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Crystal structure of cesium aquanickelo(II)undecatungstophosphate dihydrate

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Abstract

The title compound, $Cs_5[PNi(H_2O)W_{11}O_{39}] \cdot 2H_2O$, is tetragonal with space group $P4_2/ncm$ and cell dimensions $a = 20.908(5)$, $c = 10.391(6)$ Å. The single-crystal structure determination (diffractometer data, Mo radiation, $R = 0.054$ for 1484 unique reflexions) shows that two types of disorder are present: the Ni atom substituting for W in the parent α-$PW_{12}O_{40}^{3-}$ anion is distributed equally over all twelve W sites and, in addition, the anion lies at a crystal site of symmetry $2/m$ in two equally weighted orientations related by the two-fold axis. The dimensions of the anion are normal.

Introduction

Numerous examples of heteropolyoxotungstate anions are now known (Pope, 1983) in which one tungsten atom in an anion with the Keggin (α-$PW_{12}O_{40}^{3-}$) structure (Keggin, 1934; Allmann and D'Amour, 1975; Brown *et al.*, 1977) has been replaced by Mo or an atom of the 3d series. The general formula is $XZ(OH_n)W_{11}O_{39}^{x-}$, where X is tetrahedral B, P, Co, etc., and Z is the substituent atom Fe, Co, Zn, etc. at an octahedral site. No completely satisfactory X-ray structural analysis of such an anion has yet been achieved. A frequency problem is disorder: for instance, in the K^+ and NH_4^+ salts of anions of charge 7- or 8- (cubic, $Fm3m$) the anions, of actual symmetry m (C_s), adopt twelve equally weighted orientations and appear to radiation as $X(Z_{1/12}W_{11/12})_{12}$ species of $\overline{4}3m$ (T_d) symmetry containing composite heavy atoms (Baker *et al.*, 1966; Weakley, 1982). Salts of lower crystal symmetry in which disorder of the anion is not required by the space group are generally unsatisfactory for X-

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ray work although in some cases at least (Evans, 1980; Weakley, 1983) the anion is known to be polymeric through Z–O–W bridges. The substituted Keggin-structure anions in some tetragonal crystals show double disorder, as not only do X-rays ''see'' composite heavy atoms but the anion lies on a crystal inversion center in two equally weighted orientations (Evans and Pope, 1984; Weakley, 1984). The title compound is a further example of this type.

Experimental

The title compound and the Cs salts of the corresponding Co(II) and Zn complexes were prepared as described elsewhere (Weakley, 1974), reprecipitated from hot aqueous solution by the addition of CsCl(s), and recrystallized from hot water containing *ca.* 0.03 mol liter^{-1} CsCl. Well-formed air-stable tetragonal prisms were deposited from slightly supersaturated solutions on standing at room temperature. Preliminary photographic studies showed that the compounds were tetragonal and isomorphous (space group, cell dimensions, distribution of intensities in zero- and upper-level Weissenberg photographs) with the space group uniquely defined as $P4_2/ncm$.

Crystal data. $Cs_5[PCo(H_2O)W_{11}O_{39}] \cdot 3H_2O$, $a = 20.95(2)$, $c = 10.42(1)$ Å, $V = 4573$ Å^3, $Z = 4$, $d(\text{calc.}) = 5.045$ g cm^{-3}. $Cs_5[PZn(H_2O)W_{11}O_{39}] \cdot 4H_2O$, $a = 20.96(2)$, $c = 10.39(1)$ Å, $V = 4565$ Å^3, $Z = 4$, $d(\text{calc.}) = 5.067$ g cm^{-3}. $Cs_5[PNi(H_2O)W_{11}O_{39}] \cdot 3H_2O$, $a = 20.906(5)$, $c = 10.382(6)$ Å, $V = 4542$ Å, $Z = 4$, $d(\text{calc.}) = 5.052$ g cm^{-3}, $F(000) = 5806$; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 32.8$ mm^{-1}.

