X-Ray Crystallographic* and Tungsten-183 Nuclear Magnetic Resonance Structural Studies of the $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ Heteropolyanions (M = Co^{II} or Zn, X = P or As)

Howard T. Evans
U.S. Geological Survey, National Centre 959, Reston, Virginia 22092, U.S.A.
Claude M. Tourné and Gilbert F. Tourné
Laboratoire de Chimie des Solides, Université des Sciences et Techniques de Languedoc, 34060 Montpellier Cedex, France
Timothy J. R. Weakley
Department of Chemistry, Dundee University, Dundee DD1 4NH

The crystal structures of $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ (**1**) and isomorphous $K_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (**2**) have been determined {Mo-K_α radiation, space group $P2_1/n$, $Z = 2$; (**1**) $a = 15.794(2)$, $b = 21.360(2)$, $c = 12.312(1)$ Å, $\beta = 91.96°$, $R = 0.084$ for 3 242 observed reflections [$I \geqslant 3\sigma(I)$]; (**2**) $a = 15.842(4)$, $b = 21.327(5)$, $c = 12.308(4)$ Å, $\beta = 92.42(4)°$, $R = 0.066$ for 4 675 observed reflections [$F \geqslant 3\sigma(F)$]}. The anions have crystallographic symmetry $\bar{1}$ and non-crystallographic symmetry very close to $2/m$ (C_{2h}). Each consists of two $[XW_9O_{34}]^{9-}$ moieties [α-B isomers; X = P (**1**) or As (**2**)] linked *via* four $Co^{II}O_6$ or ZnO_6 groups. Two Co or Zn atoms each carry a water ligand. The ^{183}W n.m.r. spectra of the anions $[Zn_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (X = P or As) confirm that the anions retain $2/m$ symmetry in aqueous solution. Homonuclear coupling constants between ^{183}W atoms are 5.8—9.0 Hz for adjacent WO_6 octahedra sharing edges, and 19.6—25.0 Hz for octahedra sharing corners.

We briefly reported[1] several years ago the existence of a novel class of heteropolyanions of the general formula $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (M^{II} = Co, Zn, Mn, Ni, or Cu; X = P or As). The formulation is based on the structure of $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ from single-crystal *X*-ray analysis, which we also reported. The new anions were formed in a hot, near-neutral aqueous mixture of approximate composition $M^{2+}:HXO_4^{2-}:WO_4^{2-} = 2:4:18$. More recently, Finke *et al.*[2] have shown that the anions with X = P can be more rapidly obtained in good yield from M^{2+}(aq) and pre-formed $[HPW_9O_{34}]^{8-}$ and have shown using ^{183}W n.m.r. that the $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ion retains in solution the $2/m$ symmetry which it possesses in the crystalline K^+ salt. Also, the *X*-ray structure has been reported[3] for a minor by-product, $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$, of our original synthesis with M = Co. We here give details of the structures of the anions $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (M = Co, X = P; M = Zn, X = As). We also discuss the ^{183}W n.m.r. spectra of $[Zn_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (X = P or As), recorded at a higher resolution than the spectrum published earlier.[2]

Experimental

Preparations.—$K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ (**1**). The pH of a solution containing $Na_2WO_4\cdot 2H_2O$ (110 g, 0.33 mol) and $Na_2HPO_4\cdot 2H_2O$ (7.5 g, 0.042 mol) in water (350 cm^3) was adjusted to 7.0 with CH_3CO_2H. The mixture was heated to boiling and a solution of $Co(O_2CCH_3)_2\cdot 4H_2O$ (20.8 g, 0.084 mol) in water (100 cm^3) was slowly added and reflux continued for 2 h. The clear deep red solution was then treated with a hot, pH 7 solution of $K(O_2CCH_3)$ (20.8 g) and cooled. The crude crystalline product was filtered off and washed with aqueous KNO_3 followed by 50% EtOH, and stirred with two 60-cm^3 portions of water at 35—40 °C to extract $K_{16}[Co_9W_{27}P_5O_{119}H_{17}]$. The residue was twice reprecipitated from hot (85 °C) water with KNO_3, and twice recrystallised from hot water (Found: Co, 4.20; H_2O, 7.85; K, 7.05; P, 1.10; W, 60.6. Calc. for $H_{48}Co_4K_{10}O_{92}P_2W_{18}$: Co, 4.25; H_2O, 7.85; K, 7.10; P, 1.10; W, 60.0%).

Table 1. Crystallographic data for $K_{10}[M_4(H_2O)_2(XW_9O_{34})_2]\cdot nH_2O$

Complex	(1)	(2)	(3)
M, X, *n*	Co, P, 22	Zn, As, 23	Co, As, 23
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.794(2)	15.842(4)	15.822(2)
b/Å	21.360(2)	21.327(5)	21.348(2)
c/Å	12.312(1)	12.308(4)	12.313(1)
β/°	91.96(1)	92.42(4)	91.95(1)
U/Å^3	4 151.3(5)	4 154(2)	4 156.3(5)
D_c/g cm^{-3}	4.371	4.458	4.436
D_m/g cm^{-3}	4.38(1)	4.47(1)	4.39(1)
F(000)	4 888	5 004	4 980
Data collection:			
Radiation (λ/Å)	Mo-K_α (0.710 69)		
Diffractometer	Picker four-circle	Stoe two-circle	
Scan	θ–2θ	ω–2θ	
Range	6 < θ < 50°	Layers 0—3kl, hk0—9	
Crystal size/mm	0.17 × 0.17 × 0.25	0.16 × 0.23 × 0.45, 0.14 × 0.14 × 0.35	
λ/cm^{-1}	247	279	
Abs. correction	Yes	Yes	
Unique data measured	7 401	5 290	
Refinement:			
Data used	3 242 [$I \geqslant 3\sigma(I)$]	4 675 [$F \geqslant 3\sigma(F)$]	
Parameters	336	309	
R	0.084	0.066	
R'	0.073	0.071	

