Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403-1253

Single-Crystal X-ray Structures of the Polyoxotungstate Salts $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot24H_2O$ and $Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot53H_2O$

Timothy J. R. Weakley* and Richard G. Finke*

Received May 16, 1989

The structures of single crystals of the polyoxotungstate salts $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot24H_2O$ (**1**) and $Na_{14}Cu[Cu_4(H_4O)_2(P_2W_{15}O_{56})_2]\cdot53H_2O$ (**2**) have been determined by X-ray diffraction (Mo radiation). Crystal data: **1**, triclinic, $P\bar{1}$, a = 12.369 (6) Å, b = 16.957 (7) Å, c = 11.736 (6) Å, α = 108.64 (4)°, β = 98.47 (5)°, γ = 82.42 (4)°, Z = 1, $R(F)$ = 0.043 for 5714 independent data [$I \geq 3\sigma(I)$]; **2**, triclinic, $P\bar{1}$, a = 13.399 (9) Å, b = 25.017 (13) Å, c = 13.339 (9) Å, α = 104.84 (5)°, β = 114.49 (5)°, γ = 82.61 (5)°, Z = 1, $R(F)$ = 0.068 for 4615 independent data [$I \geq 3\sigma(I)$]. Two B-α-$PW_9O_{34}^{9-}$ units in **1**, and two α-$P_2W_{15}O_{56}^{12-}$ units in **2**, are linked via a set of four coplanar Cu^{2+} atoms, two of which also carry H_2O ligands. The CuO_6 octahedra in each centrosymmetric anion are all tetragonally elongated with their long axes parallel.

Introduction

The work here reported continues earlier studies of heteropolyanions of the types $[X_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ (X = P, As; M = Mn, Co, Ni, Cu, Zn)[1-3,5a] and $[P_4W_{30}M_4(H_2O)_2O_{112}]^{16-}$ (M = Co, Cu, Zn).[4,5a] The anions of the first group are known from X-ray structural analysis (X = P, M = Co; X = As, M = Zn)[1,3] to have the composition $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ in which two $[B\text{-}\alpha\text{-}XW_9O_{34}]^{9-}$ groups are linked by a planar set of four octahedrally coordinated M^{2+} atoms in a centrosymmetric arrangement (for the notation distinguishing isomeric heteropolyanions see ref 6). The anions retain their solid-state structure in aqueous solution (^{183}W NMR, M = Zn),[2,3,5a] but the *solution* stability of $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ is much lower than that of the Zn^{2+} or Co^{2+} analogues.[5b] The anions of the $[P_4W_{30}M_4(H_2O)_2O_{112}]^{16-}$ group have not been structurally characterized by single-crystal X-ray diffraction. However, all results to date, particularly ^{31}P and 1- and 2-D ^{183}W NMR spectra,[4,5a] point to the formulation $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ for this group of anions, with a central group of four M^{2+} ions separating two α-$P_2W_{15}O_{56}^{12-}$ units in a centrosymmetric arrangement with C_{2h} symmetry.

Thus, the anions of the types "$P_2W_{18}M_4$" and "$P_4W_{30}M_4$" constitute the first members of an extended class[4,5a] of heteropolyanions. However, several questions remain despite earlier studies[1-5] of this class. (1) A single-crystal X-ray analysis of a member of the $P_4W_{30}M_4$ group is needed to confirm the general structure. (2) An X-ray determination of the structure of $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ is needed (a) to confirm that the anion has the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ structure[1,3] (the K^+ salts of the two anions are *not* isomorphous), (b) to determine the magnitude of the expected Jahn-Teller distortion of the $Cu^{II}O_6$ octahedra, and (c) to answer the question "Is this distortion responsible for the greater hydrolytic instability of the Cu-containing anion compared with the Co and Zn analogue?" (3) Comparison of the structures of $P_2W_{18}Cu_4(H_2O)_2O_{68}^{10-}$ and $P_4W_{30}Cu_4(H_2O)_2O_{112}^{10-}$ is needed. Are there structural reasons for the greater stability in solution[4,5a] of the latter anion, which unlike the former can withstand prolonged boiling in unbuffered water? The thermodynamic or kinetic factors stabilizing or destabilizing heteropolyanions are little studied.[7] With the necessary structural characterizations, we anticipate that the $P_2W_{18}M_4$ and $P_4W_{30}M_4$ heteropolyanions could become a prototype system for such studies.

Table I. Crystallographic Data

	1	2
formula	$K_{8.3}Na_{1.7}[Cu_4(H_2O)_2$-$(PW_9O_{34})_2]\cdot24H_2O$	$Na_{14}Cu[Cu_4(H_2O)_2$-$(P_2W_{15}O_{56})_2]\cdot53H_2O$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.369 (8)	13.399 (9)
b, Å	16.957 (7)	25.017 (13)
c, Å	11.736 (6)	13.339 (9)
α, deg	108.64 (7)	104.84 (5)
β, deg	98.47 (5)	114.49 (5)
γ, deg	82.42 (4)	82.61 (5)
V, Å^3	2298 (2)	3933 (7)
Z	1	1
T, °C	23	23
ρ_{calc}, g cm^{-3}	3.98	3.82
μ, cm^{-1}	250.2	238.6
transm coeff	0.53-1.00	0.14-1.00
$R(F)$	0.043	0.068
$R_w(F)$	0.056	0.085

We now report the crystal structures of **1**, $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot24H_2O$ and **2**, $Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot53H_2O$. The latter salt affords satisfactory crystals for X-ray work on recrystallization from aqueous solution, unlike the nonisomorphous, microcrystalline Na^+ salts of the corresponding Co and Zn complexes.

Experimental Section

The compounds were prepared as described elsewhere.[5a] Compound **1** was recrystallized from hot water (60 °C). Pale green prismatic crystals suitable for X-ray work were deposited from a slightly supersaturated solution on standing at room temperature. Anal. (after air-drying at 20 °C). Calcd for $K_{8.3}Na_{1.7}Cu_4W_{18}O_{70}H_4\cdot24H_2O$: K, 5.85; Na, 0.71; W, 59.7. Found: K, 5.98; Na, 0.71; W, 59.9. Yellow-green block-shaped crystals of compound **2** suitable for X-ray work were obtained by recrystallization from warm (40 °C) 0.5 M aqueous NaCl. The weight loss on drying overnight in air at 195 °C indicated the presence of 53 ± 1 lattice water molecules per anion. Anal. (after air-drying at 20 °C). Calcd for $Na_{14}Cu_5P_4W_{30}O_{114}H_4\cdot53H_2O$: Na, 3.55; Cu, 3.51; P, 1.37; W, 60.9. Found: Na, 3.52; Cu, 3.47; P, 1.37; W, 61.0 (analyses by Microanalytisches Labor Pascher, Remagen, FRG). Note the extra Cu atom, in addition to the four required for the $P_4Cu_4W_{30}O_{114}H_4^{16-}$ anion, found by the elemental analysis (and by the structural study; vide infra).

X-ray Crystallography. Crystals were taken directly from their mother liquor and sealed in Lindemann glass capillaries. Intensity data for each compound were collected by use of a Rigaku AFC6R diffractometer, at the joint University of Oregon/Oregon State University (OSU) crystallographic facility for **1** and at Molecular Structures Corp., College Station, TX for **2**. Structure solution and refinement for both compounds were carried out on a MicroVAX Series II/RC computer at OSU. The

---

(1) Weakley, T. J. R.; Evans, H. T., Jr.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139.

(2) Finke, R. G.; Droege, M. W.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587.

(3) Evans, H. T., Jr.; Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2699.

(4) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *27*, 1006.

(5) (a) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886. (b) This assessment is based on (i) the lower maximum permissible temperature (ca. 60 °C) of an aqueous solution from which the K^+ salt can be recrystallized without the codeposition of a microcrystalline decomposition product and (ii) the conversion of the Cu^{2+} complex in aqueous solution at 100 °C to a second tungstophosphatocuprate anion.[5a] The IR spectrum and X-ray powder pattern of the K^+ salt of the latter anion resemble those of a byproduct formed in substantial amount during the original preparation;[5a] both substances have only been obtained as microneedles and have not yet been characterized further.

