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The Crystal Structures of Rubidium 20-Tungstocobalto(II)diarsenate(III) Hydrate, $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$, and its Zinc Analogue

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The anions in $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$ *(*I*) and* $Rb_8[As_2ZnW_{20}O_{68}(OH_2)_2]\cdot 12H_2O$ *(*II*) have the* $As_2W_{21}O_{69}(OH_2)^{6-}$ *structure, with substitution of Co or Zn for one of the W atoms in square-pyramidal coordination in the equatorial belt of the* As_2W_{21} *anion. Thus, two* α*-B* $As^{III}W_9O_{33}^{9-}$ *moieties are linked via a* $Co(OH_2)^{2+}$*, a* WO^{4+} *and a* $WO(OH_2)^{4+}$ *group whose total coordination numbers are respectively 5, 5, and 6. If the replacement of W by Co or Zn is ignored, the anions have mm symmetry, but conform to the crystal three-fold axes as the result of disorder in the equatorial belt. The crystal data include: space-group* $R\bar{3}$*, Z = 6;* I*/(*II*), a = 20.035(6) (20.030(5)), c = 32.844(10) (32.80(1))* Å*; R = 0.092 (0.092) for 3026 diffractometer data (1762 film data).*

Introduction

Heteropolyanions in which the heteroatom is an atom of a main-group element in its highest formal oxidation state [*e.g.* Si(IV), P(V)] or a d-block element [*e.g.* Mn(IV), Co(III)] have long been known [1]. More recently anions whose heteroatoms possess electron lone pairs have been studied, in particular anions containing arsenic(III) [2–5]. The anions $AsW_9O_{33}^{9-}$, $As_2W_{19}O_{67}(OH_2)_n^{14-}$, and $As_2W_{20}O_{68}(OH_2)_n^{10-}$ react [2, 3, 5] with divalent d-block cations to give complexes typified by, respectively, $As_2Co_3W_{18}O_{66}(OH_2)_3^{12-}$, $As_2Co_2W_{19}O_{67}(OH_2)_3^{10-}$, and $As_2CoW_{20}O_{68}(OH_2)_2^{8-}$. Single-crystal X-ray studies of the first of these complexes [6] and of its Cu(II) analogue [7] show them to be clearly related structurally to the limiting, non-substituted anion $As_2W_{21}O_{69}(OH_2)^{6-}$ [8] and the $As_2Z^{II}W_{20}$ anions have been similarly described [5] on the basis of spectroscopic studies. We now report the crystal structure of the $As_2Co^{II}W_{20}O_{68}(OH_2)_2^{8-}$ anion and of its zinc analogue.

Experimental

Preparation of Complexes

Salts of the tungstometalloarsenate anions were prepared without prior isolation of the tungstoarsenate(III) ligands. In a typical preparation, the pH of a solution containing $Na_2WO_4\cdot 2H_2O$ (55 g) and As_2O_3 (2.1 g) in 130 ml was adjusted to 5.7 with CH_3COOH. The mixture was heated to 70 °C and treated slowly with a concentrated solution of $Co(CH_3COO)_2\cdot 4H_2O$ (5.2 g), and was filtered after two minutes. On addition of a concentrated solution of KCl (15 g) and cooling, $K_{10}[As_2Co_2W_{19}O_{67}(OH_2)_n]\cdot(29 - n)H_2O$ was obtained as green-blue plates which were recrystallized from hot water. *Anal.* Found: K, 6.80; As, 2.61; Co, 2.05; W, 60.8%. Calcd: 6.80; 2.63; 2.13; 60.6%. A suspension of this salt, obtained by rapidly cooling a hot concentrated aqueous solution, was treated dropwise with 4 *M* HCl, with stirring, till a trace of solid just remained (pH *ca.* 2.3). The deep-pink filtrate was heated to 85 °C for several minutes, turning deep green. On treatment with concentrated aqueous KCl and cooling, green $K_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 22H_2O$ was obtained and was recrystallized from hot water. *Anal.* Found: K, 5.47; As, 2.62; Co, 1.03; W, 64.3%. Calcd: 5.68; 2.60; 1.04; 64.2%. Metathesis by use of aqueous RbCl gave $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$. *Anal.* Found: Rb, 11.6; As, 2.54; Co, 1.00; W, 62.6%. Calcd: 11.6; 2.52; 1.02; 62.6%. The rubidium salts of the zinc and manganese(II) analogues were obtained similarly and gave satisfactory analyses.