Data collection. Intensity data were collected by use of a CAD-4 diffractometer from a crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm over the range $1.5° \leq \theta \leq 25°$ (h 0 to 24, k 0 to 24, l 0 to 12), after refinement of cell dimensions from setting angles of 25 reflections in the range $12 \leq \theta \leq 14°$. The number of reflections measured was 4488; number systematically absent, 493; number of unique reflections 2088; and the merging R value was 0.074 before and 0.071 after an empirical correction of the intensities for absorption (psi-scan).

Structure solution. With four anions per cell, each must lie on a site of imposed symmetry $2/m$, mm, 222, or $\bar{4}$. The last three, though consistent with a Keggin anion in which Ni is disordered over twelve heavy-atom sites, require the anion centers to be only 5.2 Å apart, and as expected the Patterson function could be interpreted only on the basis of an anion at the $2/m$ site at the origin. This was confirmed by an E-map, generated after renormalization of the E values for the systematically weak reflections with $(h + k)$ odd, which clearly showed the four independent heavy atoms $M = Ni_{1/12}W_{11/12}$ of a cubo-octahedral ($m3m$, O_h) M_{12} framework having imposed symmetry $2/m$. The structure was expanded by difference syntheses alternating with cycles of least-squares refinement. No preferential site occupation by Ni could be deduced from Fourier peak heights or from the magnitudes of U_{iso} for M. A further empirical absorption correction was applied by use of the program DIFABS (Walker and Stuart, 1983) after isotropic refinement of all nonhydrogen atoms. Convergence for this "*m*3*m* anion" model, in which the oxygen atoms of the disordered central PO_4 group (see Discussion) were given occupancy factors of 0.5, was reached at R 0.054, wR ($= [\Sigma w(\Delta F)^2/\Sigma wF^2)^{1/2}$) 0.056; Cs, composite atoms M anisotropic, 100 parameters, 1484 unique reflections with $|F| \geq 3\sigma(F)$, weighting factor in last cycle given by $w = [\sigma^2(F) + 0.00020F^2]^{-1}$.

A difference map for the above model after isotropic refinement showed residual electron density on the edges of the associated cube of the M_{12} group, close to and on either side of M(1), M(2), and M(3), as expected if two Keggin anions shared the 2/*m* site in mutually inverted orientations. This model was also refined, with site occupancy factors of 0.5 for all atoms, M(4) now being allowed to move slightly off the crystal diad axis. Alternative positions could be discerned for Cs(2) and all oxygen atoms except O(3) and O(4). Refinement with all atoms isotropic converged at R 0.058, wR 0.062 (125 parameters, weighting factor in last cycle given by $w = [\sigma^2(F) + 0.00025F^2]^{-1}$). Attempts to introduce anisotropic thermal parameters for M and Cs resulted in nonpositive-definite thermal ellipsoids and an increase of R to 0.087.

The SHELX 76 program (Sheldrick, 1975) was used in all calculations other than for absorption correction. Atomic coordinates and isotropic thermal parameters are listed in Table 1, anisotropic parameters in Table 2, and bond lengths in Table 3. Tables of bond angles and of observed and calculated structure factors have been deposited as supplementary data.

Discussion

The anion, as it first emerges from the structure solution, has crystallographic symmetry 2/*m* but closely approximates to *m*3*m* symmetry with the Ni atom disordered over the W sites (Fig. 1). It contains 12 square-pyramidal MO_5 groups sharing basal corners; each M atom also forms a long bond to an oxygen atom of a central PO_4 tetrahedron for each of the two inversion-related orientations of the latter group. Bond lengths from M to terminal, corner-shared, and central O atoms are in the ranges 1.67–1.74, 1.86–1.94, and 2.40–2.52(3) Å respectively (Table 3). The M $\cdots$ M distances have values (3.54–3.57 Å) lying between those usually found for edge-sharing and for corner-sharing WO_6 octahedra (ca. 3.3–3.4 and 3.7 Å respectively). Each anion is closely associated with six Cs ions which lie on the local four-fold axes of the anion at 5.80 and 5.90 Å from the center, each Cs site being 5/6 occupied.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$)

(a) Imposed symmetry $2/m$ for anion ($M = Ni_{1/12}W_{11/12}$)

