

**Barium Aquacobalto(III)undecatungstoborate(6–) 26-Water,
Ba₃[BCo(H₂O)W₁₁O₃₉].26H₂O**

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Abstract. $M_r = 3613.7$, tetragonal, $P4/mnc$, $a = 12.397(1)$, $c = 18.481(1)$ Å, $V = 2840$ Å³, $Z = 2$, $D_x = 4.225$, $D_m = 4.23(1)$ Mg m⁻³, Mo $K\alpha$, $\mu = 25.1$ mm⁻¹, $\lambda = 0.71069$ Å, $F(000) = 3175$, $R = 0.063$ for 960 reflections. The $BM_{12}O_{40}H_n^{6-}$ anions ($M = Co_{1/12}W_{11/12}$) have the Keggin (α -PW₁₂O₄₀) structure. Each lies at a site of crystallographic symmetry $4/m$, in two equally weighted orientations related by inversion at the B atom.

Introduction. Numerous heteropolytungstate anions of the type $XZW_{11}O_{40}H_n^{6-}$ ($X =$ tetrahedral B, Si, P, etc.; $Z =$ octahedral Fe, Co, Zn, etc.) have been characterized since examples were first reported (Baker, Baker, Eriks, Pope, Shibata, Rollins, Fang & Koh, 1966). Each is derived from an anion having the Keggin (α -PW₁₂O₄₀) structure (Keggin, 1934) by the substitution of a $Z-OH$ or $Z-OH_2$ group for a W atom and its terminal O atom. The substitution lowers the point symmetry of the anion from $\bar{4}3m$ to m , but most diffraction studies have been confined to salts in which the anion appears to radiate as an $X(Z_{1/12}W_{11/12})_{12}$ species of $\bar{4}3m$ symmetry because of disorder of the anion over twelve equally weighted orientations which essentially differ only in the location of the Z atom (Baker, Baker, Eriks, Pope, Shibata, Rollins, Fang & Koh, 1966; Barrett, 1972; Weakley, 1982). We determined the structure of the title compound because the possible space groups ($P4nc$ or $P4/mnc$) require the two anions per cell to occupy sites of symmetry 4 or $4/m$, neither of which appears consistent with the Keggin structure even with disorder of the Co atom. Moreover, the cell dimensions are similar to those of $H_{3+n}[PV_nMo_{12-n}O_{40}].30-36H_2O$ ($n = 2, 3$) (Sergienko, Porai-Koshits & Yurchenko, 1980) which were reported to contain anions of non-Keggin but related structure on $4/m$ sites in space group $P4/mnc$.

Experimental. Green air-stable octahedra, $\{101\}$ faces (Weakley, 1973). Crystal $0.15 \times 0.15 \times 0.15$ mm. Film data initially (Weissenberg, Cu $K\alpha$ radiation, layers 0-8kl, SERC Microdensitometer Service, 758 unique reflections); subsequently four-circle diffrac-