Crystallographic Studies

Preliminary Weissenberg photographs showed that the rubidium salts, which diffracted adequately, were trigonal-rhombohedral and isomorphous, with two anions in the primitive (rhombohedral) cell. It seemed likely that the anions would prove to be disordered with respect to the crystal three-fold axes. However, crystals of the potassium salts, although apparently triclinic and therefore potentially free from disorder, always consisted of small, badly misaligned blocks and satisfactory homogeneous fragments could not be obtained.

Crystal Data

I, $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$: trigonal, space-group $R\bar{3}$, a = 20.035(6), c = 32.844(10) Å,

0020-1693/84/$3.00

$Z = 6$, $d_{calc} = 5.13$ g cm^{-3}; Mo radiation ($\lambda = 0.71069$ Å), $\mu = 356$ g cm^{-1}.

II, $Rb_8[As_2ZnW_{20}O_{68}(OH_2)_2]\cdot 12H_2O$: trigonal, space-group $R\bar{3}$, $a = 20.030(5)$, $c = 32.80(1)$ Å, $Z = 6$, $d_{calc} = 5.17$ g cm^{-3}; Cu radiation ($\lambda = 1.5418$ Å), $\mu = 638$ cm^{-1}.

III, $Rb_8[As_2MnW_{20}O_{68}(OH_2)_2]\cdot 11H_2O$: Trigonal, space-group $R3$ or $R\bar{3}$, $a = 20.14(1)$, $c = 33.01(2)$ Å, $Z = 6$, $d_{calc} = 5.06$ g cm^{-3}.

Intensity data for *I* were collected in the range $2 < 2\theta < 50°$ on the Edinburgh University CAD-4 diffractometer by ω–2θ scans, after refinement of the cell parameters from the setting angles of 25 reflections in the range $24 < 2\theta < 26°$. The intensities of two check reflections showed no evidence of crystal decay during data collection. Data reduction afforded 4464 unique reflections, of which 3026 with $|F| \geqslant 3\sigma(F)$ were used in the refinement. An attempt to correct empirically for absorption by means of a ψ-scan did not lead to a decrease in the internal consistency index or in the final residual and standard deviations, and all parameters reported here are derived from un-corrected data.

Because our allocation of diffractometer data sets was limited, intensity data for *II* were collected photographically. Equi-inclination multi-film Weissenberg photographs were recorded from a crystal mounted on the rhombohedral *a* axis (layers 0 to 10) and were scanned by use of a microdensitometer (S.E.R.C. Service, Daresbury Laboratory). Absorption corrections were applied.

The structures of *I* and *II* were solved independently as a precaution. The period of the electron density (particularly the part contributed by W(2,3,4, 5)) is roughly halved along *c* and it was necessary to re-normalize the $|E|$-values for reflections with l odd before generating E-maps in space-group $R3$. The W atoms, excluding those in the equatorial zone of the anion (see Discussion), were thereby located and the structures were expanded by difference syntheses alternating with cycles of least-squares refinement and were seen to be clearly centrosymmetric ($R\bar{3}$), successive anions along *c* being related by inversion centres. The distribution of the three equatorial heavy atoms between outer sites (further from the crystal three-fold axis) and inner sites became apparent, and the most satisfactory refinement was achieved when each inner site was occupied by 1/3W and each outer site by 1/3W and 1/3 (Co or Zn). Refinement converged at *R* 0.092, *wR* ($= [\Sigma w\Delta^2/\Sigma wF^2]^{1/2}$) 0.115 for *I* (W, Co, As anisotropic, 195 parameters, weighting factor $w = [\sigma^2(F) + 0.00167F^2]^{-1}$ in last cycle), and at *R* 0.092, *wR* 0.111 for *II* (W, Zn anisotropic, 193 parameters, unit weights). The more prominent peaks (*ca.* 4 e Å^{-1}) in the final difference maps were near the refined positions of the Rb atoms and probably reflect disorder of these atoms over several adjacent sites as a result of the orientational disorder of the anions. Other peaks may represent fractional water molecules. In the case of *I*, a residual electron-density peak between the inner equatorial atom W(7B) and the three-fold axis appears significant (see Discussion). The SHELX-76 program system [9] was used in all calculations.