$K_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (**2**). In a variant of the

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* *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table 2. Atomic co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ (**1**) (× 10^4 for P, Co, W, K; × 10^3 for oxygen)							
P	1 389(9)	747(6)	−672(11)	Co(1)	−661(4)	574(3)	−331(5)
Co(2)	−249(4)	235(3)	2 132(5)	W(1)	3 065(1)	1 457(1)	−2 322(2)
W(2)	2 018(1)	2 386(1)	−192(2)	W(3)	3 510(1)	1 102(1)	596(2)
W(4)	1 094(1)	1 100(1)	−3 461(2)	W(5)	2 435(1)	−79(1)	−2 767(2)
W(6)	54(1)	2 022(1)	−1 372(2)	W(7)	2 890(1)	−439(1)	120(2)
W(8)	474(1)	1 704(1)	1 313(2)	W(9)	1 949(1)	411(1)	2 082(2)
K(1)	7 123(11)	776(7)	5 882(12)	K(2)	5 523(9)	1 228(7)	2 914(11)
K(3)	8 483(10)	1 696(6)	3 139(14)	K(4)	5 214(8)	1 824(6)	8 789(11)
K(5)	2 694(9)	2 147(6)	2 793(9)				
O(1)	387(2)	187(1)	−286(2)	O(2)	249(2)	311(1)	−8(2)
O(3)	450(2)	138(1)	106(2)	O(4)	79(2)	128(2)	−467(2)
O(5)	288(2)	−59(1)	−358(2)	O(6)	−59(2)	257(1)	−192(2)
O(7)	354(2)	−111(2)	28(3)	O(8)	11(2)	204(1)	243(2)
O(9)	202(2)	33(1)	341(2)	O(10)	283(2)	184(1)	60(2)
O(11)	250(2)	210(1)	−150(2)	O(12)	356(2)	119(1)	−91(2)
O(13)	138(2)	122(1)	196(2)	O(14)	62(2)	179(1)	−254(2)
O(15)	297(2)	−23(1)	−140(2)	O(16)	222(2)	155(1)	−334(2)
O(17)	327(2)	62(1)	−283(2)	O(18)	101(2)	259(1)	−99(2)
O(19)	375(2)	24(1)	44(2)	O(20)	147(2)	234(2)	107(2)
O(21)	301(2)	94(1)	193(2)	O(22)	189(2)	39(1)	−381(2)
O(23)	−8(2)	212(1)	14(2)	O(24)	259(2)	−27(1)	162(2)
O(25)	178(2)	82(1)	−179(2)	O(26)	111(2)	142(1)	−36(2)
O(27)	213(2)	53(1)	22(2)	O(28)	66(2)	26(1)	−67(2)
O(29)	31(2)	53(1)	−305(2)	O(30)	151(2)	−49(1)	−239(2)
O(31)	−60(2)	128(1)	−135(2)	O(32)	186(2)	−79(1)	−10(2)
O(33)	−17(2)	98(1)	102(2)	O(34)	93(2)	1(1)	161(2)
O(35)	4(2)	75(2)	360(3)	O(36)	896(2)	55(2)	526(3)
O(37)	306(2)	137(2)	453(3)	O(38)	575(4)	126(3)	685(5)
O(39)	485(3)	150(2)	512(4)	O(40)	160(3)	241(2)	430(3)
O(41)	674(2)	186(2)	193(3)	O(42)	934(2)	233(2)	485(3)
O(43)	777(3)	155(2)	761(3)	O(44)	484(4)	1(3)	807(4)
O(45)	815(4)	203(2)	62(3)				
(*b*) $K_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (**2**) (all × 10^4)							
As	1 402(2)	746(1)	−671(3)	Zn(1)	−686(2)	601(2)	−364(4)
Zn(2)	−223(2)	256(2)	2 157(4)	W(1)	3 065(1)	1 455(1)	−2 341(1)
W(2)	2 028(1)	2 398(1)	−200(1)	W(3)	3 519(1)	1 108(1)	596(1)
W(4)	1 105(1)	1 101(1)	−3 470(1)	W(5)	2 437(1)	−75(1)	−2 768(1)
W(6)	74(1)	2 042(1)	−1 368(1)	W(7)	2 912(1)	−427(1)	137(1)
W(8)	492(1)	1 724(1)	1 322(1)	W(9)	1 971(1)	423(1)	2 090(1)
K(1)	7 135(7)	776(5)	5 868(10)	K(2)	5 542(8)	1 235(5)	2 883(11)
K(3)	8 452(8)	1 717(5)	3 008(11)	K(4)	5 252(6)	1 815(4)	8 755(9)
K(5)	2 701(5)	2 143(4)	2 761(8)	O(1)	3 922(13)	1 858(9)	−2 829(19)
O(2)	2 503(14)	3 118(10)	−46(21)	O(3)	4 494(14)	1 383(9)	1 042(20)
O(4)	769(16)	1 346(11)	−4 743(23)	O(5)	2 924(14)	−635(10)	−3 522(21)
O(6)	−612(14)	2 600(10)	−1 906(20)	O(7)	3 558(17)	−1 062(12)	257(24)
O(8)	58(13)	2 025(9)	2 475(18)	O(9)	2 018(12)	327(9)	3 452(18)
O(10)	2 840(14)	1 841(10)	548(20)	O(11)	2 507(14)	2 084(10)	−1 480(21)
O(12)	3 497(13)	1 202(9)	−928(20)	O(13)	1 374(12)	1 208(8)	1 943(18)
O(14)	692(15)	1 753(10)	−2 571(21)	O(15)	2 995(13)	−251(9)	−1 422(19)
O(16)	2 192(13)	1 579(9)	−3 445(20)	O(17)	3 291(13)	647(9)	−2 868(20)
O(18)	1 036(13)	2 606(9)	−987(19)	O(19)	3 766(13)	230(9)	398(19)
O(20)	1 404(14)	2 366(10)	1 088(21)	O(21)	3 035(12)	943(8)	1965(18)
O(22)	1 880(12)	427(8)	−3 871(18)	O(23)	−105(12)	2 176(8)	175(18)
O(24)	2 637(14)	−251(10)	1 657(21)	O(25)	1 856(12)	799(8)	−1 928(17)
O(26)	1 082(13)	1 464(9)	−330(20)	O(27)	2 196(14)	548(10)	227(21)
O(28)	601(11)	227(7)	−654(16)	O(29)	290(14)	555(10)	−3 047(20)
O(30)	1 503(13)	−447(9)	−2 410(19)	O(31)	−556(15)	1 331(10)	−1 355(21)
O(32)	1 912(15)	−747(10)	−88(22)	O(33)	−137(11)	1 021(7)	1 043(16)
O(34)	995(14)	21(10)	1 615(21)	O(35)	−9(18)	722(13)	3 586(26)
O(36)	9 005(17)	547(12)	5 281(25)	O(37)	3 049(19)	1 339(14)	4 573(28)
O(38)	5 807(36)	1 302(26)	6 959(49)	O(39)	4 887(28)	1 381(20)	5 051(37)
O(40)	1 637(21)	2 464(15)	4 421(31)	O(41)	6 666(27)	1 879(18)	1 898(38)
O(42)	9 381(21)	2 188(14)	4 922(29)	O(43)	7 896(25)	1 577(19)	7 507(35)
O(44)	4 849(23)	136(16)	8 142(33)	O(45)	8 096(23)	2 044(16)	488(32)

