Crystal structures of $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot3H_2O$ (X = P or As)

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The orthorhombic crystal structures of $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot3H_2O$ for X = P and As have been determined with data collected at room temperature, and for X = P at −100 °C, using Mo-Kα radiation. For the latter the space group is $Pna2_1$, $a = 21.670(11)$, $b = 14.805(4)$, $c = 20.393(5)$ Å and $Z = 4$. The structure consists of chains of α-Keggin-type molecules joined by W–O–Co links aligned in the *a*-axis direction. The Co/W occupancy at the link is disordered, with 61% Co on one side and 39% on the other. Further probable disorder, by lamellar merohedral twinning on (001) and by misorientation of the triethylammonium ions, has obscured the ethyl groups and the water molecules. In polarized light the crystals are deep wine-red normal to the chains (in the *b* direction), but nearly colourless in the *a* and *c* directions. The structure of the arsenate is similar to that of the phosphate.

The preparation and properties of the compounds $[NEt_3H]_5[PCo^{II}W_{11}O_{39}]\cdot3H_2O$ **1** and $[NEt_3H]_5[AsCoW_{11}O_{39}]\cdot3H_2O$ **2** have been described by Weakley,[1] together with other heteropolytungstates of the type $[XMW_{11}O_{39}]^{n-}$ with X = B, P or As and M = Co, Zn or Ni, as salts of various cations. Although these 11-tungstates are well known, no discrete crystal structure analysis has been made up to now that would allow a detailed description of the bonding environment of the monosubstituted M atom, which occupies one position in the oxometalate shell of the α-Keggin molecule. The study of the detailed structures of substituted Keggin-type heteropolyanions such as $[Co(H_2O)CoW_{11}O_{39}]^{8-}$ and $[Co(H_2O)BW_{11}O_{39}]^{6-}$ has been complicated by disorder. The monosubstituted Keggin anion has point symmetry *m*, but in most of the well diffracting salts that have hitherto been examined the anions lie at a special position of high symmetry (*e.g.* $\bar{4}3m$) with a number of equally weighted orientations so that the substituent atom is in effect randomly distributed over all twelve heavy-atom positions in the structure.[2] Even when the polyanion lies at a general position the multiple disorder is still present.[3] The results of another such structure study,[4] on $Ba_3[BCo(H_2O)W_{11}O_{39}]\cdot26H_2O$, showed that the molecule is disordered in point symmetry $4/m$ occupying two orientations related by inversion through the phosphorus atom position.

A number of years ago one of us (T. J. R. W.) observed[1] that certain salts, particularly the orthorhombic triethylammonium salts, of $[Co^{II}(H_2O)XW_{11}O_{39}]^{5-}$ (X = P or As) were strongly pleochroic. It seemed likely that the $Co(H_2O)O_5$ chromophore had a unique orientation at each polyanion site in these crystalline salts. The crystal structure analyses described here have indeed proved rewarding, but in an unexpected way: the monosubstituted Keggin groups are found to be assembled into straight chains through W–O–Co linkages.

The elimination of water from the $Co(H_2O)$ unit and its replacement by the terminal oxygen on a W atom of a second Keggin unit has occurred on crystallization of the salts described here from *aqueous* solution. Katsoulis and Pope[5] have described the extraction of $[Co^{II}(H_2O)SiW_{11}O_{39}]^{6-}$ and related anions from aqueous into toluene solution with the aid of $[N(n\text{-}C_7H_{15})_4]Br$. Marked spectral changes occur either immediately on extraction or when the toluene solutions are dried. It seems likely that in non-co-ordinating solvents the elimination of the ligand water on Co is accompanied by the formation of oligomers of Keggin units, which need not necessarily be linear as in the present structures.

Hill and Chang[6] have described further properties of the α-$[PCo^{II}W_{11}O_{39}]^{5-}$ polyanion. They found that under mildly acidic conditions this complex will catalyse epoxidation of alkenes, with the ability to restore itself following this function. As the chain complexes described here are essentially the linear chain polymer of $[PCoW_{11}O_{39}]^{5-}$, it is possible that multiply linked oligomers may play a role in this process.

It is noteworthy that another catena complex of the type found here has recently been described by an independent group[7] by means of a crystal structure analysis, namely $[bettf]_8[PMnW_{11}O_{39}]\cdot2H_2O$ [bettf = bis(ethylenedithio)-tetrathiafulvalene; tetrathiafulvalene 2-(1,3-dithiol-2-ylidene)-1,3-dithiole].