TABLE I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) for *I*, $Rb_8[As_2CoW_{20}O_{68}(OH_2)_2]\cdot 10H_2O$.

Atom	*x*	*y*	*z*	*U*
W(1)	1200(1)	398(1)	704(1)	
W(2)	1926(1)	1496(1)	1543(1)	
W(3)	322(1)	1896(1)	1548(1)	
W(4)	376(1)	1919(1)	3461(1)	
W(5)	1936(1)	1458(1)	3444(1)	
W(6)	1203(1)	399(1)	4291(1)	
W(7A)[a]	1100(4)	1673(4)	2494(2)	
W(7B)[b]	902(6)	1316(5)	2502(3)	
As(1)	0	0	1664(2)	
As(2)	0	0	3335(2)	
Rb(1)	2805(6)	1037(6)	2483(3)	105(3)
Rb(2)[c]	1718(10)	2535(10)	526(5)	110(5)
Rb(3)	1635(5)	2592(5)	4528(2)	73(2)
O(1)	1552(20)	489(20)	232(10)	33(8)
O(2)	550(20)	852(20)	640(9)	29(8)
O(3)	890(14)	314(14)	1395(7)	2(5)
O(4)	1966(17)	1343(17)	973(8)	16(7)
O(5)	107(17)	1777(16)	958(8)	13(6)
O(6)	665(19)	2848(19)	1579(9)	27(8)
O(7)	1208(17)	1856(18)	1437(8)	19(7)
O(8)	2289(18)	769(17)	1614(8)	21(7)
O(9)	372(20)	1601(21)	2073(10)	34(9)
O(10)	2804(23)	2366(22)	1580(10)	40(9)
O(11)	1553(21)	1347(21)	2088(10)	34(9)
O(12)	441(18)	1644(18)	2913(9)	23(7)
O(13)	717(21)	2873(22)	3416(10)	38(9)
O(14)	1539(18)	1302(17)	2931(8)	19(7)
O(15)	2244(18)	698(18)	3365(9)	22(7)
O(16)	1291(16)	1875(16)	3576(7)	11(6)
O(17)	2808(24)	2274(24)	3379(11)	47(10)
O(18)	163(17)	1832(17)	4045(8)	16(7)
O(19)	1986(18)	1329(18)	4033(9)	22(7)
O(20)	896(18)	306(17)	3597(8)	18(7)
O(21)	602(17)	867(18)	4355(8)	18(7)
O(22)	1595(19)	522(18)	4741(9)	23(7)
O(23)	1786(21)	2610(21)	2526(10)	34(9)
Aq(1)	3189(18)	40(18)	737(8)	18(7)
Aq(2)	2746(21)	2297(21)	208(10)	34(9)
Aq(3)	3361(27)	2693(27)	2509(13)	59(12)

[a] 0.5W + 0.5Co; site occupancy factor 2/3. [b] s.o.f. 1/3. [c] s.o.f. 2/3.

TABLE II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) for *II*, $Rb_8[As_2ZnW_{20}O_{68}(OH_2)_2]\cdot 12H_2O$.