Atoms O(36)—O(45) are in lattice water molecules in both compounds.

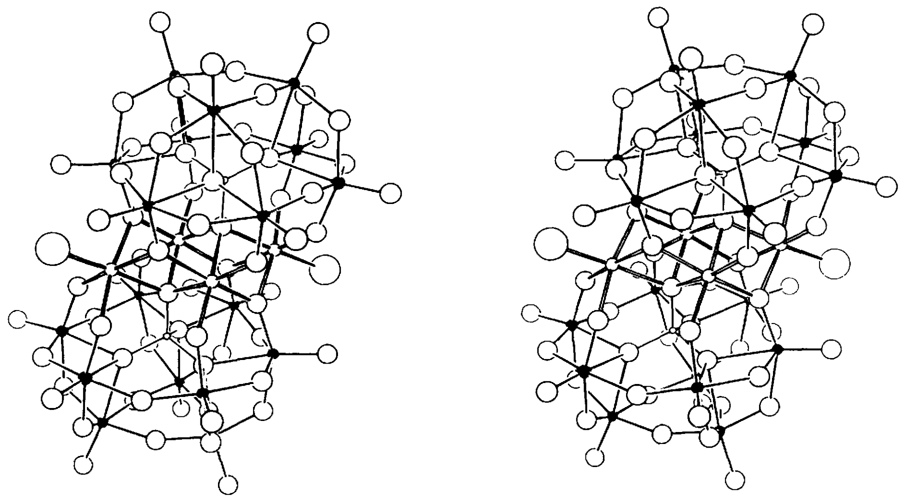

Figure 1. The $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion: general stereoview

above procedure, a boiling solution containing $ZnSO_4 \cdot 7H_2O$ (5.75 g, 0.021 mol) and 6.4 mol dm^{-3} HNO_3 (17.2 cm^3, 0.110 mol) in water (110 cm^3) was treated slowly with a solution of $Na_2WO_4 \cdot 2H_2O$ (29.7 g, 0.090 mol) and $Na_2HAsO_4 \cdot 7H_2O$ (3.15 g, 0.011 mol) in water (110 cm^3). The mixture was refluxed for 3 h and filtered while hot. The crude crystalline product was precipitated by the addition of KNO_3 (40 g) and cooling; it was twice redissolved and reprecipitated with KNO_3, and was finally recrystallised twice from hot water (Found: As, 2.60; H_2O, 8.05; K, 7.10; W, 58.5; Zn, 4.70. Calc. for $H_{50}As_2K_{10}O_{93}W_{18}Zn_4$: As, 2.65; H_2O, 7.95; K, 6.90; W, 58.6; Zn, 4.65%).

Similar procedures gave $K_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2] \cdot 23H_2O$ (**3**) and $K_{10}[Zn_4(H_2O)_2(PW_9O_{34})_2] \cdot 20H_2O$, for which satisfactory analyses were obtained.

The number of molecules of lattice water in each compound was found to be dependent on the temperature and rate at which crystallisation occurred. Values of 20—25H_2O were obtained in different preparations. The crystallinity (as judged from single-crystal photographs) and crystal habit were unaffected. As only 20 lattice water molecules could be located with confidence in the structure analyses (see below), it seems likely that the remaining water is zeolitic, as is the case for numerous heteropolyoxometalate salts.