tometer data (Edinburgh University CAD-4, graphite-monochromated Mo $K\alpha$). Cell dimensions from θ values of 25 reflections, $14^\circ < \theta < 15^\circ$. $\omega-2\theta$ scan, $2\theta_{max} = 50^\circ$. Standard reflections 647 and $\bar{4}67$, no change. Empirical absorption correction from ψ scan based on $\bar{2}3\bar{5}$. 2965 reflections scanned, 346 systematically absent, 1301 unique, $R_{int} = 0.076$; 960 reflections with $|F| \geq 3\sigma(F)$ used in refinement. Structure first solved from film data to $R = 0.093$ with the assumption that the anion had point symmetry $4/m$, with Co disordered over W sites, as suggested by the apparent isomorphism with $H_{3+n}[PV_nMo_{12-n}O_{40}].30-36H_2O$; heavy atoms located in E map, O atoms in difference synthesis; with counter data, refinement in $P4/mnc$ converged at $R = 0.073$, $wR = 0.104$ (56 parameters); an *ab initio* solution and refinement (on F) at this stage in $P4nc$ gave $R = 0.069$, $wR = 0.080$ but large σ values and strong correlation coefficients, structure still clearly centrosymmetric; with the assumption that anions of point symmetry $\bar{4}$ were present in two orientations in space group $P4/mnc$ (see Discussion) R , wR fell to 0.066, 0.095 (85 parameters), a decrease significant at the 95% confidence level; after the inclusion of Aq(4) final convergence was reached at $R = 0.063$, $wR = 0.089$; 89 parameters, $w = [\sigma^2(F) + 0.0047F^2]^{-1}$ in last cycle, maximum shift-to-error ratio 0.29; W(n) and Co(n) were constrained to have the same parameters (decoupling did not lead to a satisfactory refinement); Ba(1), all W, Co anisotropic; W(3), Co(3) non-positive-definite; the final difference synthesis (max. peak height *ca* 2 e Å⁻³) suggests partial site occupancy by those water molecules not directly located; all calculations used SHELX76 (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final coordinates and isotropic thermal parameters for anion symmetry $\bar{4}$ are listed in Table 1. When the only assumption made during the structure determination is that disorder implied by the notation $M = Co_{1/12}W_{11/12}$ must occur, the anion is found to have crystallographic point symmetry $4/m$ and virtual symmetry $m\bar{3}m$, with the M atoms at the corners of a regular cubo-octahedron; atomic coordinates have been

deposited,* and bond lengths are given in Table 2. Twelve square-pyramidal MO_5 groups share basal corners but not edges, and have short apical bonds. In addition, there are long $M-O$ bonds involving the O atoms of the central BO_4 tetrahedron which has two orientations differing by a 90° rotation about c (Fig. 1). The title compound is indeed isomorphous with $H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot 30-36H_2O$ ($n = 2, 3$) in which the heavy atoms are also disordered and whose anions have been similarly described (Sergienko, Porai-Koshits & Yurchenko, 1980). The coordinates of corresponding atoms in the anion are similar in all three compounds while the two independent Ba atoms and three of the four water molecules of the title compound correspond to five of the seven independent water molecules of the hydrated acids.

We considered the above description of the structure of the $BCo(H_2O)W_{11}O_{39}^{6-}$ and $PV_nMo_{12-n}O_{40}^{5,6-}$ anions to be inadequate, for the following reasons.

(i) There is no evidence, and no reason to expect, that in a free $XM_{12}O_{40}^{z-}$ anion the XO_4 tetrahedron can adopt alternative orientations within a defined $M_{12}O_{36}$ framework of cubic symmetry. In either orientation, a distortion of the framework would be expected, resulting in the overall tetrahedral symmetry characteristic of the Keggin anion with the heavy atoms grouped in four sets of three.

*Lists of structure factors (point symmetry $\bar{4}$), anisotropic thermal parameters ($\bar{4}$ and $4/m$) and atomic coordinates ($4/m$) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38940 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for anion point symmetry $\bar{4}$

	x	y	z	U_{iso} (\AA^2)
$M(1)^\dagger$	1606 (1)	2292 (1)	94 (5)	22‡
$M(2)$	1861 (14)	418 (17)	1311 (13)	24‡
$M(3)$	-262 (17)	2040 (14)	1343 (13)	22‡
B	0	0	0	7 (11)
O(1)	2389 (22)	3401 (20)	-101 (21)	31 (8)
O(2A)	704 (36)	2848 (35)	835 (23)	45 (11)
O(2B)	470 (24)	2592 (30)	-611 (18)	26 (8)
O(3A)	2450 (28)	1613 (29)	794 (20)	30 (8)
O(3B)	2213 (28)	1260 (30)	-560 (19)	30 (8)
O(4A)	2866 (28)	687 (31)	1983 (20)	25 (9)
O(4B)	2952 (32)	352 (32)	-2000 (22)	34 (11)
O(5)	536 (18)	836 (18)	480 (12)	9 (5)
O(6A)	968 (24)	1420 (25)	1815 (15)	22 (7)
O(6B)	721 (28)	982 (27)	-1638 (18)	31 (7)
Ba(1)	0	5000	2500	71‡
Ba(2)§	4762 (15)	3512 (16)	592 (10)	69 (5)
Aq(1)	1401 (33)	4781 (31)	1428 (20)	127 (13)
Aq(2)	4602 (43)	702 (43)	0	131 (18)
Aq(3)	0	0	3089 (35)	106 (19)
Aq(4)	1710 (55)	1567 (57)	3410 (41)	119 (21)