Atom	*x*	*y*	*z*	*U*
W(1)	1202(2)	394(2)	694(1)	
W(2)	1933(2)	1505(2)	1540(1)	
W(3)	318(2)	1903(2)	1547(1)	
W(4)	365(2)	1911(2)	3447(1)	
W(5)	1938(2)	1461(2)	3434(1)	
W(6)	1201(2)	396(2)	4283(1)	
W(7A)[a]	1148(11)	1732(7)	2486(7)	
W(7B)[b]	986(18)	1477(18)	2498(9)	
As(1)	0	0	1684(5)	11(3)
As(3)	0	0	3307(5)	13(3)
Rb(1)	2847(19)	1050(20)	2468(10)	161(11)
Rb(2)[c]	1781(32)	2530(33)	460(18)	192(20)
Rb(3)	1621(9)	2567(9)	4531(5)	75(4)
O(1)	1602(27)	498(27)	214(17)	8(10)
O(2)	513(24)	795(24)	667(16)	2(10)
O(3)	874(24)	292(24)	1413(15)	0(9)
O(4)	1998(37)	1390(38)	960(21)	29(15)
O(5)	68(35)	1777(35)	940(21)	25(14)
O(6)	667(27)	2840(27)	1583(17)	7(11)
O(7)	1188(28)	1853(28)	1435(18)	10(11)
O(8)	2297(29)	818(28)	1579(17)	10(11)
O(9)	474(30)	1675(30)	2091(18)	14(12)
O(10)	2742(40)	2346(40)	1542(24)	36(17)
O(11)	1571(42)	1371(41)	2090(24)	38(18)
O(12)	388(29)	1616(30)	2887(18)	13(11)
O(13)	720(28)	2849(28)	3399(17)	9(11)
O(14)	1500(36)	1265(36)	2898(22)	28(15)
O(15)	2228(36)	721(35)	3390(21)	26(15)
O(16)	1297(28)	1917(29)	3545(18)	10(11)
O(17)	2798(40)	2260(41)	3350(24)	37(17)
O(18)	138(41)	1827(40)	4022(23)	36(17)
O(19)	1950(40)	1343(39)	4032(22)	35(17)
O(20)	867(26)	281(27)	3578(16)	5(10)
O(21)	573(28)	803(27)	4378(17)	9(11)
O(22)	1619(29)	504(29)	4760(18)	12(11)
O(23)	1855(35)	2775(34)	2509(21)	25(14)
Aq(1)	3186(28)	93(28)	730(17)	10(11)
Aq(2)	2806(26)	2387(26)	215(16)	6(10)
Aq(3)	3309(37)	2608(27)	2481(22)	31(16)

[a] 0.5W + 0.5Zn; site occupancy factor 2/3. [b] s.o.f. 1/3. [c] s.o.f. 2/3.

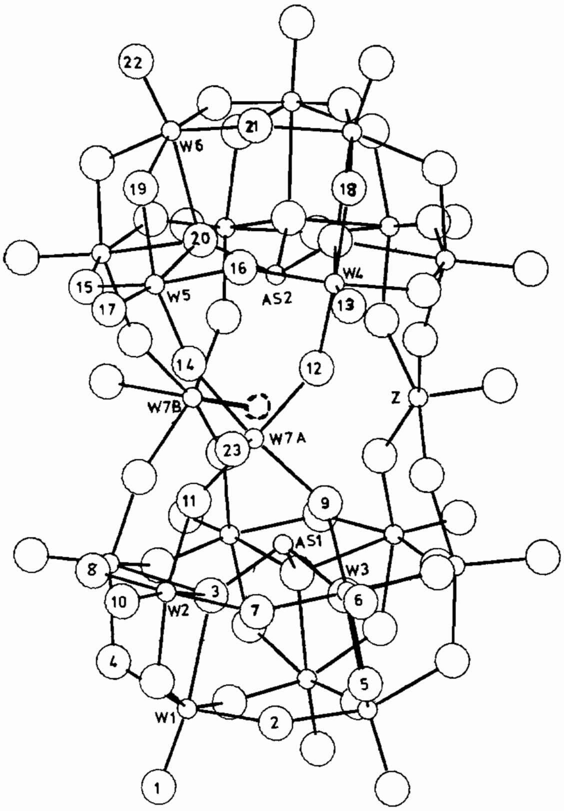

Fig. 1. The $[As_2ZW_{20}O_{68}(OH_2)_2]^{8-}$ anion (Z = Co or Zn) with atoms numbered (oxygen atoms as large circles). The atom shown as a broken circle was not refined.