(6) Pope, M. T. *Isopoly and Heteropoly Oxometalate Anions*; Springer-Verlag: Berlin, 1983; pp 26, 59.

(7) (a) Kyle, J. M. *J. Chem. Soc., Dalton Trans.* **1983**, 2609. (b) Kepert, D. L.; Kyle, J. M. *J. Chem. Soc., Dalton Trans.* **1978**, 133. (c) Kepert, D. L.; Kyle, J. M. *J. Chem. Soc., Dalton Trans.* **1978**, 137. (d) Kepert, D. L.; Kyle, J. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1781.

0020-1669/90/1329-1235$02.50/0

TEXSAN suite,[8] which included the programs MITHRIL[9] (direct methods), DIRDIF[10] (structure expansion), and DIFABS[11] (empirical absorption correction), was used for all calculations. Atomic scattering factors were taken from ref 12. Each data set clearly had a centric distribution of intensity, and the assumption of one formula unit in the triclinic cell led to a reasonable value of the calculated density of each compound. No corrections for crystal decay were needed. A summary of the crystallographic data is given in Table I and a fuller version as supplementary material, Table SI.

$K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot 24H_2O$ (1). The *E* map of highest figure of merit showed a clear image of the PW_9 atom set of the asymmetric unit whose orientation agreed with the Patterson W···W vectors but which was apparently misplaced with respect to a crystallographic inversion center. Application of the TRADIR subprogram of DIRDIF shifted the PW_9 unit to the correct position and revealed the two independent Cu atoms and some of the K and O atoms. Further cycles of DIRDIF showed the remaining O atoms of the anion. The absorption correction DIFABS was performed after isotropic refinement of the above atoms. Water oxygen atoms were located in subsequent difference syntheses. Some of the water molecules and one K^+ ion could not be located and were presumed to be disordered, nor could the Na^+ ions be positively identified (see footnote 13). The W, Cu, P, and K atoms were allowed anisotropic thermal parameters in the last cycles of full-matrix least-squares refinement. None of the stronger residual peaks (maximum 3.3 e $Å^{-3}$), many of which lay within the volume of the anion, could be identified as missing or misplaced atoms at chemically reasonable positions.

$Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$ (2). An empirical absorption correction based on azimuthal ("ψ") scans for three reflections was applied. The *E* map of highest figure of merit showed *two* complete and identically oriented, partly overlapping, images of the W_{15} framework of the asymmetric unit. The orientation of these images agreed with the strong Patterson peaks attributable to W···W vectors. Consideration of the likely C_{2h} structure of the anion,[4,5] including the presence of a central centrosymmetric set of four Cu atoms, indicated that approximate positions of the W atoms should be obtainable by averaging the positions of corresponding peaks of the two images of the W_{15} set. After this was done, repeated DIRDIF calculations gave the Cu, P, and anion O atoms. Four independent Na^+ ions and several water oxygens were revealed in a difference synthesis after isotropic least-squares refinement, and other water oxygens appeared after a further correction of the data for absorption (DIFABS). One cation, on a crystallographic inversion center, was deduced to be an extra Cu^{2+} ion [Cu(3)] from its coordination bond lengths and from its negative thermal parameter when treated as Na^+. Subsequent chemical analysis (above) supported this assignment. The W and Cu atoms were allowed anisotropic thermal parameters in the last cycles of full-matrix least-squares refinement. The strongest peaks (maximum 3.3 e $Å^{-3}$) all lay within 1.4 Å of a W atom. The high values of the residuals (Table I) seem to result from a combination of indifferent crystal quality, high absorption, and partial disorder in the interanion voids[13] (three Na^+ ions and ca. nine H_2O molecules could not be convincingly located).

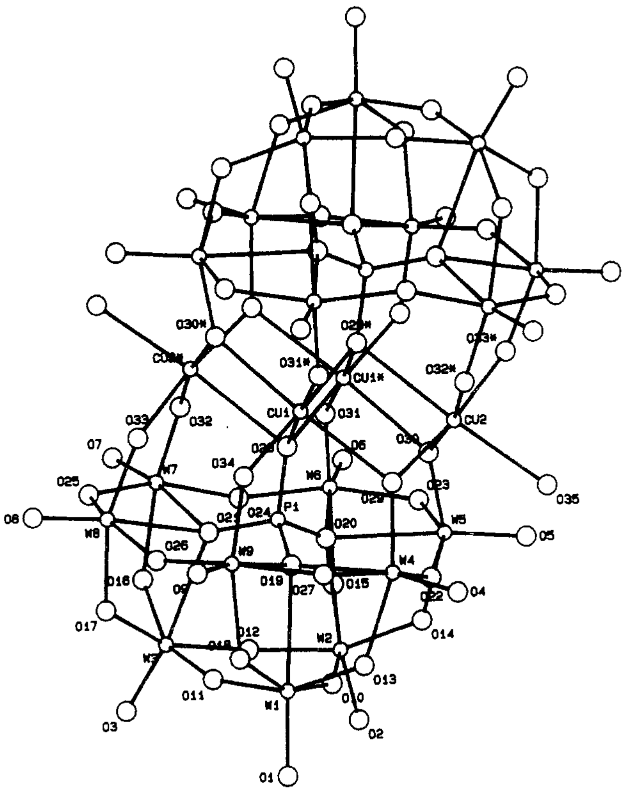

Figure 1. General view of the $[Cu_4(H_2O)_2(PW_9O_{32})_2]^{10-}$ anion in **1**.

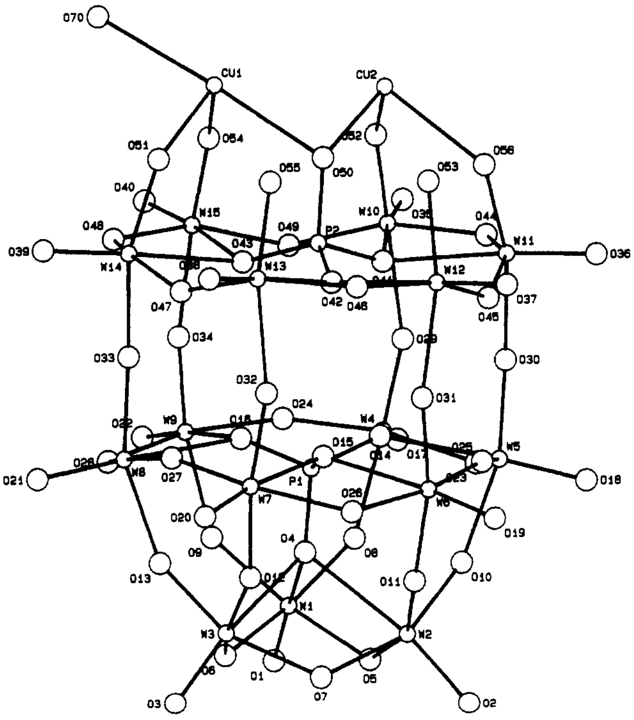

Figure 2. Asymmetric unit of the $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ anion in **2**.

Other Measurements. A Corning Model 125 pH meter with combination electrode was used in a control experiment regarding the pH of solutions of **1** and **2** (see "Solution Stabilities" under "Discussion", below).

---

(8) *TEXRAY Structural Analysis Program Suite*; Molecular Structures Corp.: College Station, TX, 1987.

(9) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(10) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 65 Ed Nijmegen, The Netherlands, 1984.

(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. C* **1983**, *39*, 158.

(12) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 148.

(13) A reviewer commented on the "incompleteness" of our determination of the structures of **1** and **2**. Unfortunately, disorder or partial disorder of the cations and lattice water in the interanion voids is common even for those crystals of heteropolyanion salts that diffract well enough to give an adequate numerical ratio of data to parameters. In the words of a second reviewer, "These large anions are a crystallographer's nightmare. Only rarely do crystals, when obtainable, produce sufficient diffraction to make data collection worth while. The structures, if solved, have large numbers of associated cations and water molecules which are inevitably disordered." We also quote from three recent reports of work in which the structures of the anions were unambiguously determined. (i) "Only one [independent water molecule] could be efficiently refined...it is believed that the other molecules are highly disordered, as frequently happens in heteropolyanion structures."[14a] (ii) "It was not possible to locate all cations required by charge balance. No attempt was made to find water molecules."[14b] (iii) "As often occurs in heteropolyanion structures, all cations were not found. Half of the rubidium atoms are missing. Water molecules were not located."[14c] For similar recent cases, see refs 14d–i.

