dashes, the remaining ones and the VO_4 tetrahedra are dotted, and the AsO_4 tetrahedra are hatched. (b) Structure of **2a** with emphasis on the six V^{IV}–V^{IV} pairs with rather short distances (V^{IV} = black, V^{V} = dotted). (c) Arrangement of the nine octahedrally coordinated V atoms (black) that belong to the chiral ϵ Keggin fragment in **1a** and **2a**. The completion to a distorted "truncated tetrahedron" spanned by the V atoms of the hypothetical ϵ Keggin ion is indicated by three white V atoms with dashed lines. (d) The twelve V atoms in **2a** that are important for the magnetic properties and belong to the two penetrated ϵ Keggin fragments. The six common atoms are black, and nine V atoms of one fragment are shown with solid "bonds". (e) The nonuniform solid (truncated tetrahedron capped by a trigonal cupola), which is spanned (in a strongly distorted way) by the twelve V^{IV} and a set of three V^{V} centers in **2a**. (If the other set is used, the resulting solid is rotated by 180° perpendicular to the view direction.)

the capping moieties are not taken into consideration.

A 60° rotation of every $\{M_3O_{13}\}$ unit of the α Keggin ion (which is unknown for vanadium) formally generates the ϵ isomer with T_d symmetry,[2b] where the metal atoms form a truncated tetrahedron (VIII in Table IV), but the bridging oxygen atoms cannot be attributed to a regular polyhedron. This isomer is unknown (for reasons, see below), but **1a** contains three-fourths of it,[8] as shown in Figure 3a,c. (By neglecting the different coordination spheres and connectivities, one sees that the peripheral As atoms and their terminal O atoms complete the fragment in a distorted way.) **1a** can be derived formally (without considering the H atoms) from $[H_9V_{18}O_{46}(VO_4)]^{8-}$ (**2a**, in $(NH_4)_8[H_9V_{18}O_{46}(VO_4)]\cdot 11H_2O$[9]) by replacing a $\{V_3O_7\}$ group by a capping potassium ion and four tetrahedrally coordinated V atoms by As atoms (see Figure 3a), which is rather unusual in polyoxometalate chemistry. Without the H atoms and the $V^{V}O_4$ tetrahedra, **2a** can be described as *two chiral fragments of the ϵ Keggin ion which are penetrated* so that they have six VO_6 octahedra in common (see Figure 3a,d) and form a *new basic polyoxometalate structure*. (As in **1a**, one set of three tetrahedra can be considered only formally as completing one ϵ Keggin fragment.) Each of the two ϵ Keggin fragments of **2a** contains three V^{IV}–V^{IV} pairs (Figure 3b) with rather short distances (2.896–2.994 Å) showing very strong exchange coupling.[10] Short distances like this between the V centers of two edge-shared VO_6 octahedra can only occur if the shared edges include no O atom which is trans to the terminal ones and therefore has a rather large distance to the V atoms. The rotation of the $\{V_3O_{13}\}$ units of the hypothetical α Keggin isomer can generate additional edge-sharing between the VO_6 octahedra. There are no shared edges of the described kind, which make short V–V distances possible, in the α or β isomer,

Table IV. Idealized Polyhedra Spanned by Oxygen and/or Metal Atoms of Polyoxometalates