Crystal Structure Analysis.—Beautiful violet [(**1**) and (**3**)] or colourless [(**2**)] crystals were deposited from slightly supersaturated aqueous solutions on standing at room temperature. Cell dimensions for (**2**) were originally obtained from NaCl-calibrated Weissenberg photographs and were refined on the diffractometer. Cell dimensions for (**1**) and (**3**) were also refined on the diffractometer and improved values were obtained from powder photographs (Guinier–Hagg focusing camera; Cr-K_α radiation, λ = 2.289 62 Å; CaF_2 internal standard, a = 5.4638 Å). The final values are listed in Table 1, together with other information relevant to data collection and refinement. {A second data set for (**2**) was independently collected, and the structure solved: CAD-4F four-circle diffractometer, Mo-K_α radiation, $\theta_{max.}$ 21°, 4 260 unique data [$I \geqslant 2.5\sigma(I)$]; R 0.047, R' 0.056 for 3 177 data with $|F_o| \geqslant 0.06|F_o|_{max.}$. The final parameters, standard deviations, and derived dimensions are not significantly different from the values obtained with the first data set, which are the ones reported here.} Data were not collected for (**3**), which was clearly isostructural with (**1**) and (**2**) (cell dimensions, space group, distribution of intensities). The structural analyses were straightforward. The heavy atoms in both compounds (W, P or As, Co or Zn) were readily located in E maps, following the assignment of signs by a symbolic-addition procedure [(**1**); reflections with $\theta < 15°$] or by the EEES sub-program of SHELX-76[4] [(**2**), all data]. The K and O atoms were located in difference syntheses alternating with cycles of refinement. The W, Co, P, and K atoms in (**1**) and the W, As, and Zn atoms in (**2**) were allowed anisotropic thermal parameters during block-diagonal least-squares refinement [(**1**), XRAY-76;[5] (**2**), SHELX-76[4]]. For (**1**), an isotropic extinction parameter was included and the data were weighted by $1/\sigma$ based on counting statistics. For (**2**) the weights in the last cycle were given by $w = [\sigma^2(F) + 0.013F^2]^{-1}$. The maximum peak heights in the final difference synthesis were *ca.* 2 e Å^{-3}. There were indications that some K^+ ions and lattice H_2O molecules were disordered over two or more adjacent sites. No attempt was made to model this since the structural features of the anions, which did not appear to be affected by disorder, were already clear when convergence was reached at the R values given in Table 1. The somewhat high residual for (**1**) may be the consequence of the loss of some zeolitic water from the crystals during transit, with enhancement of the disorder for the cations and remaining water molecules.

Atomic co-ordinates for (**1**) and (**2**) are given in Table 2.

^{183}W *Nuclear Magnetic Resonance Spectra.*—Measurements were made on concentrated solutons of $Li_{10}[Zn_4(H_2O)_2(XW_9O_{34})_2] \cdot 40H_2O$ (X = P or As) which were prepared by passage of the aqueous K^+ salts through a cation-exchange resin in the Li^+ form until the effluent showed no reaction with $NaBPh_4$, and evaporation to dryness. Spectra were recorded by use of a Bruker WP-360 spectrometer fitted with a 15-mm low-frequency multinuclear probe. The two-dimensional experiment (COSY-45) was performed as described previously,[6] except that a 45° φ_2 mixing pulse was used.

Discussion

Structure of the Anions.—The anions $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ are isostructural. A general stereoview of the Co anion is given in Figure 1, and the atomic numbering shown in Figure 2. Like many other heteropolyanions,[7] they contain portions of the well known Keggin[8] (α-$XW_{12}O_{40}{}^{n-}$) structure. The latter has T_d symmetry and contains four groups of three edge-sharing WO_6 octahedra, with corner sharing between adjacent octahedra of

Table 3. Bond lengths and distances between heavy atoms (Å) for $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ (**1**) and $K_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (**2**) [X, M = P, Co in (**1**) and As, Zn in (**2**)]