(14) (a) Jeannin, Y.; Launay, J. P.; Sedjadi, M. A. S. *Inorg. Chem.* **1980**, *19*, 2933. (b) Martin-Frère, J.; Jeannin, Y. *Inorg. Chem.* **1984**, *23*, 3394. (c) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1986**, *25*, 2114. (d) Robert, F.; Leyrie, M.; Hervé, G.; Tézé, A.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1746. (e) Jameson, G. B.; Pope, M. T.; Wasfi, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 4911. (f) Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577. (g) Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2237. (h) Liu, B.-Y.; Ku, Y.-T.; Wang, M.; Zheng, P.-J. *Inorg. Chem.* **1988**, *27*, 3868. (i) Tourné, C. M.; Tourné, G. F. *J. Chem. Soc., Dalton Trans.* **1988**, 2411.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic (O) or Equivalent Isotropic (W, Cu, P, K) Thermal Parameters (Å^2) for **1**, $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot 24H_2O$

atom	*x*	*y*	*z*	*B*
W(1)	2732.0 (7)	2273.7 (5)	1108.1 (7)	0.98 (3)
W(2)	3022.4 (7)	1748.8 (5)	3963.7 (7)	0.98 (3)
W(3)	5286.2 (7)	1114.0 (5)	2016.4 (7)	0.96 (3)
W(4)	2145.9 (7)	4357.3 (5)	2693.0 (7)	0.79 (3)
W(5)	2425.2 (7)	3833.5 (5)	5513.2 (7)	0.81 (3)
W(6)	4822.2 (7)	2798.1 (5)	622.2 (7)	0.83 (3)
W(7)	7085.3 (7)	2144.7 (5)	4405.3 (7)	0.97 (3)
W(8)	6829.8 (7)	2621.6 (5)	1808.3 (7)	0.90 (3)
W(9)	4275.4 (7)	3792.8 (5)	967.9 (7)	0.78 (3)
Cu(1)	4871 (2)	5226 (1)	3813 (2)	0.82 (8)
Cu(2)	2837 (2)	5771 (1)	5445 (2)	0.92 (9)
K(1)	4923 (5)	1519 (3)	8914 (4)	2.5 (2)
K(2)	6420 (7)	4010 (5)	8933 (6)	5.2 (3)
K(3)	8934 (6)	4148 (5)	2023 (7)	5.3 (4)
P(1)	4639 (4)	3337 (3)	3679 (4)	0.7 (2)
O(1)	1910 (13)	1627 (9)	−33 (13)	2.0 (3)
O(2)	2297 (13)	911 (9)	3832 (12)	1.9 (3)
O(3)	5329 (12)	87 (9)	1248 (12)	1.9 (3)
O(4)	912 (12)	4895 (9)	2487 (12)	1.9 (3)
O(5)	1304 (13)	4208 (9)	6288 (13)	2.1 (3)
O(6)	5190 (12)	2568 (8)	7643 (12)	1.5 (3)
O(7)	8158 (13)	1650 (9)	5063 (13)	2.3 (3)
O(8)	7732 (13)	2460 (9)	768 (13)	2.2 (3)
O(9)	4366 (12)	4053 (8)	−310 (12)	1.5 (3)
O(10)	2504 (11)	2012 (8)	2520 (11)	1.1 (2)
O(11)	4055 (12)	1585 (8)	1183 (12)	1.4 (3)
O(12)	4264 (11)	1246 (8)	3136 (11)	1.1 (2)
O(13)	1765 (12)	3242 (8)	1577 (12)	1.4 (3)
O(14)	2092 (11)	2643 (8)	4759 (11)	1.0 (2)
O(15)	3957 (11)	1842 (8)	5412 (11)	1.0 (2)
O(16)	6415 (11)	1139 (7)	3258 (11)	0.9 (2)
O(17)	6181 (11)	1509 (8)	1210 (11)	1.1 (2)
O(18)	3411 (11)	2800 (8)	250 (11)	1.0 (2)
O(19)	3820 (11)	3424 (7)	2599 (10)	0.8 (2)
O(20)	4024 (10)	3056 (7)	4511 (10)	0.5 (2)
O(21)	5568 (11)	2652 (8)	3213 (11)	1.1 (2)
O(22)	1901 (11)	3933 (8)	3948 (11)	1.3 (2)
O(23)	3387 (11)	3390 (8)	6627 (11)	1.1 (2)
O(24)	5970 (11)	2191 (8)	5392 (11)	1.0 (2)
O(25)	7645 (12)	2111 (8)	2939 (12)	1.5 (3)
O(26)	5530 (11)	3020 (8)	978 (11)	1.1 (2)
O(27)	2839 (11)	4388 (7)	1365 (11)	0.9 (2)
O(28)	5093 (11)	4181 (7)	4365 (10)	0.8 (2)
O(29)	2982 (11)	5122 (7)	3776 (11)	0.8 (2)
O(30)	3220 (11)	4730 (8)	5849 (11)	1.3 (3)
O(31)	5373 (11)	3757 (8)	6589 (11)	1.0 (2)
O(32)	7292 (11)	3221 (8)	5036 (11)	1.3 (3)
O(33)	2912 (12)	6379 (8)	7170 (12)	1.5 (3)
O(34)	5076 (11)	5419 (8)	7836 (11)	1.0 (2)
O(35)	934 (14)	5817 (10)	5361 (15)	2.9 (3)
O(36)	197 (11)	3661 (8)	7819 (11)	1.2 (2)
O(37)	3084 (11)	5200 (8)	8615 (11)	1.1 (2)
O(38)	33 (20)	2827 (14)	2948 (20)	5.8 (5)
O(39)	2186 (20)	2879 (14)	8067 (20)	5.7 (5)
O(40)	1076 (24)	4812 (18)	9638 (25)	8.1 (7)
O(41)	9858 (27)	3164 (20)	9870 (28)	9.8 (9)
O(42)	8175 (20)	3453 (14)	7525 (21)	5.9 (5)
O(43)	1297 (26)	1351 (19)	7349 (27)	8.9 (8)
O(44)	5879 (22)	370 (16)	5094 (22)	6.8 (6)
O(45)	3373 (23)	942 (17)	6929 (24)	7.4 (7)
O(46)	6658 (26)	815 (19)	7556 (27)	9.1 (8)
O(47)	2631 (28)	−113 (21)	401 (29)	10.1 (9)
O(48)	8781 (30)	−23 (22)	5001 (31)	11.1 (10)
O(49)	7800 (32)	2151 (23)	−1829 (33)	12.1 (11)

Results

Atomic coordinates and isotropic or isotropic equivalent thermal parameters for $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot 24H_2O$ (**1**) are given in Table II, bond lengths in Table III, and distances between heavy atoms in Table IV. Anisotropic thermal parameters (Table S2), bond angles (Table S3), and observed and calculated structure factors (Table S4) are listed in the supplementary material. Atomic coordinates and isotropic or isotropic equivalent thermal parameters for $Na_{10}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$ (**2**) are given in Table V, bond lengths in Table VI, and distances between heavy atoms in Table VII. Anisotropic thermal parameters (Table S5), bond angles (Table S6), and observed and calculated structure factors (Table S7) are listed in the supplementary material.