M_x polyhedron					O_y polyhedron						
x	polyhedron	no.	type[a]	sym[b]	y	polyhedron	no.	type[a]	sym[b]	examples	ref
6	octahedron	I	P	O_h	12	cuboctahedron	II	A	O_h	$[Mo_6O_{19}]^{2-}$	2b
9	triangular cupola	III	N	C_{3v}						$[W_9O_{30}(PO_4)]^{9-}$	2b
10	gyroelongated square bipyramid	IV	N	D_{4d}	16	square gyrobicupola	V	N	D_{4d}	$[V_{10}O_{26}]^{4-}$	c
10	elongated square bipyramid	VI	N	D_{4h}						$[W_{10}O_{32}]^{4-}$	2b
12	icosahedron	VII	P	I_h	12[d]	icosahedron	VII	P	I_h	$[Mo_{12}O_{42}(Ce)]^{8-}$	2b
12	truncated tetrahedron	VIII	A	T_d	12[d]	cuboctahedron	II	A	O_h	$[Mo_{12}(HOAsO_3)_4O_{34}]^{4-}$	2b
12	cuboctahedron	II	A	O_h	24[11]	rhombicuboctahedron	IX	A	O_h	$[Mo_{12}O_{36}(PO_4)]^{3-}$ (α Keggin)	2b
12	triangular bicupola ("anticuboctahedron")	X	N	D_{3h}						$[W_{12}O_{36}(SiO_4)]^{4-}$ (β Keggin)	2b
12	truncated tetrahedron	VIII	A	T_d						$[H_3V_{12}Mn_3O_{40}]^{5-}$ ("ϵ Keggin")	11
12	cuboctahedron	II	A	O_h						$[V_{14}O_{40}(Al)]^{9-}$ and $[V_{14}O_{40}(As)]^{7-}$ (central unit of sherwoodite)	2b, *e*
					24	rhombicuboctahedron	IX	A	O_h	$[V_{18}O_{42}(SO_4)]^{8-}$	*f*
					24	elongated square gyrobicupola ("14th Archimedean solid")	XI	N	D_{4d}	$[H_4V_{18}O_{42}(X)]^{9-}$ (X = Cl, Br, I)	*g*
18	elongated triangular bicupola	XII	N	D_{3h}						α-$[W_{18}P_2O_{62}]^{6-}$	2b
18	elongated triangular gyrobicupola	XIII	N	D_{3d}						β-$[W_{18}P_2O_{62}]^{6-}$	2b
30	elongated pentagonal bicupola	XIV	N	D_{5h}						$[W_{30}P_5O_{110}(Na)]^{14-}$	*h*

[a] P = Platonic solid (all vertices and all faces equivalent); A = Archimedean solid (all vertices equivalent); N = nonuniform solid (at least two different types of vertices). [b] Real symmetry is generally reduced by distortions. [c] Bino, A.; Cohen, S.; Heitner-Wirguin, C. *Inorg. Chem.* **1982**, *21*, 429. [d] Inner shell of oxygen atoms. [e] Müller, A.; Döring, J.; Khan, M. I.; Wittneben, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 210. [f] Müller, A.; Döring, J.; Bögge, H.; Krickemeyer, E. *Chimia* **1988**, *42*, 300. [g] Müller, A.; Penk, M.; Rohlfing, R.; Krickemeyer, E.; Döring, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 926. Cf. also: Johnson, G. K.; Schlemper, E. O. *J. Am. Chem. Soc.* **1978**, *100*, 3645. [h] Alizadeh, M. H.; Harmalker, S. P.; Jeannin, Y.; Martin-Frère, J.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662.

---

(8) Cf. also the anion $[HV_{19}O_{45}(VO_4)]^{8-}$ in ref 2b.

(9) Müller, A.; Penk, M.; Krickemeyer, E.; Bögge, H.; Walberg, H.-J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1719.

(10) Müller, A.; Rohlfing, R.; Döring, J.; Penk, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 588.

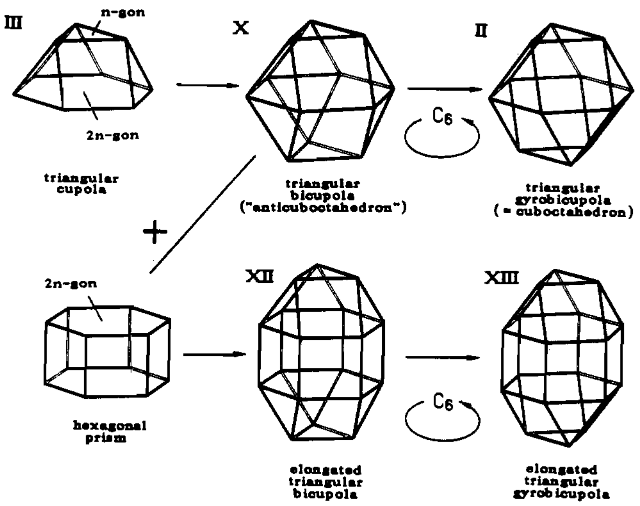

Figure 4. Relationships between some polyhedra of Table IV together with an elucidation of the nomenclature of these solids, demonstrating the function of cupolas for the construction of nonuniform solids like that in **2a** (Figure 3e).

but six in the ε isomer. (In the *only* other derivative of the ε isomer, at least named as such, $[H_3V_{12}Mn_3O_{40}]^{5-}$, the symmetry is reduced to C_{3v} by the additional Mn and H atoms.[11])

The 12 V^{IV} centers of **2a** (cf. Figure 3d) can, *alternatively* to the discussion above, be described as spanning a to some extent twisted and strongly distorted fragment of a *nonuniform solid*: an "augmented truncated tetrahedron".[7] It consists of a truncated tetrahedron capped by a trigonal cupola (definition see below) and is shown in Figure 3e. (Again, this solid is "completed" by a set of three V^V atoms.) This geometrically idealized polyhedron and its related distorted version as it is spanned by a part of the V atoms of **2a** are *topologically equivalent*.