The present compounds $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot3H_2O$ (X = P or As) produced beautiful, orthorhombic crystals from aqueous solution, which offered a new possibility for obtaining structural information on the monosubstituted Keggin complex. Unfortunately, the structures are found to suffer from three types of disorder. Despite these problems, a new, unique arrangement of the Keggin-type molecules was revealed, in which they are joined by Co–O–W bridges into chains, like beads on a string. Although this study failed to yield the structural detail that we had hoped for, we present here the results that we have obtained for these unusual complexes.

Experimental

Crystallography

Both the arsenate and phosphate forms of $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot3H_2O$ have been analysed, but the latter has been subjected to a more detailed study. The crystals of both are orthorhombic, forming stubby, prismatic crystals from aqueous solution (Fig 1). Precession X-ray photography showed the space group to be *Pnam* (no. 62) or $Pna2_1$ (no. 33). Lack of *hk*0 extinctions precludes glides normal to *c*, and the determined structure is incompatible with a mirror, so the space group $Pna2_1$ was assumed throughout the analysis. The unit-cell constants given in Table 1 were measured for the phosphate by least-squares analysis of X-ray powder data obtained from Guinier–Hägg patterns using Cr-Kα radiation (λ = 2.2897 Å); for the arsenate compound by least-squares analysis of 2θ values in the range 30–40° measured for 20 reflections on a Nonius CAD4 automatic diffractometer.

Morphological measurements of the phosphate complex with a two-circle optical goniometer showed a simple habit with the forms (101) (prism direction), and (110), plus sometimes a minor (011) (Fig. 1); no tendency for hemimorphism was apparent. These forms are consistent with space-group extinctions and the Donnay–Harker Law. There is perfect (010) cleavage. The crystals are transparent but dark coloured, purple with a greenish cast. In polarized light they are pale blue in the *a* and *c* directions (purple in thick sections), and deep wine-red in the *b* direction. Optically the crystals are biaxial positive, with indices of refraction parallel to *a* (α) of 1.694(2), to *b* (γ) of 1.740(2) and to *c* (β) of 1.698(2).

Twinning is frequent on (110), producing penetration forms, crossed at an angle of 54°. Merohedral twinning on (001) is possible but not detectible morphologically or optically. Some subtle evidence for it was found in the structure analysis.

The crystals used for the structure analysis were obtained from the preparation described in 1973.[1] The structure of compound **1** was first solved in 1975, yielding a result entirely similar to that given here for the arsenic compound **2**, based on a data set limited by large thermal and disorder effects prevailing at room temperature. These structures are identical, within the degree of resolution, to that obtained by the considerably improved low-temperature analysis described below, which still suffered from disorder in the intermolecular material. No degradation of structural or optical properties have been observed over the intervening time, and the crystals are assumed to be indefinitely stable.

For compound **1** a prismatic crystal was mounted with the *b* axis parallel to the φ axis; the scan peaks at −100 °C were about 0.3° at half height and well shaped. The range of X-ray scattering was nearly twice ($2\theta > 60°$) that for either compound at room temperature, thus leading to substantial improvement in the estimated errors.

Structure analysis. The crystals of both compounds **1** and **2** were weakly diffracting, and no reflections were detectable at room temperature beyond $2\theta = 45°$. Intensity measurements made with **1** at about −100 °C (crystal cooled by means of a cold stream of N_2 gas) were considerably stronger, yielding a data set more than three times as large as that at room temperature; this set was used in the final structure analysis (Table 1). Even so, owing to the presence of severe disorder, resolution was relatively poor.

The Patterson map immediately showed the presence of an α-Keggin molecule located on the *a*-glide plane at $y = \frac{1}{4}$. This configuration implies a link between adjacent molecules along the *a* axis, forming a chain. The W atoms from two adjacent molecules are involved with this link through the sharing of an oxygen atom. One of the W atoms showed strongly reduced electron density, indicating an unequal substitution by Co on each side of the link. Except in the region of the W–O–Co link, the molecular dimensions and atom densities found were normal for a dodecatungstophosphate α-Keggin molecule.

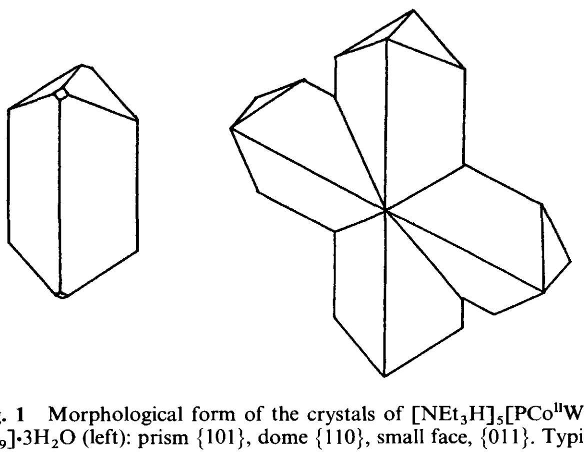

Fig. 1 Morphological form of the crystals of $[NEt_3H]_5[PCo^{II}W_{11}O_{39}]\cdot 3H_2O$ (left): prism {101}, dome {110}, small face, {011}. Typical twin habit (right): twin plane (110)