	(1)	(2)		(1)	(2)		(1)	(2)
X–O(25)	1.54(3)	1.74(2)	W(2)–O(11)	1.97(2)	1.95(2)	W(6)–O(14)	1.79(2)	1.91(2)
X–O(26)	1.56(3)	1.67(2)	W(2)–O(18)	1.89(2)	1.86(2)	W(6)–O(18)	1.98(2)	1.98(2)
X–O(27)	1.65(3)	1.69(2)	W(2)–O(20)	1.82(2)	1.90(2)	W(6)–O(23)	1.89(2)	1.95(2)
X–O(28)	1.56(3)	1.68(2)	W(2)–O(26)	2.50(3)	2.49(3)	W(6)–O(26)	2.42(3)	2.35(2)
M(1)–O(28)	2.17(3)	2.17(2)	W(3)–O(3)	1.75(2)	1.72(2)	W(6)–O(31)	1.89(2)	1.82(2)
M(1)–O(28^{i})	2.24(3)	2.23(2)	W(3)–O(10)	1.91(2)	1.90(2)	W(7)–O(7)	1.78(2)	1.70(2)
M(1)–O(31)	1.98(3)	1.99(2)	W(3)–O(12)	1.87(2)	1.89(2)	W(7)–O(15)	1.93(2)	1.97(2)
M(1)–O(32)	2.04(3)	2.07(2)	W(3)–O(19)	1.88(2)	1.93(2)	W(7)–O(19)	2.03(2)	1.97(2)
M(1)–O(33)	2.01(3)	2.11(2)	W(3)–O(21)	1.88(2)	1.91(2)	W(7)–O(24)	1.96(2)	1.98(2)
M(1)–O(34)	2.04(3)	2.08(2)	W(3)–O(27)	2.53(3)	2.44(2)	W(7)–O(27)	2.39(3)	2.37(3)
M(2)–O(28)	2.17(3)	2.18(2)	W(4)–O(4)	1.60(2)	1.72(2)	W(7)–O(32)	1.80(2)	1.74(2)
M(2)–O(29)	1.99(3)	2.05(2)	W(4)–O(14)	2.01(2)	1.91(2)	W(8)–O(8)	1.68(2)	1.73(2)
M(2)–O(30)	2.10(3)	2.10(2)	W(4)–O(16)	2.02(2)	2.00(2)	W(8)–O(13)	1.91(2)	1.87(2)
M(2)–O(33)	2.11(3)	2.14(2)	W(4)–O(22)	2.03(2)	1.97(2)	W(8)–O(20)	2.10(2)	2.02(2)
M(2)–O(34)	2.04(3)	2.13(2)	W(4)–O(25)	2.36(2)	2.29(2)	W(8)–O(23)	1.90(2)	1.92(2)
M(2)–O(35)	2.15(4)	2.04(3)	W(4)–O(29)	1.82(2)	1.83(2)	W(8)–O(26)	2.41(3)	2.34(2)
W(1)–O(1)	1.71(2)	1.73(2)	W(5)–O(5)	1.66(2)	1.72(2)	W(8)–O(33)	1.88(2)	1.83(2)
W(1)–O(11)	1.93(2)	1.95(2)	W(5)–O(15)	1.89(2)	1.88(2)	W(9)–O(9)	1.65(2)	1.69(2)
W(1)–O(12)	1.97(2)	1.92(2)	W(5)–O(17)	1.99(2)	2.06(2)	W(9)–O(13)	1.96(2)	1.93(2)
W(1)–O(16)	1.80(2)	1.92(2)	W(5)–O(22)	1.81(2)	1.91(2)	W(9)–O(21)	2.03(2)	2.03(2)
W(1)–O(17)	1.92(2)	1.88(2)	W(5)–O(25)	2.51(3)	2.34(2)	W(9)–O(24)	1.88(2)	1.87(2)
W(1)–O(25)	2.55(3)	2.44(2)	W(5)–O(30)	1.78(2)	1.75(2)	W(9)–O(27)	2.33(3)	2.35(2)
W(2)–O(2)	1.73(2)	1.72(2)	W(6)–O(6)	1.69(2)	1.72(2)	W(9)–O(34)	1.89(2)	1.84(2)
W(2)–O(10)	1.97(2)	1.95(2)						
K(1)–O(2)	2.72(5)	2.69(3)	K(3)–O(1)	3.37(6)	3.30(4)	K(4)–O(8)	2.94(5)	2.94(5)
K(1)–O(5)	2.86(5)	2.90(3)	K(3)–O(2)	2.77(5)	2.90(3)	K(4)–O(12)	2.99(5)	3.11(3)
K(1)–O(9)	2.83(5)	2.82(3)	K(3)–O(5)	3.25(6)	3.26(4)	K(4)–O(38)	2.83(6)	2.65(4)
K(1)–O(24)	3.27(5)	3.25(3)	K(3)–O(8)	2.84(5)	2.73(3)	K(4)–O(40)	2.80(6)	2.78(4)
K(1)–O(36)	3.06(6)	3.12(4)	K(3)–O(11)	3.05(5)	3.04(3)	K(4)–O(42)	2.80(6)	2.94(4)
K(1)–O(38)	2.71(6)	2.78(4)	K(3)–O(30)	2.75(5)	2.81(3)	K(5)–O(6)	2.78(5)	2.74(3)
K(1)–O(43)	2.86(6)	2.87(4)	K(3)–O(35)	3.23(6)	3.29(4)	K(5)–O(10)	2.80(5)	2.82(3)
K(2)–O(3)	2.77(5)	2.77(3)	K(3)–O(41)	3.10(6)	3.11(4)	K(5)–O(13)	3.03(5)	3.04(3)
K(2)–O(5)	2.96(5)	2.83(3)	K(3)–O(42)	2.72(6)	2.90(4)	K(5)–O(20)	2.85(5)	2.89(3)
K(2)–O(6)	3.11(5)	3.10(3)	K(3)–O(45)	3.21(6)	3.21(4)	K(5)–O(21)	2.85(5)	2.80(3)
K(2)–O(18)	2.96(5)	2.93(4)	K(4)–O(1)	2.89(5)	2.81(3)	K(5)–O(37)	2.75(6)	2.85(4)
K(2)–O(39)	3.01(6)	2.92(4)	K(4)–O(3)	3.20(5)	3.24(4)	K(5)–O(40)	2.65(6)	2.79(4)
K(2)–O(41)	2.67(6)	2.59(6)	K(4)–O(7)	2.71(5)	2.72(3)	K(5)–O(43)	2.80(6)	2.77(4)
K(2)–O(44)	2.67(6)	2.59(4)						
W(1)···W(2)	3.721(5)	3.745(3)	W(7)···W(9)	3.404(5)	3.404(3)	X···W(1)	3.715(10)	3.730(6)
W(1)···W(3)	3.715(5)	3.730(3)	W(8)···W(9)	3.715(5)	3.728(3)	X···W(2)	3.681(10)	3.699(6)
W(1)···W(4)	3.455(5)	3.432(3)	W(4)···M(2^{i})	3.569(9)	3.624(7)	X···W(3)	3.725(10)	3.719(6)
W(1)···W(5)	3.467(5)	3.445(3)	W(5)···M(2^{i})	3.581(9)	3.639(7)	X···W(4)	3.531(10)	3.539(6)
W(2)···W(3)	3.723(5)	3.730(3)	W(6)···M(1)	3.547(9)	3.542(6)	X···W(5)	3.576(10)	3.574(6)
W(2)···W(6)	3.468(5)	3.442(3)	W(7)···M(1^{i})	3.551(9)	3.569(7)	X···W(6)	3.533(10)	3.557(6)
W(2)···W(8)	3.437(5)	3.447(3)	W(8)···M(1)	3.590(9)	3.633(6)	X···W(7)	3.582(10)	3.573(6)
W(3)···W(7)	3.478(5)	3.452(3)	W(9)···M(1^{i})	3.593(9)	3.614(6)	X···W(8)	3.533(10)	3.570(6)
W(3)···W(9)	3.451(5)	3.451(3)	W(8)···M(2)	3.499(9)	3.500(6)	X···W(9)	3.548(10)	3.546(6)
W(4)···W(5)	3.381(5)	3.367(3)	W(9)···M(2)	3.494(9)	3.498(6)	X···M(1)	3.300(14)	3.359(10)
W(4)···W(6)	3.672(5)	3.707(3)	M(1)···M(1^{i})	3.305(12)	3.455(10)	X···M(1^{i})	3.302(14)	3.359(10)
W(5)···W(7)	3.683(5)	3.700(3)	M(1)···M(2^{i})	3.192(12)	3.248(10)	X···M(2^{i})	3.264(14)	3.333(10)
W(6)···W(8)	3.418(5)	3.417(3)	M(1^{i})···M(2^{i})	3.164(12)	3.243(10)			