Atom	x	y	z	U_{iso}
M(1)	663(1)	663(1)	2856(2)	18(1)[a]
M(2)	−977(1)	229(1)	2778(1)	15(1)[a]
M(3)	446(1)	1645(1)	83(1)	16(1)[a]
M(4)	−1192(1)	1192(1)	0	17(1)[a]
P	0	0	0	9(2)
O(1)	1003(9)	1003(9)	4177(28)	33(7)
O(2)	−1452(11)	340(10)	4053(23)	49(6)
O(3)	684(9)	2440(10)	128(19)	37(5)
O(4)	−1761(11)	1761(11)	0	50(9)
O(12)	−214(11)	682(11)	3169(24)	52(6)
O(13)	508(11)	1419(11)	1816(24)	52(6)
O(22)	−536(11)	−536(11)	3143(32)	49(8)
O(23)	270(9)	1505(9)	−1691(21)	36(5)
O(24)	−1209(1)	961(11)	1791(24)	55(7)
O(33)	1235(13)	1235(13)	−191(39)	70(11)
O(34)	−446(10)	1688(10)	362(21)	43(6)
OP(12)	−17(15)	−17(15)	1455(40)	11(9)
OP(13)	481(13)	481(13)	509(40)	7(9)
OP(24)	−669(14)	193(13)	439(29)	9(7)
Cs(1)	1595(1)	1595(1)	−3403(3)	25(1)[a]
Cs(2)	−667(1)	2127(1)	3314(2)	20(1)[a]
Aq(1)	1934(32)	1934(32)	2706(90)	226(41)
Aq(2)	2500	2500	5032(89)	149(33)

(b) Imposed symmetry m for anion ($M = Ni_{1/12}W_{11/12}$)

Atom	x	y	z	U_{iso}
M(1A)	−710(2)	−710(2)	−2784(5)	13(2)
M(1B)	621(2)	621(2)	2922(5)	7(1)
M(2A)	−257(2)	1018(2)	−2727(4)	10(1)
M(2B)	−936(2)	200(2)	2831(4)	11(1)
M(3A)	−1638(2)	−503(2)	−119(4)	8(1)
M(3B)	384(2)	1651(2)	45(4)	10(1)
M(4)	−1171(3)	1212(3)	−68(6)	14(1)
P	0	0	0	11(3)
O(1A)	−996(24)	−996(24)	−4354(77)	28(20)
O(1B)	1024(25)	1024(25)	4026(80)	11(22)
O(2A)	−413(26)	1338(27)	−4208(55)	46(15)
O(2B)	−1545(15)	301(19)	3951(41)	15(9)
O(3)	679(10)	2438(11)	146(22)	41(6)
O(4)	−1763(12)	1763(12)	0	50(10)
O(12A)	−664(20)	195(20)	−2910(47)	22(10)
O(12B)	−224(20)	691(20)	3500(44)	19(10)
O(13A)	−1472(19)	−602(19)	−1891(39)	13(9)
O(13B)	401(26)	1337(26)	1719(54)	42(15)
O(22A)	591(19)	591(19)	−3396(59)	21(13)
O(22B)	−490(24)	−490(24)	2941(74)	27(19)
O(23A)	−1434(24)	−286(24)	1545(51)	13(15)

Table 1. Continued

(b) Imposed symmetry m for anion ($M = Ni_{1/12}W_{11/12}$)

Atom	x	y	z	U_{iso}
O(23B)	256(16)	1586(17)	−1874(37)	23(8)
O(24A)	−989(18)	1321(18)	−1880(37)	11(9)
O(24B)	−1070(23)	918(22)	1683(47)	28(12)
O(33A)	−1360(19)	−1360(19)	85(56)	18(12)
O(33B)	1130(20)	1130(20)	−309(53)	19(13)
O(34A)	−1603(18)	390(18)	−428(36)	9(9)
O(34B)	−536(20)	1822(20)	302(39)	19(10)
OP(12)	−22(18)	−22(18)	1495(48)	16(11)
OP(13)	−489(15)	−489(15)	−519(45)	7(10)
OP(24)	−194(14)	653(15)	−448(30)	5(7)
Cs(1)	1595(1)	1595(1)	−3401(4)	25(1)
Cs(2A)	−738(3)	2112(3)	3355(7)	12(2)
Cs(2B)	−2144(3)	598(3)	−3276(6)	10(2)
Aq(1)	1921(31)	1921(31)	2663(87)	202(37)