Table III. Bond Lengths (Å) for **1**, $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot 24H_2O$

	(a) Anion		
W(1)–O(1)	1.73 (1)	W(4)–O(13)	2.00 (1)
W(1)–O(13)	1.88 (1)	W(4)–O(19)	2.43 (1)
W(1)–O(18)	1.88 (1)	W(5)–O(5)	1.71 (2)
W(1)–O(11)	1.89 (1)	W(5)–O(30)	1.83 (1)
W(1)–O(10)	1.92 (1)	W(5)–O(23)	1.91 (1)
W(1)–O(19)	2.55 (1)	W(5)–O(22)	1.91 (1)
W(2)–O(2)	1.74 (1)	W(5)–O(14)	2.00 (1)
W(2)–O(14)	1.86 (1)	W(5)–O(20)	2.46 (1)
W(2)–O(15)	1.89 (1)	W(6)–O(6)	1.70 (1)
W(2)–O(10)	1.89 (1)	W(6)–O(31)	1.77 (1)
W(2)–O(12)	1.90 (1)	W(6)–O(24)	1.90 (1)
W(2)–O(20)	2.54 (1)	W(6)–O(23)	1.94 (1)
W(3)–O(3)	1.69 (1)	W(6)–O(15)	1.98 (1)
W(3)–O(16)	1.86 (1)	W(6)–O(20)	2.36 (1)
W(3)–O(17)	1.87 (1)	W(7)–O(7)	1.70 (2)
W(3)–O(12)	1.90 (7)	W(7)–O(32)	1.78 (1)
W(3)–O(11)	1.92 (1)	W(7)–O(24)	1.91 (1)
W(3)–O(21)	2.58 (1)	W(7)–O(25)	1.93 (1)
W(4)–O(4)	1.70 (2)	W(7)–O(16)	2.00 (1)
W(4)–O(29)	1.81 (1)	W(7)–O(21)	2.41 (1)
W(4)–O(27)	1.91 (1)	W(8)–O(8)	1.71 (2)
W(4)–O(22)	1.91 (1)	W(8)–O(33)	1.78 (1)
W(8)–O(25)	1.91 (1)	Cu(1)–O(28′)	2.05 (1)
W(8)–O(26)	1.90 (1)	Cu(1)–O(30)	2.35 (1)
W(8)–O(17)	2.02 (1)	Cu(1)–O(29)	2.36 (1)
W(8)–O(21)	2.42 (1)	Cu(2)–O(29)	1.94 (1)
W(9)–O(9)	1.72 (1)	Cu(2)–O(32)	1.95 (1)
W(9)–O(34)	1.87 (1)	Cu(2)–O(33)	1.95 (1)
W(9)–O(26)	1.90 (1)	Cu(2)–O(30)	1.96 (1)
W(9)–O(27)	1.97 (1)	Cu(2)–O(35)	2.34 (2)
W(9)–O(18)	2.00 (1)	Cu(2)–O(28)	2.55 (1)
W(9)–O(19)	2.35 (1)	P(1)–O(28)	1.55 (1)
Cu(1)–O(34)	1.90 (1)	P(1)–O(19)	1.54 (1)
Cu(1)–O(31)	1.91 (1)	P(1)–O(20)	1.54 (1)
Cu(1)–O(28)	2.05 (1)	P(1)–O(21)	1.55 (1)
	(b) Cations		
K(1)–O(3)	2.73 (2)	K(2)–O(9)	2.80 (2)
K(1)–O(6)	2.75 (1)	K(2)–O(42)	2.80 (3)
K(1)–O(46)	2.78 (3)	K(2)–O(6)	2.92 (2)
K(1)–O(45)	2.80 (3)	K(3)–O(37)	2.70 (2)
K(1)–O(18)	2.88 (1)	K(3)–O(4)	2.81 (2)
K(1)–O(17)	2.91 (1)	K(3)–O(41)	2.85 (3)
K(1)–O(11)	2.98 (1)	K(3)–O(5)	2.87 (2)
K(1)–O(26)	2.99 (1)	K(3)–O(38)	2.90 (3)
K(2)–O(37)	2.78 (1)	K(3)–O(33)	2.94 (2)
K(2)–O(31)	2.79 (1)	K(3)–O(40)	3.02 (3)

Table IV. Distances (Å) between W, Cu, and P Atoms in **1**, $K_{8.3}Na_{1.7}[Cu_4(H_2O)_2(PW_9O_{34})_2]\cdot 24H_2O$

W(1)···W(2)	3.698 (2)	W(3)···W(8)	3.478 (2)
W(1)···W(3)	3.708 (2)	W(4)···W(5)	3.658 (2)
W(2)···W(3)	3.709 (2)	W(4)···W(9)	3.411 (2)
W(1)···W(4)	3.467 (2)	W(5)···W(6)	3.418 (2)
W(1)···W(9)	3.425 (2)	W(6)···W(7)	3.686 (2)
W(2)···W(5)	3.461 (2)	W(7)···W(8)	3.364 (2)
W(2)···W(6)	3.450 (2)	W(8)···W(9)	3.692 (2)
W(3)···W(7)	3.459 (2)		
W(4)···Cu(2)	3.423 (3)	W(5)···Cu(1*)	3.769 (3)
W(4)···Cu(1)	3.750 (3)	W(6)···Cu(1*)	3.484 (3)
W(5)···Cu(2)	3.423 (3)	W(7)···Cu(2*)	3.501 (3)
W(9)···Cu(1)	3.491 (3)	W(8)···Cu(2)	3.500 (3)
Cu(1)···Cu(1*)	3.087 (4)	Cu(1*)···Cu(2)	3.263 (4)
Cu(1)···Cu(2)	3.246 (4)		
W(1)···P(1)	3.656 (5)	W(6)···P(1)	3.480 (5)
W(2)···P(1)	3.687 (5)	W(7)···P(1)	3.468 (5)
W(3)···P(1)	3.695 (5)	W(8)···P(1)	3.583 (5)
W(4)···P(1)	3.566 (5)	W(9)···P(1)	3.469 (5)
W(5)···P(1)	3.581 (5)		
Cu(1)···P(1)	3.211 (6)	Cu(2)···P(1)	3.525 (6)
Cu(1*)···P(1)	3.205 (6)		

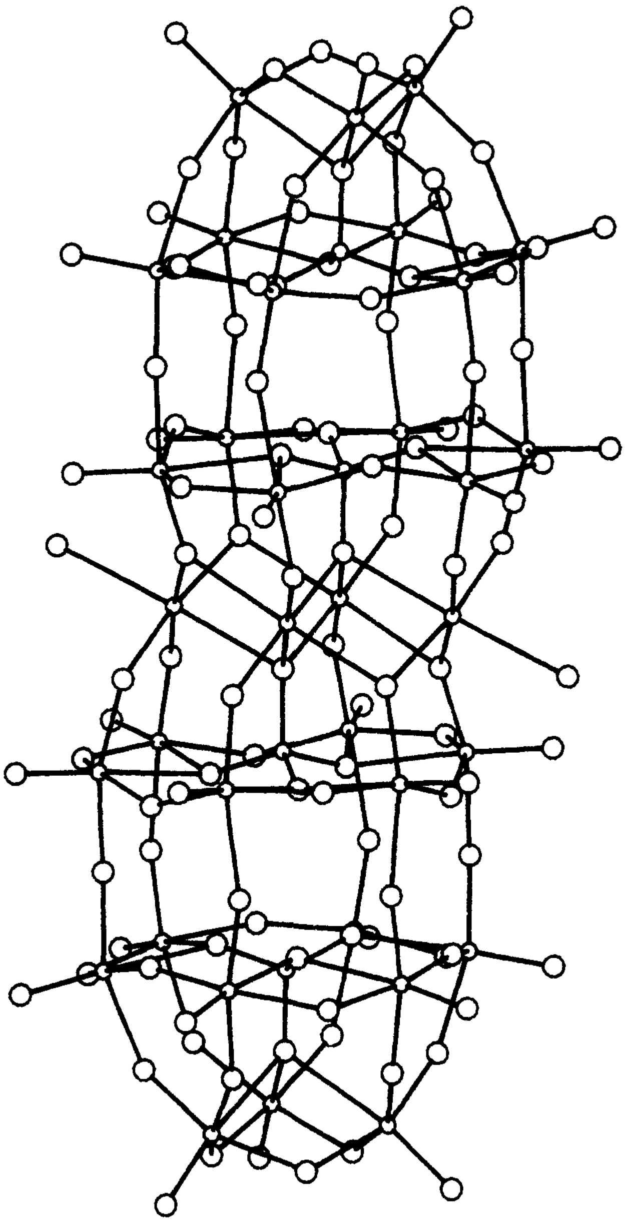

Figure 3. General view of the $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ anion in **2**.

The anions in both **1** and **2** lie on crystallographic inversion centers and have approximate symmetry $2/m$ (C_{2h}). A view of the anion $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in **1** is shown in Figure 1 with atoms labeled. The asymmetric unit of the anion $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ in **2** is shown in Figure 2 with atoms labeled, and the whole anion is shown in Figure 3. The local diad axes pass through Cu(1) and Cu(1*) in **1** and through Cu(2) and Cu(2*) in **2**, where the star implies the inversion operation.