different groups. The removal of three adjacent corner sharing octahedra (*i.e.* related by a C_3 axis of the anion) gives an α-A-$XW_9O_{34}{}^{n-}$ anion; the removal of one trio of edge-sharing octahedra gives an α-B-$XW_9O_{34}{}^{n-}$ anion. The α, β, A, and B notation is discussed, and the Keggin-derivative structures are illustrated, elsewhere.[7,9] Single-crystal *X*-ray studies have revealed an α-A-PW_9 moiety in several tungstophosphates.[10,11] The present anions, however, each contain two α-B-XW_9 units (X = P or As). The oxygen atoms 'exposed' in the notional formation of these units, including one oxygen of each XO_4 tetrahedron, are shared with the planar set of four Co or Zn atoms, M, which thus act as the filling in a sandwich. The M atoms have distorted octahedral co-ordination. The ligand oxygens on M(1) are all shared with XW_9 units, but one oxygen, O(35), on M(2) is unshared. Chemical analysis in conjunction with the location of 70 oxygens in the anions requires that each anion contains four non-acidic H atoms, and these are assigned to the two terminal O(35) atoms to give aqua ligands, as in the $[M(H_2O)(XW_{11}O_{39})]^{n-}$ series.[12]

The $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ anions in the K^+ salts have crystallographic symmetry $\bar{1}$, but almost exact non-crystallographic symmetry 2/*m* (see Figure 2); the two-fold axis passes through M(1) and M(1^{i}), and the mirror plane through W(1), P or As, M(2), and inversion-related atoms. The P···Co, P···W, Co···W, Co···Co, and W···W distances in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ are similar to those in $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$, which also contains α-B-PW_9 units.[3] The biggest change in the skeletal distances

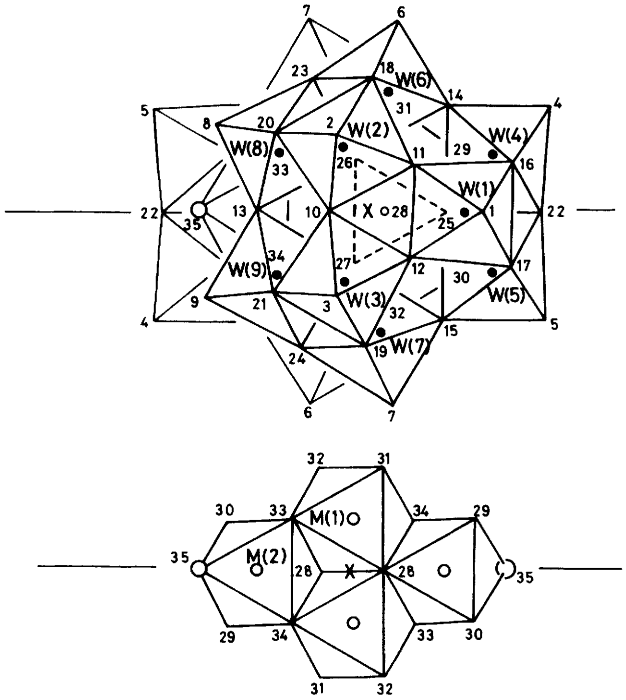

Figure 2. Numbering of atoms for $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$

Table 4. Mean bond lengths (Å) in $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$

Complex	(1)	(2)
M, X	Co, P	Zn, As
X–O	1.58	1.70
M–O	2.09	2.11
W(1)–O	1.98	1.98
W(2,3)–O	1.97	1.97
W(4,5)–O	1.96	1.95
W(6,7)–O	1.96	1.96
W(8,9)–O	1.97	1.95
All W–O	1.968	1.962
W–O, O also bonded to:		
Unshared	1.69	1.72
W(corner sharing)	1.92	1.92
W(edge sharing)	1.94	1.95
Two W, X	2.44	2.38
M	1.84	1.82

Table 5. ^{183}W N.m.r. data for anions $[Zn_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ in *ca.* 60% D_2O at 303 K. The upper and lower entries in each pair are respectively for X = P and X = As. Entries connecting W atoms of the same type are chemical shifts (p.p.m.) relative to 2 mol dm^{-3} Na_2WO_4 (±0.1 Hz), other entries are ^2J coupling constants (Hz) (±0.2 Hz for X = P, ±0.4 Hz for X = As)

	W(1)	W(2,3)	W(8,9)	W(6,7)	W(4,5)	^2J(P–O–W)
Line	A	B	C	D	E	
	A	C	B	D	E	
W(1)	−90.7	19.6			7.3	1.3
	−79.7	19.6			6.2	
W(2,3)	19.6	−105.8	7.1	7.1		1.1
	19.6	−99.6	5.8	5.8		
W(8,9)		7.1	−117.8	9.0		See text
		5.8	−93.9	9.0		
W(6,7)		7.1	9.0	−130.5	23.7	1.8
		5.8	9.0	−126.1	25.0	
W(4,5)	7.3			23.7	−135.6	1.6
	6.2			25.0	−129.0	

in going from $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ to $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ is in M(1) ··· M(1^i) (3.31, 3.45 Å respectively) with smaller increases in some M ··· W distances. Corresponding P(As) ··· W and W ··· W distances in the two anions (Table 3) are not significantly different, despite the somewhat greater size of As (av. P–O 1.58, av. As–O 1.70 Å). Also, the average bond length about a given W atom is the same in the two anions, as is the average W–O bond length, for an oxygen atom of a given connectivity (Table 4). Thus, any strain introduced by the substitution of As for P is taken up as small changes in bond angles.