This information was obtained from a room-temperature data set measured on a modified Picker automatic diffractometer using Zr-filtered Mo-Kα radiation (λ = 0.7107 Å). The best refinement of the structure with this data set (based upon 1017 observed reflections) reached a weighted reliability factor of $R' = 0.054$, but O atom positions were highly irregular and their positional estimated errors were about 0.3 Å. Eventually, a new data set was measured at low temperature with a Siemens P4/RA automatic diffractometer. The final refinement with these data, while arriving at a higher reliability factor (Table 1), yielded molecular O atom errors of ±0.04 Å. Carbon atoms in the triethylammonium groups still could not be resolved, probably because of positional disorder.

Experimental procedure: no H atoms were refined, corrections were made for Lorentz and polarization factors and for absorption corrections using the GAUSSIAN method.[8] The computer system XTAL 2.4[9] was used for all calculations, weights were determined according to counting statistics ($1/\sigma$), with refinement on *F*.

After much work was spent on attempts to resolve the remaining details of the crystal structure, the following strategy was finally adopted, using the low-temperature data set. (1) An 'ideal' $PW_{12}O_{40}$ molecule[10] was located with its centre (P atom) at *x*, *y*, *z* = 0.110, 0.250, 0.250 (number of variable parameters $p = 0$, weighted reliability factor $R' = 0.35$). (2) The ideal model was given rigid-molecule refinement ($p = 10$, $R' = 0.178$). (3) One O atom was removed (at the link), Co/W disorder at the link was set at 0.33/0.67, and rigid refinement was continued ($p = 10$, $R' = 0.158$). (4) Eleven atoms and (W, Co) were then allowed freely to refine isotropically (O fixed, $p = 54$, $R = 0.149$). (5) The tungsten atoms were further refined alone in anisotropic mode ($p = 114$, $R' = 0.109$). The W–O bond lengths did not vary more than 0.01 Å from the ideal values at this stage. (6) Ghosts of W atoms that appeared on the *F* map were added at 0.041 weight, shifted ±0.15 Å along the *z* axis from the tungsten positions (no refinement, $R' = 0.092$; ghosts disappeared from map). (7) Keggin O atoms were refined isotropically with anisotropic W ($p = 264$, $R' = 0.080$). (8) Five N atoms were located in the electron-density and difference maps, and refined with the molecule ($p = 284$, $R' = 0.077$).

According to Hamilton's test[11] the improvement is significant at each stage. At the end of step (7) the estimated standard

Table 1 Crystallography and diffractometry[a] for $[NEt_3H]_5[XCo^{II}W_{11}O_{39}]\cdot 3H_2O$

	X = P **1**	As **2**
M	3301	3345
a/Å	21.715(10)[b]	21.656(5)[c]
b/Å	14.753(4)	14.773(3)
c/Å	20.782(6)	20.865(10)
U/Å^3	6658(4)	6682(4)
D_m/g cm^{-3} (25 °C)	3.23(1)	
D_c/g cm^{-3}	3.293	3.328
Crystal dimensions/mm	0.3 × 0.2 × 0.2	0.25 × 0.2 × 0.15
μ/cm^{-1}	191	201
F(000)	5972	6044
Total reflections	7633	7701
Independent reflections	5919	6487
Observed reflections [$X > 3\sigma(X)$]	3886 ($X = F$)	2749 ($X = I$)
No. parameters	284	275
R	0.092	0.076
R'	0.077	0.082
Goodness of fit	2.70	2.08

[a] Details in common: orthorhombic, space group $Pna2_1$, $Z = 4$; Mo-Kα radiation; $2\theta_{max} = 50°$. [b] At 25 °C. Values at −100 °C: *a* 21.670(11), *b* 14.805(4), *c* 20.393(5) Å, *U* 6543(4) Å^3. [c] At 20 °C.