[a] $U_{eq} = 1/3\ \Sigma_{ij}\ U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 2. Anisotropic thermal parameters[a] ($\times 10^4$) and anion symmetry $2/m$ ($M = Ni_{1/12}W_{11/12}$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	214(5)	214(5)	123(8)	−92(5)	−92(5)	91(7)
M(2)	188(6)	154(5)	112(5)	−40(5)	61(5)	−32(5)
M(3)	261(6)	76(5)	135(6)	−1(5)	41(5)	−22(4)
M(4)	163(5)	163(5)	198(8)	−19(5)	−19(5)	24(6)
Cs(1)	274(11)	274(11)	198(18)	−6(10)	−6(10)	−65(15)
Cs(2)	347(13)	112(10)	146(11)	−120(9)	−39(10)	20(10)

[a] The temperature factor is given by $T = \exp\left[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})\right]$.

Table 3. Bond lengths and interatomic distances (Å) ($M = Ni_{1/12}W_{11/12}$)

(a) Anion symmetry $2/m$

W(1)-O(1)	1.70(3)	W(3)-OP(13)	2.47(3)
W(1)-O(12)	1.86(2)	W(3)-OP(24)	2.50(3)
W(1)-O(13)	1.94(2)	W(4)-O(4)	1.68(3)
W(1)-OP(12)	2.48(4)	W(4)-O(24)	1.92(3)
W(1)-OP(13)	2.50(4)	W(4)-O(34)	1.91(2)
W(2)-O(2)	1.67(2)	W(4)-OP(24)	2.40(3)
W(2)-O(12)	1.90(2)	P-OP(12)	1.51(4)
W(2)-O(22)	1.88(2)	P-OP(13)	1.52(4)
W(2)-O(23')	1.89(2)	P-OP(24)	1.53(3)
W(2)-O(24)	1.91(2)	Cs(1)-O(1)	3.06(3)
W(2)-OP(12)	2.49(3)	Cs(1)-O(23)	3.30(2)
W(2)-OP(24)	2.52(3)	Cs(1)-O(33)	3.50(4)

Table 3. Continued

(a) Anion symmetry 2/*m*

W(3)-O(3)	1.74(2)	Cs(1)-Aq(2)	3.13(5)
W(3)-O(13)	1.87(3)	Cs(2)-O(12)	3.17(2)
W(3)-O(23)	1.90(2)	Cs(2)-O(13)	3.26(2)
W(3)-O(33)	1.88(2)	Cs(2)-O(24)	3.12(3)
W(3)-O(34)	1.89(2)	Cs(2)-O(34)	3.24(2)
W(1) ··· W(2)	3.549(3)	W(3) ··· W(4)	3.552(3)
W(1) ··· W(3)	3.567(3)	W(1) ··· P	3.557(3)
W(2) ··· W(2^{ii})	3.567(3)	W(2) ··· P	3.569(3)
W(2) ··· W(4)	3.548(3)	W(3) ··· P	3.563(3)
W(2) ··· W(3^{i})	3.574(3)	W(4) ··· P	3.523(3)
W(3) ··· W(3^{ii})	3.545(3)		