The anions can be regarded as consisting of two XW_9M_3 units with two M atoms, M(1) and M(1^i), in common. Each XW_9M_3 group taken alone has the β-$XW_{12}O_{40}{}^{n-}$ structure (known for X = Si[13]) which differs from the α or Keggin structure by a 60° rotation of one set of three edge-linked octahedra. Here, the M_3 set has been rotated. The rotation serves to increase the distance between the aqua ligand O(35) on M(2) in one XW_9M_3 unit and a W–O–W bridging oxygen in the other unit. It is remarkable that $H_2O(35)$ cannot be replaced by, *e.g.*, pyridine, acetonitrile, or thiocyanate, in contrast with the rapid replacement of H_2O in such anions as $[Co(H_2O)(PW_{11}O_{39})]^{5-}$(aq).[12] In the crystal, O(35) makes several contacts with oxygens outside the $M(2)O_6$ octahedron. The shortest are with O(4) in the adjacent anion along *c* and with a lattice water molecule O(36) {respectively 2.65, 2.74 Å for $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and 2.70, 2.69 Å for $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$}, but significantly the next-shortest contacts are with the terminal oxygen atoms O(8) and O(9) on W(8) and W(9) {3.11, 3.33 Å in $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$; 3.10, 3.27 Å in $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$}, and these may represent weak hydrogen bonds whose stabilising energy would be lost on replacement of $H_2O(35)$. We return to this point later.

^{183}W *N.M.R. Spectra.*—The ^{183}W nucleus has spin ½ and is 14.28% abundant. The $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ anions both show five-line spectra (Figures 3 and 4). The lines have relative intensities 2:4:4:4:4 in order of decreasing frequency, and will be referred to as A, B, C, D, and E. Frequencies are listed in Table 5. The spectrum of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (Figure 3) is very similar to that obtained earlier at lower resolution.[2] The five-line spectra and intensity patterns are expected if the 2/*m* symmetry effective for the anions in the crystal is retained in solution. The groups of symmetry-equivalent W atoms are W(1,1^i), W(2,2^i,3,3^i), W(4,4^i,5,5^i), W(6,6^i,7,7^i), and W(8,8^i,9,9^i), where the superscript denotes inversion at the anion centre (see also Figure 2). Lines A, B, D, and E in $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (Figure 3) are split as the result of $^2J(^{31}P\text{–}O\text{–}^{183}W)$ heteronuclear coupling (1—1.8 Hz). Line C is discussed below. Also, homonuclear $^2J(^{183}W\text{–}O\text{–}^{183}W)$ coupling creates weak satellite lines near the feet of all five main lines in each spectrum. Coupling constants are included in Table 5. Previous work[14] has established that the ^2J(W–O–W) values are smaller if the WO_6 octahedra share an edge (weak coupling, 5—10 Hz) than if they share a corner (strong coupling, 15—26 Hz). Line A belongs to W(1), from its intensity. Line B for the As anion and line C for the P anion show only weak coupling and must therefore be attributed to W(8,9). Lines A and B in the spectrum of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ show strong coupling with the same ^2J values. Line B for this anion is therefore attributed to W(2,3) which alone share octahedron corners with W(1). For the same reason, line C in the spectrum of $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ is

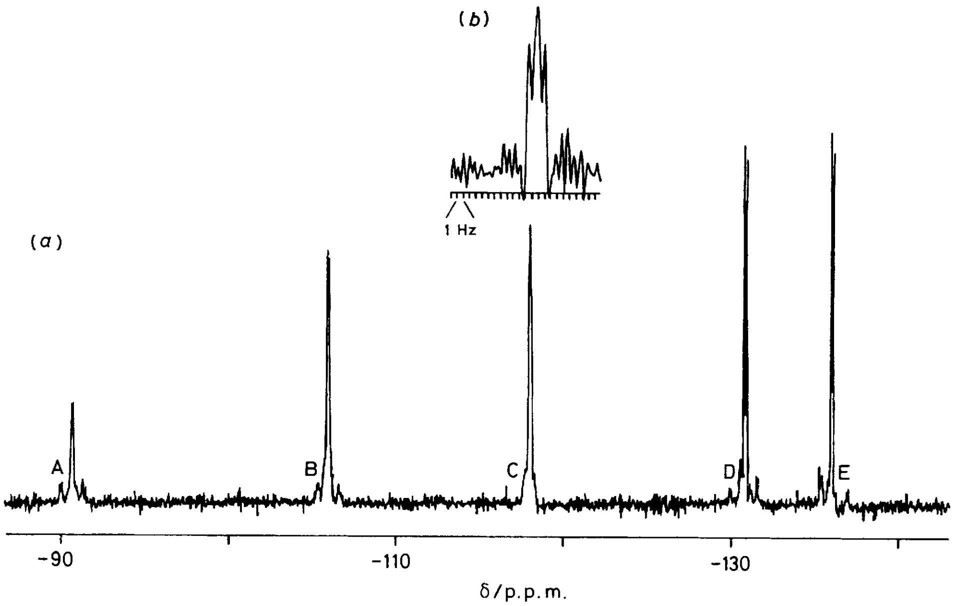

Figure 3. (*a*) ^{183}W 15.0046-MHz n.m.r. spectrum of $Li_{10}[Zn_4(H_2O)_2(PW_9O_{34})_2]$ (0.6 mol kg^{-1} in *ca.* 60% D_2O at 303 K, 7 000 scans, reference 2 mol dm^{-3} Na_2WO_4 in D_2O). (*b*) Line C after Gaussian deconvolution of free induction decay