Discussion

Atomid coordinates and thermal parameters are listed in Tables I to III, and bond lengths and other distances in Tables IV to VI.

The structures of the anions in *I* and *II* (Figs. 1 and 2) can be described as follows. Eighteen of the W atoms are present in two α-B [10] $AsW_9O_{33}^{9-}$ units, each of which has three-fold symmetry and is derived from an $AsW_{12}O_{40}^{3-}$ anion with the familiar Keggin [11] (α-$PW_{12}O_{40}^{3-}$) structure by removal of three edge-sharing WO_6 octahedra including an

TABLE III. Anisotropic Thermal Parameters (×10^4) for $Rb_8As_2ZW_{20}O_{68}(OH_2)_2\cdot nH_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I (Z = Co)						
W(1)	173(11)	192(11)	46(8)	16(7)	19(6)	89(9)
W(2)	150(10)	145(10)	100(8)	−4(7)	−12(7)	45(8)
W(3)	190(11)	147(10)	99(8)	−18(7)	−25(7)	81(9)
W(4)	215(12)	177(11)	115(9)	−6(7)	12(7)	93(9)
W(5)	164(11)	182(11)	118(9)	0(7)	−21(7)	64(9)

(continued overleaf)

TABLE III. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(6)	245(12)	275(12)	56(8)	−34(7)	−63(7)	129(10)
W(7A)	169(39)	239(39)	12(20)	2(31)	21(22)	41(35)
W(7B)	205(53)	175(49)	44(27)	31(41)	14(28)	−54(46)
As(1)	118(25)	118(25)	1(28)	0	0	59(12)
As(2)	145(26)	145(26)	2(28)	0	0	73(13)
II (Z = Zn)						
W(1)	91(17)	137(17)	68(28)	26(15)	26(14)	54(15)
W(2)	92(17)	120(18)	102(28)	−7(15)	−19(15)	20(14)
W(3)	155(18)	87(17)	127(28)	−23(15)	−52(15)	61(15)
W(4)	210(21)	151(19)	161(31)	17(17)	11(17)	93(17)
W(5)	111(18)	159(19)	149(29)	20(17)	16(16)	48(15)
W(6)	155(18)	187(19)	81(30)	−14(17)	−35(16)	89(16)
W(7A)	64(52)	50(44)	249(106)	−48(48)	−1(48)	−10(40)
W(7B)[a]	480(188)	1200(265)	−242(116)	150(162)	16(107)	596(195)

[a] Non-positive-definite.

TABLE IV. Bond Lengths (Å) within $As_2ZW_{20}O_{68}(OH_2)_2^{8-}$ Anions (*I*, Z = Co; *II*, Z = Zn).