† $M = Co_{1/12}W_{11/12}$.

‡ $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

§ Site-occupancy factor $\frac{1}{3}$.

(ii) The $BCo^{III}(H_2O)W_{11}O_{39}^{6-}$ anion is similar in all properties to $BeCo^{III}(H_2O)W_{11}O_{39}^{7-}$ and is obtained by mild oxidation of $BCo^{II}(H_2O)W_{11}O_{39}^{7-}$. The latter anions both have the Keggin structure (Weakley, 1973, 1982).

(iii) Several heteropolyanions in which one or several Mo or W atoms have been replaced by V atoms have been shown to have the Keggin structure (Nishikawa, Kobayashi & Sasaki, 1975; Björnberg & Hedman, 1980; Klevtsova, Yurchenko, Glinskaya, Detusheva &

Table 2. Interatomic distances (\AA)

(a) For anion point symmetry $4/m$ ($M = Co_{1/12}W_{11/12}$)			
B-O(5)	1.51 (3)	W(2)-O(2 ^h)	1.81 (3)
W(1)-O(1)	1.66 (3)	W(2)-O(6 ^h)	1.92 (3)
W(1)-O(2)	1.93 (3)	W(2)-O(5)	2.44 (3)
W(1)-O(3)	1.86 (3)	W(2)-O(5 ^h)	2.39 (3)
W(1)-O(5)	2.39 (3)	Ba(1)-Aq(1)	2.54 (5)
W(2)-O(3)	1.86 (3)	Ba(1)-O(4 ^h)	2.81 (5)
W(2)-O(4)	1.75 (3)	Ba(2)-O(1 ^h)	2.92 (5)
W(2)-O(6)	1.87 (3)	Ba(2)-Aq(3 ^h)	2.91 (5)
W(1)⋯W(2)	3.471 (4)	B⋯W(1)	3.471 (4)
W(1)⋯W(2 ^h)	3.468 (4)	B⋯W(2)	3.471 (4)
W(2)⋯W(2 ^h)	3.474 (4)		

Symmetry code: (i) $y, -x, z$; (ii) $-y, x, z$; (iii) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$.

(b) For anion point symmetry $\bar{4}$ ($M = Co_{1/12}W_{11/12}$)			
B-O(5)	1.52 (2)	$M(3)-O(4B^{III})$	1.66 (4)
$M(1)-O(1)$	1.72 (3)	$M(3)-O(2A)$	1.82 (5)
$M(1)-O(2A)$	1.90 (4)	$M(3)-O(6A)$	1.92 (4)
$M(1)-O(2B)$	1.96 (3)	$M(3)-O(3B^{III})$	1.92 (4)
$M(1)-O(3A)$	1.87 (4)	$M(3)-O(6B^{III})$	1.94 (5)
$M(1)-O(3B)$	1.92 (3)	$M(3)-O(5)$	2.40 (3)
$M(1)-O(5)$	2.35 (2)	Ba(1)-Aq(1)	2.65 (4)
$M(2)-O(4A)$	1.79 (4)	Ba(1)-O(4A ^h)	2.94 (5)
$M(2)-O(3A)$	1.91 (4)	Ba(1)-O(4B ^h)	2.74 (4)
$M(2)-O(6A)$	1.91 (3)	Ba(2)-O(1 ^h)	2.82 (5)
$M(2)-O(2B^h)$	1.93 (3)	Ba(2)-O(1 ^h)	2.96 (5)
$M(2)-O(6B^h)$	1.88 (3)	Ba(2)-Aq(3 ^h)	3.07 (5)
$M(2)-O(5)$	2.31 (3)		
$M(1) \cdots M(2)$	3.248 (14)	$M(3) \cdots M(2^v)$	3.637 (16)
$M(1) \cdots M(3)$	3.284 (14)	B⋯M(1)	3.474 (10)
$M(2) \cdots M(3)$	3.312 (16)	B⋯M(2)	3.385 (13)
$M(1) \cdots M(2^{III})$	3.650 (14)	B⋯M(3)	3.558 (13)
$M(1) \cdots M(3^h)$	3.699 (14)		