(b) Anion symmetry *m*

W(1A)-O(1A)	1.84(8)	W(3A)-OP(13)	2.44(3)
W(1A)-O(12A)	1.90(4)	W(3B)-O(3)	1.76(3)
W(1A)-O(13A)	1.86(4)	W(3B)-O(13B)	1.86(6)
W(1A)-OP(13)	2.44(5)	W(3B)-O(23B)	2.02(4)
W(1B)-O(1B)	1.65(8)	W(3B)-O(33B)	1.94(2)
W(1B)-O(12B)	1.87(4)	W(3B)-O(34B)	1.97(4)
W(1B)-O(13B)	2.00(6)	W(3B)-OP(24)	2.46(3)
W(1B)-OP(12)	2.41(5)	W(4)-O(4)	1.69(4)
W(2A)-O(2A)	1.71(6)	W(4)-O(24A)	1.93(4)
W(2A)-O(12A)	1.93(4)	W(4)-O(24B)	1.93(5)
W(2A)-O(22A)	2.10(3)	W(4)-O(34A)	1.98(4)
W(2A)-O(23B)	1.83(3)	W(4)-O(34B)	1.88(4)
W(2A)-O(24A)	1.88(4)	W(4)-OP(24)	2.39(3)
W(2A)-OP(24)	2.49(3)	P-OP(12)	1.56(5)
W(2B)-O(2B)	1.74(4)	P-OP(13)	1.54(4)
W(2B)-O(12B)	1.94(4)	P-OP(24)	1.50(3)
W(2B)-O(22B)	1.72(2)	Cs(1)-O(1B)	3.16(8)
W(2B)-O(23A)	1.98(5)	Cs(1)-O(22A)	2.97(6)
W(2B)-O(24B)	1.94(5)	Cs(1)-O(33B)	3.49(6)
W(2B)-OP(12)	2.41(4)	Cs(2A)-O(2A)	3.08(6)
W(3A)-O(3)	1.71(3)	Cs(2A)-O(12B)	3.16(4)
W(3A)-O(13A)	1.89(4)	Cs(2A)-O(24B)	3.12(5)
W(3A)-O(23A)	1.84(5)	Cs(2B)-O(2B)	3.20(4)
W(3A)-O(33A)	1.90(3)	Cs(2B)-O(24A)	3.20(4)
W(3A)-O(34A)	1.90(4)	Cs(2B)-O(34A)	3.20(4)
W(1A) ··· W(2A)	3.735(5)	W(3A) ··· W(4)	3.717(5)
W(1A) ··· W(3A)	3.410(5)	W(3B) ··· W(3B^{ii})	3.746(5)
W(1B) ··· W(2B)	3.372(5)	W(3B) ··· W(4)	3.381(5)
W(1B) ··· W(3B)	3.718(5)	P ··· W(1A)	3.574(5)
W(2A) ··· W(2A^{ii})	3.770(5)	P ··· W(1B)	3.547(5)
W(2A) ··· W(3B)	3.442(5)	P ··· W(2A)	3.584(5)
W(2A) ··· W(4)	3.383(5)	P ··· W(2B)	3.558(5)
W(2B) ··· W(2B^{ii})	3.360(5)	P ··· W(3A)	3.584(5)
W(2B) ··· W(3A)	3.702(5)	P ··· W(3B)	3.544(5)
W(2B) ··· W(4)	3.714(5)	P ··· W(4)	3.524(5)
W(3A) ··· W(3A^{ii})	3.356(5)		

Symmetry code: (i) $-y, -x, -z$; (ii) y, x, z

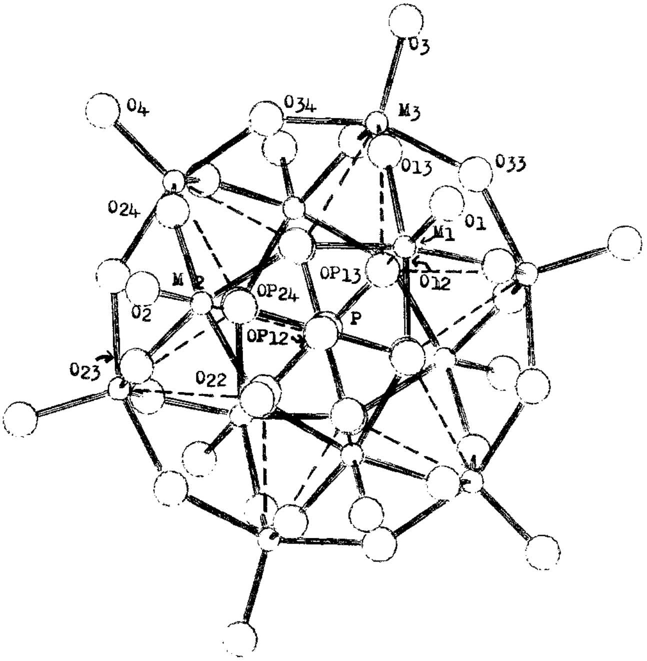

Fig. 1. Imposed symmetry 2/*m* for anion: *c*-axis projection.