	I	*II*		*I*	*II*
W(1)–O(1)	1.68(3)	1.73(5)	W(5)–O(14)	1.82(3)	1.92(7)
W(1)–O(2)	1.94(3)	1.92(5)	W(5)–O(15)	1.92(3)	1.85(6)
W(1)–O(2^{i})	1.86(3)	1.83(5)	W(5)–O(16)	1.91(3)	1.95(5)
W(1)–O(3)	2.34(2)	2.43(5)	W(5)–O(17)	1.71(4)	1.69(7)
W(1)–O(4)	1.95(3)	2.03(7)	W(5)–O(19)	1.96(3)	1.93(8)
W(1)–O(5^{i})	1.89(3)	1.86(5)	W(5)–O(20)	2.26(3)	2.31(5)
W(2)–O(3)	2.29(2)	2.33(4)	W(6)–O(18^{i})	1.96(3)	1.97(5)
W(2)–O(4)	1.90(3)	1.93(7)	W(6)–O(19)	1.93(3)	1.92(7)
W(2)–O(7)	1.94(3)	1.97(5)	W(6)–O(20)	2.35(3)	2.39(5)
W(2)–O(8)	1.94(3)	1.85(5)	W(6)–O(21)	1.87(3)	1.84(5)
W(2)–O(10)	1.76(4)	1.65(7)	W(6)–O(21^{i})	1.96(3)	1.97(5)
W(2)–O(11)	1.91(3)	1.91(8)	W(6)–O(22)	1.63(3)	1.74(6)
W(3)–O(3^{ii})	2.34(4)	2.34(6)	W(7A)–O(9)	1.96(4)	1.83(6)
W(3)–O(5)	1.97(3)	2.04(7)	W(7A)–O(11)	1.90(4)	1.88(8)
W(3)–O(6)	1.68(3)	1.65(5)	W(7A)–O(12)	1.89(3)	1.93(6)
W(3)–O(7)	1.85(3)	1.83(5)	W(7A)–O(14)	2.01(3)	1.96(7)
W(3)–O(8^{ii})	1.94(3)	1.99(5)	W(7A)–O(23)	1.69(4)	1.85(6)
W(3)–O(9)	1.84(3)	1.90(6)	W(7B)–O(9)	2.01(4)	1.84(6)
W(4)–O(12)	1.90(3)	1.94(6)	W(7B)–O(11)	1.87(4)	1.86(8)
W(4)–O(13)	1.68(4)	1.65(5)	W(7B)–O(12)	1.93(3)	1.86(7)
W(4)–O(15^{ii})	1.92(3)	1.91(5)	W(7B)–O(14)	1.91(3)	1.84(7)
W(4)–O(16)	1.92(3)	1.89(5)	W(7B)–O(23)	2.30(4)	2.30(7)
W(4)–O(18)	1.96(3)	1.93(8)	As(1)–O(3)	1.80(3)	1.78(4)
W(4)–O(20^{ii})	2.35(4)	2.34(7)	As(2)–O(20)	1.80(3)	1.77(5)

Symmetry code: (i) y − x, −x, z (II) −y, x − y, z

oxygen atom of the central AsO_4 group. The oxygen atoms thus exposed are bonded to two W atoms and one Co or Zn atom which occupy the equatorial plane of the anion between the AsW_9O_{33} units. The Co or Zn atom is in square-pyramidal coordination with an axial H_2O ligand. One equatorial W atom (W(7A)) also has a square-pyramidal coordination, but with an axial W=O bond; the other (W(7B)) is closer to the anion axis and has octahedral coordination, the ligand atoms being four oxygens of AsW_9-

TABLE V. Distances between Heavy Atoms within Anions (Å).

	I	*II*		*I*	*II*
W(1)–W(1^{i})	3.675(4)	3.68(1)	W(3)–W(7A)	3.601(8)	3.60(2)
W(1)–W(2)	3.367(4)	3.40(1)	W(3)–W(7B)	3.725(11)	3.66(2)
W(1^{ii})–W(3)	3.376(4)	3.40( )	W(4)–W(7A)	3.626(8)	3.62(2)
W(2)–W(3)	3.681(4)	3.70(1)	W(4)–W(7B)	3.708(11)	3.62(2)
W(2)–W(3^{i})	3.345(4)	3.36(1)	W(5)–W(7A)	3.668(8)	3.65(2)
W(4^{i})–W(5)	3.351(4)	3.34(1)	W(5)–W(7B)	3.653(11)	3.63(2)
W(4^{i})–W(6)	3.372(4)	3.37(1)	As(1)–W(1)	3.799(7)	3.88(1)
W(4)–W(5)	3.677(4)	3.69(1)	As(1)–W(2)	3.573(7)	3.55(1)
W(5)–W(6)	3.360(4)	3.37(1)	As(1)–W(3)	3.541(7)	3.57(1)
W(6)–W(6^{i})	3.685(4)	3.68(1)	As(2)–W(4)	3.553(7)	3.55(1)
W(2)–W(7A)	3.634(8)	3.61(2)	As(2)–W(5)	3.518(7)	3.53(1)
W(2)–W(7B)	3.679(11)	3.66(2)	As(2)–W(6)	3.794(7)	3.84(1)

(i) y – x, –x, z

TABLE VI. Bond Lengths around Rubidium Atoms (Å).