Symmetry code: (i) $y, -x, -z$; (ii) $-y, x, z$; (iii) $-y, x, -z$; (iv) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$; (v) $-x, -y, z$.

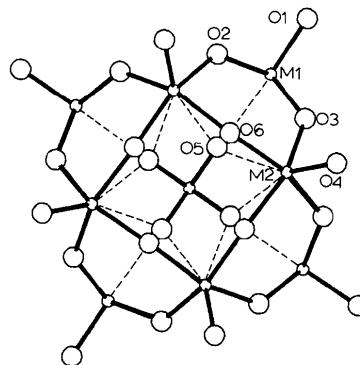


Fig. 1. The $BCo(H_2O)W_{11}O_{39}^{6-}$ anion, $4/m$ symmetry, c -axis projection. $M(1)$ and $O(1)$ lie in the mirror plane.

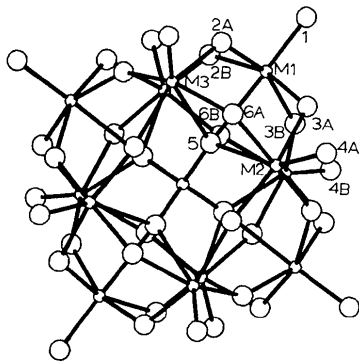


Fig. 2. The $\text{BCo}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{6-}$ anion, $\bar{4}$ symmetry (one orientation), c -axis projection.

Kuznetsova, 1981), including the $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$ anion in its sodium salt (Sergienko, Detusheva, Yurchenko & Porai-Koshits, 1981). In the present case, our alternative model assumes that the anion has the Keggin structure, with a disordered Co atom, and has crystallographic symmetry $\bar{4}$ (Fig. 2). The $4/m$ site is then occupied by two equally weighted anions related by inversion at the B atom. The act of inversion (here equivalent to reflection in the plane $z = 0$) brings the heavy-atom set into near self-coincidence. The less strongly scattering set of O atoms is brought into rougher self-coincidence, *except* for the atoms of the BO_4 group. These coincidences generate the $4/m$ structure shown in Fig. 1. The interatomic distances which result from refinement in this model are given in Table 2(b). As usual, the lengths of $M\text{—O}$ bonds increase with the coordination number of the O atom. The values are reasonable in view of the implicit double disorder, except for the bond to the terminal atom

O(4A) which appears to be somewhat misplaced. The possible presence of a Keggin anion in two orientations was apparently not considered in the case of $\text{H}_{3+n}[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]\cdot 30\text{--}36\text{H}_2\text{O}$, or in that of $(\text{NBu}_4)_3[\gamma\text{-PW}_{12}\text{O}_{40}]$ (Fuchs, Thiele & Palm, 1982) where the anion lies at an inversion centre in space group $P\bar{1}$.

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Structure of Strontium Selenate, SrSeO_4

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Abstract. $M_r = 230.58$, monoclinic, space group $P2_1/n$, $a = 6.853$ (1), $b = 7.352$ (1), $c = 7.102$ (2) Å, $\beta = 103.43$ (1)°, $V = 348.0$ (1) Å³, $Z = 4$, $D_x =$

4.401 (1) Mg m⁻³, $F(000) = 416$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 25.23$ mm⁻¹, $T = 291$ K. Single crystals were obtained by hydrothermal syn-