Discussion

Structures of the Anions. The general features of $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$—the presence of the PW_9O_{34} units in the B-α isomeric form, the planar central set of four atoms of the 3d series, and the W···W distances—resemble, as expected, those of the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ anions[3] and the more recently reported $[Cu_4(H_2O)_2Fe_2(FeW_9O_{34}H)_2]^{10-}$ anion.[15]

The $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ anion has the structure deduced earlier[4,5a] for the $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ series on the basis of chemical synthesis [M(II) = Co, Cu, Zn], electronic spectra (M = Co, Cu) and ^{31}P and ^{183}W NMR spectroscopy (M = Zn). Two α-$P_2W_{15}O_{56}{}^{12-}$ units each share seven oxygen atoms, including an oxygen on P(2), with a central set of four edge-sharing CuO_6 octahedra in which the Cu atoms are coplanar. As in **1**, water ligands lie at the two unshared CuO_6 vertices. The structural relationship to the anions of the $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ series is clear (compare Figures 1 and 3). The α-$P_2W_{15}O_{56}{}^{12-}$ ligand, originally regarded[16] as $P_2W_{16}O_{59}{}^{12-}$, results from degradation of α-$P_2W_{18}O_{62}{}^{6-}$ in aqueous solution at pH 9. The structure of noncoordinated $P_2W_{15}O_{56}{}^{12-}$ has not yet been determined, but is unlikely to differ in connectivity from the structure adopted in the present complex and previously deduced[17] from the ^{183}W NMR spectrum of the derivative $P_2W_{15}Mo_3O_{62}{}^{6-}$: namely, the Dawson (α-$P_2W_{18}O_{62}{}^{6-}$) structure[18] with one end cap of three edge-sharing WO_6 octahedra missing.

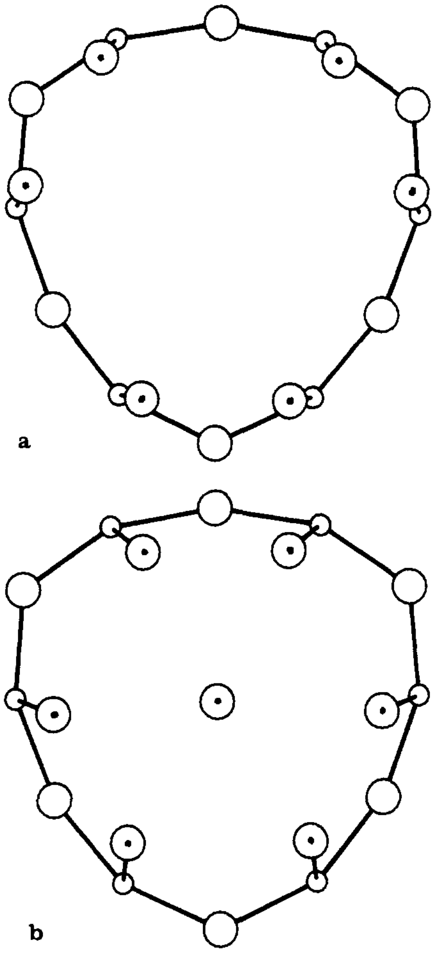

Figure 4. Belt of tungsten and oxygen atoms (small and large circles respectively) and attached ligand oxygen atoms (with dots) in (a) A-α-$PW_9O_{34}{}^{9-}$ and (b) B-α-$PW_9O_{34}{}^{9-}$. Atomic positions were taken from data of ref 19 for α-$PW_{12}O_{40}{}^{3-}$.

An unexpected feature of **2** is the additional Cu atom, Cu(3). The *un*recrystallized material contains[5a] only *four* Cu atoms per formula. Sited at ($^1/_2$, $^1/_2$, $^1/_2$), Cu(3) forms long trans bonds (Table VI) to the anion oxygen O(37) and the corresponding atom at ($1 - x$, $1 - y$, $1 - z$) and four shorter bonds to water molecules; thus the anion, centered at (0, $^1/_2$, $^1/_2$), is linked to its neighbors in the ±*a* directions.

The similarity in the mode of bonding to the Cu atoms by the tungstophosphate ligands in **1** and **2** follows from the close structural relationships known to exist between α-$PW_{12}O_{40}{}^{3-}$ and α-$P_2W_{18}O_{62}{}^{6-}$. The removal of one edge-sharing cap in each case exposes a set of seven ligand oxygen atoms. These are shown in

---

(15) Wasfi, S. H.; Rheingold, A. L.; Kokoszka, G. F.; Goldstein, A. S. *Inorg. Chem.* **1987**, *26*, 2934.

(16) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* **1977**, 2601; *J. Chem. Res., Synop.* **1977**, 222.

(17) Acerete, R.; Hammer, C. A.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478.

(18) (a) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113. (b) D'Amour, H. *Acta Crystallogr., Sect. B* **1976**, *32*, 729.

Table V. Atomic Coordinates (×10⁴) and Isotropic (P, Na, O) or Equivalent Isotropic (W, Cu) Thermal Parameters (Å²) for **2**, $Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$