Similar descriptions have been given for the anions in $H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot 30\text{–}36H_2O$ ($n = 2,3$) (Sergienko *et al.*, 1980) and $(NBu_4)_3[\gamma\text{-}PW_{12}O_{40}]$ (Fuchs *et al.*, 1982), but these have been criticized by Evans and Pope (1984) who showed that the apparent high anisotropic motion of the O atoms in the first two anions was consistent with the presence of a tetrahedral Keggin anion lying on a crystal inversion center in two orientations. The act of inversion brings the set of heavy atoms into near self-coincidence, and the set of oxygen atoms (except for the central four) into more approximate self-coincidence. The same conclusion was reached by Weakley (1984), who showed that the anion in $Ba_3[BCo(H_2O)W_{11}O_{39}] \cdot 26H_2O$ also had apparent *m*3*m* symmetry but could be refined as two mutually inverted Keggin anions.

The anion in the title compound is clearly similarly disordered. It was apparent after the identification of alternative sites for M and for most oxygen atoms that a Keggin anion was present in two orientations related by inversion at the P atom or equivalently by the crystal diad axis, the crystallographic mirror plane being coincident with a mirror plane of the (Ni-disordered) anion in each orientation. One of the two orientations is shown in Fig. 2. The MO_6 octahedra are grouped in four sets of three, with edge sharing within groups and corner

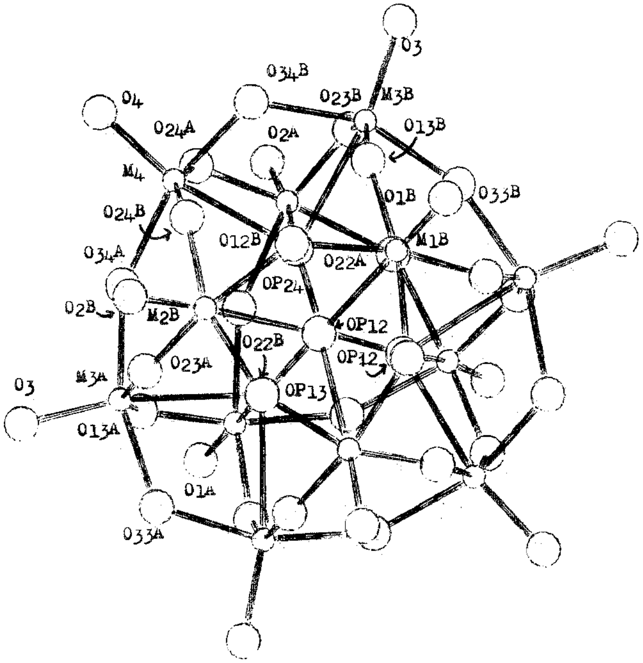

Fig. 2. Imposed symmetry *m* for anion: one orientation, *o*-axis projection.

sharing between them, the M · · · M distances (3.36–3.44 and 3.72–3.77 Å respectively) lying in the expected ranges. Most bond lengths to oxygen atoms have reasonable lengths (Table 3), although the terminal atom O(1A) and the bridging atom O(22B) must be somewhat misplaced and it was not evident which alternative position of Cs(2) corresponded to a given orientation of the anion. We conclude that disorder of this type is to be expected whenever the space group and number of anions per cell constrain a heteropolyoxometallate anion to lie at a crystallographic inversion center if the anion is believed from other evidence (e.g., synthesis) to have the Keggin structure and, therefore, to contain a unique atom (here, P) which is normally tetrahedrally bonded. In the present case each anion has two nearest neighbors at 10.39 Å, eight at 11.67 Å, and four at 14.78 Å; the array is not close-packed, and inversion of the quasi-spherical anion can occur without introducing local strain in the crystal.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63050 (11 pages).