	I	*II*		*I*	*II*
Rb(1)–O(4^{iii})	3.31(4)	3.18(7)	Rb(2)–O(2)	3.02(4)	3.19(8)
Rb(I)–O(8)	2.99(3)	3.07(7)	Rb(2)–O(4)	3.05(3)	3.02(9)
Rb(1)–O(9^{i})	3.29(4)	3.41(8)	Rb(2)–O(5)	3.14(3)	3.37(8)
Rb(1)–O(10^{iii})	3.25(4)	3.14(7)	Rb(2)–O(7)	3.24(4)	3.45(8)
Rb(1)–O(11)	3.15(4)	3.18(7)	Rb(2)–O(17^{v})	2.91(3)	2.83(7)
Rb(1)–O(12^{i})	3.40(4)	3.37(8)	Rb(3)–O(6^{vi})	2.93(3)	2.96(7)
Rb(1)–O(14)	3.20(3)	3.26(7)	Rb(3)–O(16)	3.37(4)	3.43(8)
Rb(1)–O(15)	3.06(3)	3.21(7)	Rb(3)–O(18)	3.01(3)	3.07(7)
Rb(1)–Aq(2^{iii})	3.07(3)	3.02(7)	Rb(3)–O(19)	3.36(4)	3.28(8)
Rb(1)–Ag(3)	2.92(3)	2.78(7)	Rb(3)–O(21)	3.07(3)	3.12(5)
Rb(2)–O(1^{iv})	3.03(4)	2.77(7)	Rb(3)–O(22^{vii})	2.96(3)	2.85(7–

(i) y - x, –x, z; (iii) 2/3 – x, 1/3 – y, 1/3 – z; (iv) x – y, x, –z; (v) 1/3 + y – x, 2/3 – x, –1/3 + z; (vi) 1/3 – x, 2/3 – y, 2/3 – z; (vii) x – y, x, 1 – z

O_{33} units and, in the equatorial plane, an *exterior* H_2O molecule and an *interior* unshared oxygen atom. Although chemically distinct, the three exterior equatorial O atoms appear as a single atom O(23) as a result of disorder (see below). This description accords with the following observations.

(i) The final difference synthesis for *I* showed a weak peak at 0.038, 0.036, 0.253 in the equatorial plane, 1.67 Å from W(7B) and interior to it. Because of disorder the peak should correspond to only 1/3 of an oxygen atom, and no attempt was made to refine its coordinates.

(ii) The ^{183}W NMR spectrum for *II* has been interpreted [12] as showing the presence of one penta-coordinate and nine pairs of hexa-coordinate W atoms plus a unique, well-shielded, probably hexa-coordinate W atom.

(iii) The anions in *I* and *II* are very clearly structural derivatives of the 21-tungsto species $As_2W_{21}O_{69}(OH_2)^{6-}$ [8]. In the latter, one W atom in the equatorial plane has octahedral coordination as described for W(7B); the other two lie further from the anion axis and have square-pyramidal coordination.

Thus, the replacement of a square-pyramidal W atom in the As_2W_{21} anion gives the present anions, which should also be regarded as complexes of the ligand $As_2W_{20}O_{68}(OH_2)^{10-}$; the postulated [5] structure of the latter and its tetradentate character are confirmed. The bond lengths and W··W distances in *I* and *II* (Tables IV and V) are in satisfactory agreement with those found for $As_2W_{21}O_{69}(OH_2)^{6-}$.