atom	*x*	*y*	*z*	B_{eq}
W(1)	492 (2)	849 (1)	3050 (2)	1.4 (1)
W(2)	2623 (2)	1226 (1)	2639 (2)	1.4 (1)
W(3)	2973 (2)	1125 (1)	5262 (2)	1.3 (1)
W(4)	−1186 (2)	2015 (1)	1852 (2)	1.1 (1)
W(5)	904 (2)	2379 (1)	1438 (2)	1.05 (9)
W(6)	3580 (2)	2666 (1)	3861 (2)	0.92 (6)
W(7)	3899 (2)	2582 (1)	6436 (2)	0.96 (9)
W(8)	1592 (2)	2148 (1)	6846 (2)	1.0 (1)
W(9)	−838 (2)	1885 (1)	4682 (2)	1.2 (1)
W(10)	−2037 (2)	3541 (1)	2545 (2)	0.81 (9)
W(11)	46 (2)	3891 (1)	2083 (2)	0.79 (9)
W(12)	2664 (2)	4175 (1)	4465 (2)	0.69 (8)
W(13)	2928 (2)	4085 (1)	7028 (2)	0.73 (9)
W(14)	685 (2)	3647 (1)	7495 (2)	0.85 (9)
W(15)	−1726 (2)	3399 (1)	5322 (2)	0.78 (9)
Cu(1)	−862 (4)	4769 (3)	6442 (5)	1.0 (2)
Cu(2)	−1109 (4)	4873 (3)	4013 (5)	1.0 (2)
Cu(3)	5000	5000	5000	2.3 (4)
P(1)	1370 (10)	2206 (7)	4162 (12)	1.3 (3)
P(2)	384 (10)	3863 (6)	4863 (11)	0.9 (3)
Na(1)	1754 (16)	4261 (10)	719 (18)	2.5 (5)
Na(2)	2369 (21)	2793 (13)	−186 (25)	5.4 (7)
Na(3)	6783 (18)	3270 (11)	8017 (21)	3.7 (3)
Na(4)	5686 (22)	3010 (14)	−328 (25)	5.6 (7)
O(1)	−153 (28)	234 (18)	2490 (32)	2.9 (9)
O(2)	3277 (25)	854 (16)	1813 (29)	2.0 (8)
O(3)	3847 (29)	679 (19)	6028 (34)	3.4 (9)
O(4)	1717 (22)	1566 (14)	3902 (26)	0.9 (7)
O(5)	1478 (26)	737 (16)	2274 (30)	2.2 (8)
O(6)	1772 (23)	676 (15)	4331 (27)	1.2 (7)
O(7)	3400 (23)	963 (15)	4013 (27)	1.2 (7)
O(8)	−353 (26)	1304 (16)	2078 (30)	2.2 (8)
O(9)	−124 (22)	1221 (14)	4118 (26)	0.8 (6)
O(10)	1611 (23)	1658 (15)	1757 (27)	1.4 (7)
O(11)	3454 (22)	1851 (14)	3382 (29)	0.9 (6)
O(12)	3768 (23)	1779 (14)	5808 (26)	1.0 (7)
O(13)	2204 (25)	1502 (16)	6148 (30)	2.1 (8)
O(14)	555 (24)	2377 (15)	2979 (28)	1.6 (7)
O(15)	2399 (19)	2557 (12)	4727 (22)	−0.5 (5)
O(16)	812 (25)	2232 (16)	4949 (29)	2.0 (8)
O(17)	−2376 (25)	1690 (16)	871 (29)	1.8 (7)
O(18)	1020 (27)	2316 (17)	203 (31)	2.6 (8)
O(19)	4559 (29)	2719 (16)	3395 (29)	1.9 (7)
O(20)	5132 (22)	2560 (14)	7621 (26)	0.8 (6)
O(21)	2042 (28)	2016 (17)	8157 (32)	2.8 (8)
O(22)	−1910 (23)	1560 (15)	4573 (27)	1.4 (7)
O(23)	−471 (23)	2029 (14)	862 (26)	1.1 (7)
O(24)	−1336 (23)	1982 (14)	3160 (27)	1.1 (7)
O(25)	2307 (23)	2651 (14)	2538 (26)	1.1 (7)
O(26)	4490 (23)	2588 (14)	5317 (26)	1.0 (7)
O(27)	2859 (25)	2483 (16)	6973 (30)	2.1 (8)
O(28)	185 (23)	1805 (15)	6166 (27)	1.2 (7)
O(29)	−1560 (24)	2729 (15)	1938 (28)	1.7 (7)
O(30)	268 (22)	3062 (14)	1598 (25)	0.7 (6)
O(31)	3350 (24)	3390 (15)	4379 (28)	1.7 (7)
O(32)	3574 (23)	3327 (15)	6640 (27)	1.3 (7)
O(33)	942 (24)	2835 (15)	7032 (27)	1.4 (7)
O(34)	−1181 (26)	2594 (17)	5177 (30)	2.3 (8)
O(35)	−3410 (23)	3442 (15)	1639 (27)	1.3 (7)
O(36)	115 (23)	3985 (15)	913 (27)	1.2 (7)
O(37)	3577 (25)	4420 (16)	4073 (29)	1.8 (7)
O(38)	4052 (22)	4288 (14)	8353 (25)	0.8 (6)
O(39)	1064 (25)	3672 (15)	8893 (28)	1.8 (7)
O(40)	−3004 (23)	3259 (14)	5264 (26)	1.0 (7)
O(41)	−206 (23)	3649 (14)	3517 (26)	1.1 (7)
O(42)	1620 (20)	3831 (12)	5216 (23)	−0.2 (6)
O(43)	73 (21)	3574 (13)	5570 (24)	0.5 (6)
O(44)	−1462 (21)	3687 (13)	1534 (25)	0.5 (6)
O(45)	1570 (22)	3870 (14)	3004 (26)	0.9 (7)
O(46)	3515 (21)	4261 (13)	6064 (25)	0.5 (6)
O(47)	2085 (23)	3726 (14)	7464 (26)	1.0 (7)
O(48)	−829 (21)	3418 (13)	6860 (24)	0.3 (6)
O(49)	−2026 (25)	3276 (16)	3732 (29)	1.8 (7)
O(50)	29 (25)	4480 (16)	5112 (29)	1.9 (8)
O(51)	196 (23)	4343 (15)	7389 (26)	1.1 (7)
O(52)	−2056 (21)	4250 (13)	3231 (24)	0.3 (6)
O(53)	1864 (26)	4791 (17)	4665 (31)	2.4 (8)
O(54)	−1816 (24)	4122 (16)	5585 (28)	1.7 (7)
O(55)	2106 (26)	4693 (17)	6964 (31)	2.5 (8)
O(56)	−69 (23)	4587 (15)	2836 (27)	1.3 (7)
O(70)	−1995 (27)	4952 (17)	7686 (31)	2.6 (8)
O(71)	5095 (30)	3552 (19)	2668 (35)	3.7 (9)
O(72)	6786 (29)	957 (19)	4356 (33)	3.3 (9)
O(73)	2710 (25)	3478 (16)	1471 (29)	2.0 (8)
O(74)	5965 (30)	4430 (19)	4504 (34)	3.5 (9)
O(75)	5447 (40)	2198 (26)	−36 (47)	7 (2)
O(76)	5564 (26)	4776 (17)	6536 (30)	2.4 (8)
O(77)	901 (30)	4939 (19)	−300 (35)	4 (1)
O(78)	6029 (27)	3818 (17)	9303 (31)	2.6 (8)
O(79)	8290 (32)	3913 (20)	8543 (36)	4 (1)
O(80)	3389 (30)	4329 (19)	454 (34)	3.6 (9)
O(81)	3672 (28)	3202 (17)	−650 (32)	2.7 (8)
O(82)	5662 (26)	3668 (17)	6416 (31)	2.5 (8)
O(83)	7279 (35)	4776 (23)	604 (41)	6 (1)
O(84)	4478 (28)	5328 (18)	7970 (34)	3.3 (9)
O(85)	3706 (43)	2126 (28)	766 (49)	8 (2)
O(86)	6324 (36)	2336 (23)	2612 (41)	6 (1)
O(87)	7600 (37)	2816 (24)	9560 (43)	6 (1)
O(88)	7235 (35)	2559 (23)	6706 (41)	5 (1)

Figure 4b for the derivative B-α-$PW_9O_{34}^{9-}$; as the detailed structure of the latter has not yet been determined, the atomic positions have been taken from the known structure[19] of α-$PW_{12}O_{40}^{3-}$. A key feature is the unshared oxygen atom of a PO_4 group, situated at the center of the hexagon of ligand oxygens attached to W atoms; in both the $M_4(PW_9)_2$ and the $M_4(P_2W_{15})_2$ complexes, this atom can form bonds to three M atoms of the central compact set of four edge-sharing MO_6 octahedra so that each tungstophosphate unit becomes capped by three octahedra. It is *not* at present clear why the $M_4(XW_9)_2$ (X = P, As)[3] and $M_4(P_2W_{15})_2$ anions are formed in preference to simpler trisubstituted anions $XW_9M_3O_{40}H_x^{(15-x)-}$ and $P_2M_3W_{15}O_{62}H_x^{(18-x)-}$ with the α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$ structures.

The above set of ligand atoms is to be contrasted with the set resulting from the removal of three *corner*-sharing octahedra from α-$PW_{12}O_{40}^{3-}$. In A-α-$PW_9O_{34}^{9-}$ an O(P) atom is absent from the center of the hexagon of O(W) ligand atoms (Figure 4a). Derivatives of the type $M_3(PW_9)_2$ are formed in which each M atom is linked to only two oxygens in each $PW_9O_{34}^{9-}$ unit; in addition, the M atoms may carry terminal oxo or aquo ligands or share oxo or other additional groups with one another or both. The structures of $[W_3O_3(H_2O)_3(PW_9O_{34})_2]^{6-}$,[14g] $[Ce_3O_3(H_2O)_2(PW_9O_{34})_2]^{12-}$,[14f] and $[Cu_3(NO_3)(PW_9O_{34})_2]^{13-}$[14f] have been determined; $[Zr_3(OH)_3(SiW_9O_{34})_2]^{11-}$ is a related species[20] derived from A-β-$SiW_9O_{34}^{10-}$, while $[Co_3(H_2O)_3(PW_9O_{34})_2]^{12-}$ has also been shown[21] to contain A-$PW_9O_{34}^{9-}$ (note that Co^{2+} and Cu^{2+} can form complexes with both A- and B-α-$PW_9O_{34}^{9-}$). The probable greater alternation in O···O distances within the hexagon of O(W) ligand atoms in A-α- compared with B-α-$PW_9O_{34}^{9-}$ (Figure 4) would also favor the $M_3(PW_9)_2$ over the $M_4(PW_9)_2$ structure.

Three additional structural features merit brief mention. We believe that these are real, as each feature is found for both anions, but we caution that the problems experienced during the structural analyses (disorder and residual electron density) should be taken as implying that the calculated standard deviations in bond lengths (Tables III and VI) and other distances (Tables IV and VII) have

---

(19) Brown, G. M.; Noe-Spirlet, M.-R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr., Sect. B* **1977**, *33*, 1038.