Several polyhedra spanned by the metal and/or oxygen atoms of other polyoxometalates are listed in Table IV. Some of these polyhedra of Table IV exist as pairs, which are related by a rotation C_{2n} of one "*cupola*",[7] *which also occurs in the description of the structure of* ***2a***. (An *n*-gonal cupola with C_{nv} symmetry has *n* triangular and *n* square faces separating two polygons with *n* and 2*n* vertices; see Figure 4.) These pairs are II and X (C_6), IX and XI (C_8), XII and XIII (C_6), and also, in a similar way, IV and VI (C_8) where the central square antiprism becomes a cube. Additionally, "elongated" solids can be generated by insertion of a 2*n*-gonal prism or antiprism into a "bicupola".[7] Examples for the "elongation" are polyhedra II and XIII (2*n* = 6), V and XI (2*n* = 8), X and XII (2*n* = 6), and (as a simplified case with 2n = 4) I and VI (prism) or IV (antiprism). The fundamental relationships between these polyhedra are important for common basic type structures like the Keggin or Dawson[2b] ones (which both exist as a series of various isomers as indicated in Table IV), but also for the basic type structures derived from these (like penetrated fragments as in the case of **2a**).

These considerations can of course be extended to solids not belonging to the 92 nonuniform ones.[12] An example therefore is the polyhedron spanned by all of the 18 peripheral V atoms in **2a**. It can be described as an "augmented truncated tetrahedron" of (12 + 3) V atoms (see above) with three hexagons being capped by the remaining three V^V atoms. This kind of capping leads to the nonregular faces of this polyhedron, which cannot be idealized to regular ones. All faces are additionally distorted, so that the approximate D_3 symmetry of the original V–O cluster shell of **2a** is retained.

It may be shown, that topological and/or geometrical aspects can help to classify several features (like magnetic properties) and also isomerisms of polyoxometalates. Stability considerations can be related to the symmetry of the polyhedra spanned by the metal or oxygen atoms, as in the case of the known topologically different Keggin isomers. By means of calculations of the repulsion energy of the metal atoms, it can been shown that the α and β isomers of the Keggin ion are more stable than the others, for instance the ε one.[13] Also, the density of the packing of the oxygen atoms decreases continuously from the α or the β to the ε isomer, leading to a lacunary arrangement of the oxygen atoms. In the more stable species, the atoms tend to form convex polyhedra as in the α or β species, *whereby "connected" fragments of the less stable species like the ε isomer seem to be stable, too (example* ***2a****)*. This seems to be also correct for species like **1a** consisting of one ε fragment which is stabilized by other groups (in the case of **1a** by a capping potassium ion and by additional VO_4 tetrahedra). The tendency of the metal centers to form polyhedra with a minimization of Coulombic repulsions seems to be obvious. But, the connection between the extent of the metal–metal interaction and the kind of polyhedron thereby formed is not completely understood.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Dr. H. Bögge for his help with the X-ray structure analysis.

Registry No. 1, 137233-81-9; KVO_3, 13769-43-2; As_2O_5, 1303-28-2; KSCN, 333-20-0.

Supplementary Material Available: Tables giving the details of the crystal structure determination, thermal parameters, potassium–oxygen distances, and bond angles for **1** (11 pages); a listing of calculated and observed structure factors for **1** (36 pages). Ordering information is given on any current masthead page.

---

(11) Ichida, H.; Nagai, K.; Sasaki, Y.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 586. The poly*cation* $[Al_{12}(OH)_{24}(H_2O)_{12}(AlO_4)]^{7+}$ also has ε Keggin structure (Johansson, G. *Ark. Kemi* **1963**, *20*, 305, 321).

(12) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1981**, *20*, 1333.

(13) Favas, M. C.; Kepert, D. L. *Prog. Inorg. Chem.* **1981**, *28*, 309.