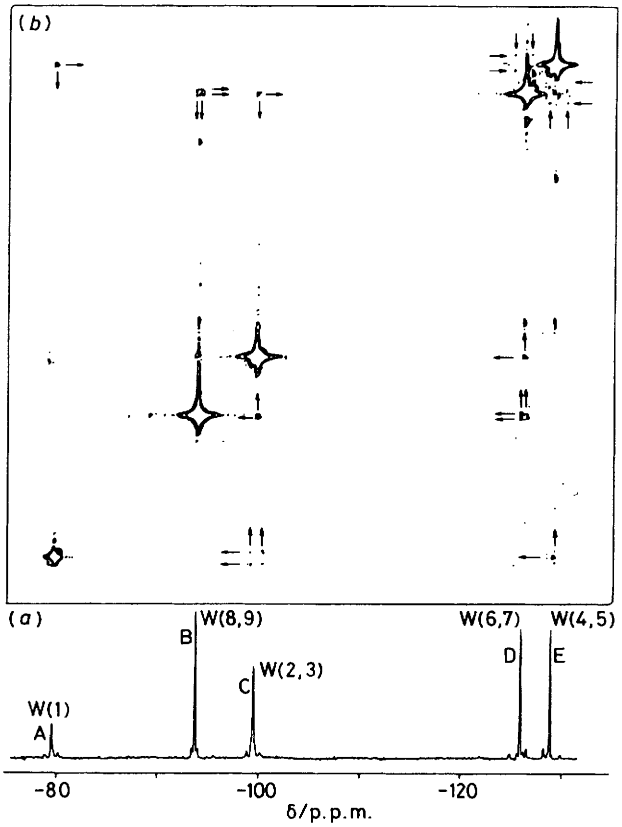

Figure 4. ^{183}W 15.0046-MHz n.m.r. spectra of $Li_{10}[Zn_4(H_2O)_2(AsW_9O_{34})_2]$ (0.6 mol kg^{-1} in *ca.* 60% D_2O at 303 K, reference 2 mol dm^{-3} Na_2WO_4 in D_2O). (*a*) One-dimensional spectrum, 10 600 scans. (*b*) Two-dimensional (COSY-45) spectrum (not symmetrised) (single arrows denote weak couplings and paired arrows denote strong couplings)

assigned to W(2,3). There remain the pairs of atoms W(4,5) and W(6,7) whose expected strong coupling to one another is seen in lines D and E. Line D in each spectrum is assigned to W(6,7) [weak coupling to W(2,3) and to W(8,9)], and line E to W(4,5) [weak coupling to W(1) only]. These assignments are supported by the COSY-45 two-dimensional spectrum (Figure 4) which shows the coupling pattern described above. No splitting of line C, assigned to W(8,9), can be seen in the spectrum of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in D_2O–H_2O (Figure 3). However, Gaussian convolution shows that line C has solvent-dependent fine structure. In H_2O (external lock) it is weakly resolved into two peaks separated by *ca.* 0.9 Hz. This splitting may result from coupling to ^{31}P. However, convolution of line C recorded in *ca.* 50% D_2O reveals a triplet structure, with a separation of *ca.* 2 Hz between the outer lines (Figure 3). The triplet could be an overlapping pair of doublets which might indicate that the mirror-plane effective symmetry of the anion was inexact for W(8) and W(9) only. An alternative explanation, however, is that we are seeing the effect on the W(8,9) resonance of slow isotope exchange between H in the anion, close to W(8) and W(9), and solvent H (β-effect[15]). We have observed a similar phenomenon for the $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ anion.[11] In the present case, the hydrogen atoms belong to the H_2O ligand, O(35), on Zn(2) which (see above) may form hydrogen bonds to the terminal oxygen atoms on W(8) and W(9). Slow H/D exchange on O(35) in 50% D_2O then gives three W(8,9) resonances in the ratio 1:2:1, corresponding to the isotopomeric forms H_2O, HDO, D_2O of the aqua ligand. No resolution of the corresponding line, B, for $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ could be achieved for reasons of linewidth. Because the main features of the anions are already clear, and because of the expense of the n.m.r. work, we have not pursued this matter further. We note, however, that although our tentative interpretation that slow H/D exchange is taking place on H_2O bound to Zn is clearly invalid if the ligand is undergoing the rapid exchange with bulk water which would normally be expected, the inability of even small, sterically-unhindered species to replace ligand H_2O in $[Co_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ (X = P or As) is consistent with a marked reduction in the lability of the H_2O–M bond in these complexes.

Further Comments.— It is reasonable to suppose that in the synthesis of the anions described above, a nonatungstate heteropolyanion is first formed and then reacts with M^{2+}(aq). Two groups of workers have reported[16,17] the preparation of Na^+ or K^+ salts of $[XW_9O_{34}]^{9-}$ anions (X = P or As). Each anion exists in isomeric α- or β-forms which differ in their polarographic behaviour[17] and which on acidification give the α- and β-$[XW_{11}O_{39}]^{7-}$ anions respectively (*i.e.* the α- and β-$[XW_{12}O_{40}]^{3-}$ structures with one W and its terminal oxygen atom missing). Both the α- and β-$[XW_9O_{34}]^{9-}$ anions can potentially exist in both A and B forms depending on whether they are derived from the parent $[XW_{12}O_{40}]^{3-}$ anion by the removal of three adjacent corner-linked WO_6 octahedra or three edged-linked ones. The β-$[XW_9O_{34}]^{9-}$ anions are presumed to be of type A, as the β-$[B\text{-}XW_9O_{34}]^{9-}$ structure would include a WO_6 group with three terminal O atoms and would be expected to be unstable for that reason.[7] A salt described as $Na_8H[\beta\text{-}PW_9O_{34}]\cdot 24H_2O$[18] reacts rapidly with aqueous M^{2+} to give $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ if previously air-dried at 140 °C, but gives a different initial product if previously dried at 60 °C or below.[2] Recent studies[19] of this 'β-PW_9' salt using solid-state ^{31}P n.m.r. indicate, however, that the anion is the α-A isomer which is converted on heating to the α-B form present as a constituent of the $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions. There is obviously scope for *X*-ray studies of the $[XW_9O_{34}]^{9-}$ anions themselves, if disorder-free single crystals come to hand.

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