(20) Finke, R. G.; Rapko, B.; Weakley, T. J. R. *Inorg. Chem.* **1989**, *28*, 1573.

(21) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62.

Table VI. Bond Lengths (Å) for **2**, $Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$[a]

(a) In Anion			
W(1)–O(1)	1.70 (4)	W(10)–O(52)	1.78 (3)
W(1)–O(8)	1.86 (4)	W(10)–O(49)	1.86 (4)
W(1)–O(9)	1.92 (3)	W(10)–O(44)	1.93 (3)
W(1)–O(5)	1.95 (3)	W(10)–O(29)	2.11 (4)
W(1)–O(6)	1.95 (3)	W(10)–O(41)	2.27 (3)
W(1)–O(4)	2.32 (3)	W(11)–O(36)	1.68 (3)
W(2)–O(2)	1.71 (3)	W(11)–O(56)	1.80 (3)
W(2)–O(10)	1.83 (3)	W(11)–O(45)	1.90 (3)
W(2)–O(11)	1.85 (3)	W(11)–O(44)	1.93 (3)
W(2)–O(5)	1.91 (4)	W(11)–O(30)	2.03 (3)
W(2)–O(7)	1.93 (3)	W(11)–O(41)	2.31 (3)
W(2)–O(4)	2.39 (3)	W(12)–O(37)	1.74 (4)
W(3)–O(3)	1.71 (4)	W(12)–O(53)	1.79 (4)
W(3)–O(6)	1.87 (3)	W(12)–O(45)	1.92 (3)
W(3)–O(12)	1.88 (3)	W(12)–O(46)	1.93 (3)
W(3)–O(13)	1.88 (3)	W(12)–O(31)	2.05 (4)
W(3)–O(7)	1.91 (3)	W(12)–O(42)	2.37 (3)
W(3)–O(4)	2.31 (3)	W(13)–O(55)	1.76 (4)
W(4)–O(17)	1.72 (3)	W(13)–O(38)	1.78 (3)
W(4)–O(29)	1.78 (4)	W(13)–O(47)	1.87 (3)
W(4)–O(24)	1.86 (3)	W(13)–O(46)	1.92 (3)
W(4)–O(23)	1.93 (3)	W(13)–O(32)	2.01 (3)
W(4)–O(8)	2.00 (4)	W(13)–O(42)	2.30 (3)
W(4)–O(14)	2.34 (3)	W(14)–O(39)	1.70 (3)
W(5)–O(18)	1.68 (4)	W(14)–O(51)	1.80 (3)
W(5)–O(30)	1.81 (3)	W(14)–O(47)	1.93 (3)
W(5)–O(23)	1.91 (3)	W(14)–O(48)	1.95 (3)
W(5)–O(25)	1.92 (3)	W(14)–O(33)	2.00 (3)
W(5)–O(10)	1.99 (4)	W(14)–O(43)	2.31 (3)
W(5)–O(14)	2.29 (3)	W(15)–O(54)	1.75 (4)
W(6)–O(19)	1.70 (3)	W(15)–O(40)	1.76 (3)
W(6)–O(31)	1.80 (4)	W(15)–O(48)	1.89 (3)
W(6)–O(26)	1.86 (3)	W(15)–O(49)	1.94 (3)
W(6)–O(25)	1.87 (3)	W(15)–O(34)	2.04 (4)
W(6)–O(11)	1.98 (3)	W(15)–O(43)	2.38 (3)
W(6)–O(15)	2.39 (3)	Cu(1)–O(51)	1.89 (3)
W(7)–O(20)	1.76 (3)	Cu(1)–O(56*)	1.95 (3)
W(7)–O(32)	1.83 (4)	Cu(1)–O(54)	1.98 (4)
W(7)–O(27)	1.88 (3)	Cu(1)–O(53*)	2.00 (4)
W(7)–O(26)	1.96 (3)	Cu(1)–O(50)	2.44 (4)
W(7)–O(12)	1.97 (3)	Cu(1)–O(70)	2.61 (4)
W(7)–O(15)	2.32 (2)	Cu(2)–O(55*)	1.89 (4)
W(8)–O(21)	1.70 (4)	Cu(2)–O(52)	1.92 (3)
W(8)–O(33)	1.83 (3)	Cu(2)–O(50)	1.99 (4)
W(8)–O(13)	1.91 (3)	Cu(2)–O(50*)	2.08 (4)
W(8)–O(27)	1.92 (3)	Cu(2)–O(53*)	2.31 (4)
W(8)–O(28)	1.93 (3)	Cu(2)–O(56)	2.43 (3)
W(8)–O(16)	2.36 (4)	P(1)–O(16)	1.51 (4)
W(9)–O(22)	1.68 (3)	P(1)–O(15)	1.53 (3)
W(9)–O(34)	1.80 (4)	P(1)–O(4)	1.60 (4)
W(9)–O(24)	1.93 (3)	P(1)–O(14)	1.63 (4)
W(9)–O(28)	1.93 (3)	P(2)–O(42)	1.52 (3)
W(9)–O(9)	1.95 (3)	P(2)–O(43)	1.53 (4)
W(9)–O(16)	2.33 (3)	P(2)–O(50)	1.55 (4)
W(10)–O(35)	1.74 (3)	P(2)–O(41)	1.60 (3)
(b) Around Cations			
Cu(3)–O(74)	1.97 (4)	Na(2)–O(18)	2.57 (5)
Cu(3)–O(76)	2.07 (4)	Na(3)–O(88)	2.37 (5)
Cu(3)–O(37)	2.26 (3)	Na(3)–O(78)	2.39 (4)
Na(1)–O(77)	2.33 (5)	Na(3)–O(87)	2.39 (6)
Na(1)–O(39*)	2.37 (4)	Na(3)–O(82)	2.42 (5)
Na(1)–O(80)	2.39 (4)	Na(3)–O(79)	2.50 (5)
Na(1)–O(73)	2.40 (4)	Na(4)–O(75)	2.25 (7)
Na(1)–O(70*)	2.44 (4)	Na(4)–O(78*)	2.34 (5)
Na(1)–O(36)	2.51 (4)	Na(4)–O(35*)	2.40 (4)
Na(2)–O(73)	2.34 (5)	Na(4)–O(20*)	2.50 (4)
Na(2)–O(85)	2.46 (7)	Na(4)–O(81)	2.55 (4)
Na(2)–O(21*)	2.46 (5)	Na(4)–O(87*)	2.61 (5)
Na(2)–O(81)	2.48 (5)		

[a] An asterisk denotes the symmetry operation $-x$, $1 - y$, $1 - z$.

Table VII. Distances (Å) between W, Cu, and P Atoms in **2**, $Na_{14}Cu[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$

W(1)···W(2)	3.406 (4)	W(6)···W(7)	3.339 (4)
W(1)···W(3)	3.413 (4)	W(6)···W(12)	3.804 (4)
W(1)···W(4)	3.719 (4)	W(7)···W(8)	3.689 (4)
W(1)···W(9)	3.711 (4)	W(7)···W(13)	3.811 (4)
W(2)···W(3)	3.405 (4)	W(8)···W(9)	3.339 (4)
W(2)···W(5)	3.713 (4)	W(8)···W(14)	3.787 (4)
W(2)···W(6)	3.704 (4)	W(9)···W(15)	3.810 (4)
W(3)···W(7)	3.731 (4)	W(10)···W(11)	3.357 (4)
W(3)···W(8)	3.700 (4)	W(10)···W(15)	3.658 (4)
W(4)···W(5)	3.343 (4)	W(11)···W(12)	3.626 (4)
W(4)···W(9)	3.702 (4)	W(12)···W(13)	3.352 (4)
W(4)···W(10)	3.832 (4)	W(13)···W(14)	3.656 (4)
W(5)···W(6)	3.699 (4)	W(14)···W(15)	3.325 (4)
W(5)···W(11)	3.794 (4)		
W(10)···Cu(2)	3.491 (7)	W(12)···Cu(2*)	3.728 (7)
W(11)···Cu(2)	3.762 (7)	W(13)···Cu(2*)	3.475 (7)
W(11)···Cu(1*)	3.477 (7)	W(14)···Cu(1)	3.499 (7)
W(12)···Cu(1*)	3.444 (7)	W(15)···Cu(1)	3.505 (7)
W(1)···P(1)	3.48 (2)	W(9)···P(1)	3.53 (1)
W(2)···P(1)	3.49 (1)	W(10)···P(2)	3.44 (1)
W(3)···P(1)	3.46 (2)	W(11)···P(2)	3.56 (1)
W(4)···P(1)	3.52 (1)	W(12)···P(2)	3.52 (1)
W(5)···P(1)	3.56 (2)	W(13)···P(2)	3.43 (1)
W(6)···P(1)	3.52 (1)	W(14)···P(2)	3.54 (1)
W(7)···P(1)	3.52 (1)	W(15)···P(2)	3.52 (1)
W(8)···P(1)	3.51 (2)		
Cu(1)···Cu(2)	3.19 (1)	Cu(1)···Cu(2*)	3.22 (1)
Cu(2)···Cu(2*)	3.05 (1)		
Cu(1)···P(2)	3.44 (1)	Cu(2)···P(2)	3.16 (2)
Cu(2*)···P(2)	3.22 (2)		