The arsenic atoms lie on a crystal three-fold axis, each at the apex of a trigonal pyramid with the sterically-active electron lone pair directed along the axis into a region avoided by other atoms. The anions have overall virtual symmetry C_{2v}, if the replacement of one W atom is neglected, and adopt three equally-

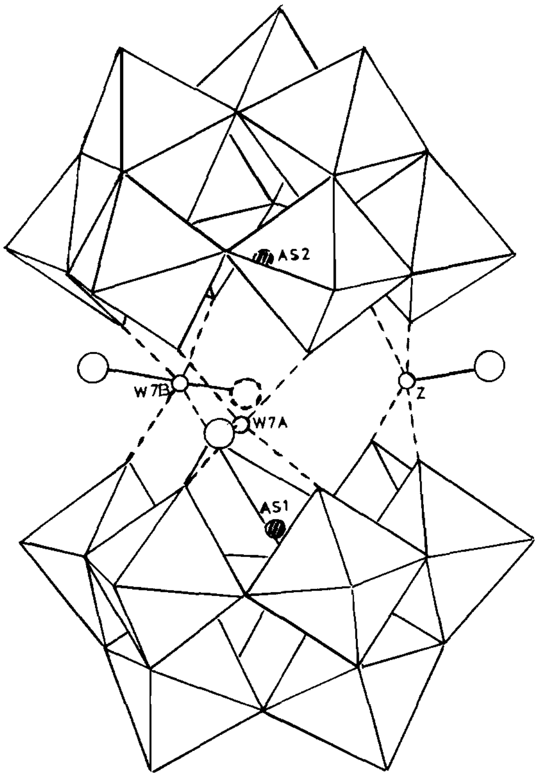

Fig. 2. The AsW_9O_{33} units, shown as groups of vertex-sharing octahedra, and the linking equatorial atoms.

weighted orientations about the crystal axis. Because the AsW_9O_{33} moieties have essentially three-fold symmetry, the disorder is only apparent as the presence of inner and outer heavy-atom sites in the equatorial plane, occupied respectively by 1/3W(7B) and 1/3(W(7A) + Co or Zn), and perhaps also as the generally larger thermal parameters U_{11} and U_{22} compared with U_{33} for the heavy atoms in *I*. Exactly the same sort of disorder occurs in $Rb_4H_2[As_2W_{21}O_{69}(OH_2)]\cdot 34H_2O$ [8].

Interestingly, the tri-substituted anion in $K_{12}[As_2Cu_3W_{18}O_{66}(OH_2)_2]\cdot 11H_2O$ [7] is well-ordered and shows a marked departure from three-fold symmetry; one AsW_9O_{33} unit is offset with respect to the other by displacement parallel to the equatorial (Cu_3) plane. The fact that it was possible to solve and refine the present disordered structures suggests that, as with $As_2W_{21}O_{69}(OH_2)^{6-}$, any 'shear' between AsW_9O_{33} units is here small, although the question must remain open until satisfactory disorder-free crystals are available.

The rubidium cations link the anion centred at 0, 0, ¼ to the eight neighbours related to it by the inversion centres at 0, 0, 0 and 0, 0, ½ and at 1/3, 1/6, 1/6 and equivalent positions, and to the six other neighbours generated by the primitive (R) lattice translations. Atom Rb(1) is coordinated in the equatorial plane 60° from the heavy atoms and corresponds to the one independent Rb atom identified in $Rb_4H_2[As_2W_{21}O_{69}(OH_2)]\cdot 34H_2O$ [8].

An anion $As_4Co_2W_{40}O_{140}(OH_2)_2{}^{24-}$ is known [3] and its structure has been determined as the ammonium salt [13]. It is not an exact dimer of the $As_2CoW_{20}O_{68}(OH_2)_2{}^{10-}$ anion, as the charge:As ratios are different. Nevetheless, the anions have salient features in common, namely the presence of α-B AsW_9O_{33} units linked through additional tungsten atoms, with sites for binding Co^{2+} (and a NH_4^+ ion also, in the case of the dimer).

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