[a] An asterisk denotes the symmetry operation $-x$, $1 - y$, $1 - z$.

been considerably underestimated.

(1) Jahn–Teller distortion of the CuO_6 groups is predicted and is accommodated by the tungstophosphate ligands. Each CuO_6 octahedron exhibits marked axial elongation [bond lengths 1.90–2.05, 2.34–2.55 (1) Å in **1**, and 1.89–2.08, 2.31–2.61 (3) Å in **2**]. The long axes within each anion are parallel, and corresponding octahedra in **1** and **2** are oriented similarly. In contrast, the MO_6 octahedra in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ show smaller distortions,[3] and the exact geometries differ both within and between the anions. It is of interest that in the related $[Cu_4(H_2O)_2Fe_2(FeW_9O_{34}H)_2]^{10-}$ anion,[15] in which the atoms of the central Cu_2Fe_2 group were identified by refinement of site occupancy factors, the bonds about the Cu(II) atom [corresponding to Cu(2) of **1**] span a *smaller* range that the bonds about Fe(III).

(2) The noncoordinated α-$PW_9O_{34}^{9-}$ and α-$P_2W_{15}O_{56}^{12-}$ ligands are presumed to have 3-fold symmetry, which is lost when they are bonded to Cu. The loss is implied by the following two points.

(i) The first is the deviations of the belt of six W atoms nearest the Cu atoms from their mean plane. The atoms furthest from, and related by, the approximate mirror plane of the whole anion are displaced toward the Cu atoms [**1**: W(6), W(9), 0.030 (2) Å; **2**: W(10), W(13), 0.034, 0.047 (2) Å]; the other atoms are displaced away from the Cu atoms [**1**: W(4,5,7,8), 0.013–0.018 (2) Å; **2**, W(11,12,14,15), 0.005–0.034 (2) Å]. Similar displacements occur for the atoms corresponding to W(10,13) in the other W_6 belt in **2** [W(4), W(7); 0.018, 0.034 (2) Å toward the Cu atoms]. The distortion of the heavy-atom framework in each anion may serve to accommodate the steric requirements of the Cu atoms; this question would be answered if the detailed structure were known for the $Zn_4(P_2W_{15})_2$ complex, for instance, where no Jahn–Teller distortion is expected.

(ii) Each ligand, $PW_9O_{34}^{9-}$ or $P_2W_{15}O_{56}^{12-}$, is capped by three of the central CuO_6 groups, which share a vertex of the PO_4 tetrahedron [P(2) in **2**]. The Cu atoms, however, are asymmetrically placed with respect to the normal through P to the Cu_4 plane; this may be seen from the Cu···P distances (Tables IV and VII), the longest of which in each case involves the Cu atom on the local mirror plane of the anion.

(3) The effective substitution of three Cu^{2+} for a capping group of three W^{6+} in α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$ is accompanied by changes in W–O bond lengths. In particular, the bonds from the belt W atoms W(4–9) in **1** and W(10–15) in **2** to the oxygens

shared with the Cu atoms are shorter than the bonds trans to them [1.77–1.83 (1) Å vs 1.98–2.02 (1) Å in **1** and 1.76–1.81 (3) Å vs 1.86–1.94 (3) Å in **2**]. Although the differences are barely significant in the case of **2** (see earlier caveat) they are consistent with findings[3,15] for the congeners of $[Cu_2(H_2O)_2(PW_9O_{34})_2]^{10-}$ and with the requirement that changes in bond lengths should maintain the bond valence sum[22] at each W atom at a value close to 6.0.

Solution Stabilities. As noted earlier (a) $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is much less stable in solution than its Zn^{2+} and Co^{2+} analogues,[5a] and (b) the kinetic and thermodynamic factors affecting the solution stabilities of polyoxoanions are little studied.[7] Some factors that are known to be important are pH, solvent effects (e.g. H_2O vs. organic solvents like CH_3CN), and the nature of the countercation. As regards the last, we note that a countercation/ion-pairing effect on the *rate* of hydrolysis of polyoxoanions has been demonstrated.[7]

In the present case, the fact that the more stable $P_4W_{30}Cu_4$ anion is obtained as an Na^+ salt (**2**) and the less stable $P_2W_{18}Cu_4$ anion as a mostly K^+ salt (**1**)[5] is counterbalanced by the fact that the relatively stable Co and Zn congeners of the $P_2W_{18}Cu_4$ anion are prepared and recrystallized[1,3] as wholly K^+ salts. In any case, neither the positions of the K^+ ions in the solid-state structure of **1** nor the positions of the Na^+ ions in crystalline **2** give any hint that these ions might be closely involved in stabilizing either anion in aqueous solution. As regards pH effects, a simple control experiment has shown that the pH values of 0.0145 M aqueous solutions of **1** and **2** are in the same (6–7) range, 6.27 and 6.85, respectively.

We hope to gain insight into the reduced stability of the $P_2W_{18}Cu_4$ anion indirectly, by establishing the composition and structure of the product of solution thermolysis. We also note that ^{17}O NMR spectroscopy (with ^{183}W enrichment) to investigate the initial site(s) of hydrolysis and detailed kinetic studies as a function of pH and countercations would be valuable.

Summary and Conclusions

The major findings of this work are as follows:

(1) X-ray single-crystal analysis has confirmed the structure previously[4,5] deduced for the $P_4W_{30}M_4(H_2O)_2O_{112}{}^{16-}$ anions and has shown that the structure of $P_2W_{18}Cu_4(H_2O)_2O_{68}{}^{10-}$ closely resembles that of the related Co_4 and Zn_4 complexes.

(2) The environments of corresponding Cu atoms in **1** and **2** are similar; in particular, the tungstophosphate ligands permit Jahn–Teller distortions (tetragonal elongation) of similar magnitude for the CuO_6 octahedra.

(3) However, further structural studies are needed: namely, the X-ray structures of the $P_2W_{15}O_{56}{}^{12-}$ anion itself, of a $P_4W_{30}M_4(H_2O)_2O_{112}{}^{16-}$ anion (e.g. $M = Zn^{2+}$) in which no distortion is predicted for the MO_6 groups, and, especially, of the product of solution thermolysis of the $P_2W_{18}Cu_4(H_2O)_2O_{68}{}^{10-}$ anion.

(4) No obvious *solid-state* structural reasons for the lower solution stability of the $P_2W_{18}Cu_4(H_2O)_2O_{68}{}^{10-}$ anion, in relation both to its Co and Zn congeners and to the $P_4W_{30}Cu_4$ anion, were found, but experiments that may reveal further insights were suggested.

Acknowledgment. We gratefully acknowledge support of this work by NSF Grant CHE-8612924. T.J.R.W. thanks the University of Oregon for a visiting Associate Professorship during leave of absence from Dundee University, Dundee, UK, in 1987–1988.

Supplementary Material Available: Tables of full crystallographic data (Table S1), anisotropic thermal parameters (Tables S2 and S5), and bond angles for anions (Tables S3 and S6) (18 pages); tables of observed and calculated structure factors (Tables S4 and S7) (71 pages). Ordering information is given on any current masthead page.

---

[22] Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.