Table 2 Tungsten–oxygen bond lengths in the polytungstate **1** (values for **2** are given in parentheses). Typical e.s.d. 0.06 Å

W(1)–O(1)	1.62 (1.82)	W(5)–O(5)	1.70 (1.74)	W(9)–O(9)	1.73 (1.71)
W(1)–O(27)	1.72 (1.73)	W(5)–O(32)	1.84 (1.74)	W(9)–O(33)	1.82 (1.85)
W(1)–O(15)	1.87 (1.99)	W(5)–O(25)	1.91 (1.65)	W(9)–O(29)	1.87 (1.95)
W(1)–(26)	1.95 (1.99)	W(5)–O(19)	1.98 (1.89)	W(9)–O(18)	1.89 (1.92)
W(1)–O(13)	2.02 (1.89)	W(5)–O(16)	2.03 (1.91)	W(9)–O(24)	1.95 (2.20)
W(1)–O(37)	2.63 (2.30)	W(5)–O(38)	2.35 (2.34)	W(9)–O(39)	2.46 (2.46)
W(2)–O(2)	1.82 (1.70)	W(6)–O(7)	2.00 (1.97)	W(10)–O(10)	1.70 (1.59)
W(2)–O(13)	1.87 (2.08)	W(6)–O(17)	1.89 (1.99)	W(10)–O(19)	1.84 (1.94)
W(2)–O(14)	1.95 (1.79)	W(6)–O(31)	2.03 (1.93)	W(10)–O(34)	1.89 (1.84)
W(2)–O(28)	1.95 (2.00)	W(6)–O(21)	2.07 (1.94)	W(10)–O(20)	1.90 (1.84)
W(2)–O(25)	2.01 (2.29)	W(6)–O(27)	2.08 (2.03)	W(10)–O(35)	2.04 (2.07)
W(2)–O(38)	2.37 (2.21)	W(6)–O(37)	2.48 (2.27)	W(10)–O(40)	2.47 (2.50)
W(3)–O(3)	1.69 (1.62)	W(7)–O(7)	1.84 (1.81)	W(11)–O(11)	1.77 (1.68)
W(3)–O(14)	1.82 (1.97)	W(7)–O(32)	1.87 (2.02)	W(11)–O(21)	1.71 (1.82)
W(3)–O(15)	1.89 (1.84)	W(7)–O(18)	1.90 (1.97)	W(11)–O(35)	1.93 (1.92)
W(3)–O(29)	1.97 (1.84)	W(7)–O(22)	1.92 (2.00)	W(11)–O(36)	1.95 (1.94)
W(3)–O(30)	1.98 (1.95)	W(7)–O(28)	2.06 (2.01)	W(11)–O(23)	2.14 (2.00)
W(3)–O(39)	2.60 (2.32)	W(7)–O(38)	2.41 (2.11)	W(11)–O(40)	2.46 (2.32)
W(4)–O(4)	1.65 (1.55)	W(8)–O(8)	1.99 (1.86)	W(12)–O(12)	1.80 (1.75)
W(4)–O(31)	1.81 (1.86)	W(8)–O(23)	1.84 (1.90)	W(12)–O(34)	1.89 (2.05)
W(4)–O(20)	1.92 (1.94)	W(8)–O(17)	1.89 (2.07)	W(12)–O(24)	1.93 (1.71)
W(4)–O(16)	1.91 (1.97)	W(8)–O(30)	1.95 (1.89)	W(12)–O(22)	1.94 (1.92)
W(4)–O(26)	2.01 (1.90)	W(8)–O(33)	2.16 (1.81)	W(12)–O(36)	2.14 (1.96)
W(4)–O(37)	2.35 (2.33)	W(8)–O(39)	2.47 (2.26)	W(12)–O(40)	2.33 (2.26)

deviation (e.s.d.) for O atom positions was *ca.* 0.07 Å, which is about one-fourth that obtained by free-atom refinement based upon room-temperature data. The intermolecular atoms appeared as five peaks in the electron-density map, which may be tentatively assigned to N atoms, as they are surrounded by many, small, highly distorted peaks. The difference electron-density map showed many noise maxima and minima in the range ± 6 e Å^{-3}, thus preventing the unambiguous identification of water molecules or triethyl groups in the intermolecular region.

The polarity along the *z* axis was pinned by holding *z* parameters for six W atoms constant for one cycle, and for the other six for the next cycle. The data were weighted for least-squares analysis according to counting statistics. No evidence for extinction was detected.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/73.

Results and Discussion

Features of the crystal structure

The best W–O bond lengths as obtained from stage (8) of the refinement based upon the low-temperature data are given in Table 2. Various averages of these are listed in Table 3 compared with the 'ideal'[10] values. [The variations within the various types of bonds (A–D) suggest that the actual e.s.d.s for W–O bonds are somewhat larger than the standard errors given by the least-squares analysis.] No unusual features appear in the molecule except in the region of the W–O–Co link. The Co atom was found by least-squares analysis to lie 39% on one side of the link and 61% on the other. [This disorder limits the interpretation of the bond lengths in this link; the lengths found were 2.00(5) Å on the 61% side, and 1.84(5) Å on the 39% side.]

It is worth noting that while the crystals are transparent and nearly colourless in two polarized directions, they are deep wine-red in the third direction. The last direction (prism, *b* axis) is normal to the chain direction, instead of parallel as one might intuitively expect.

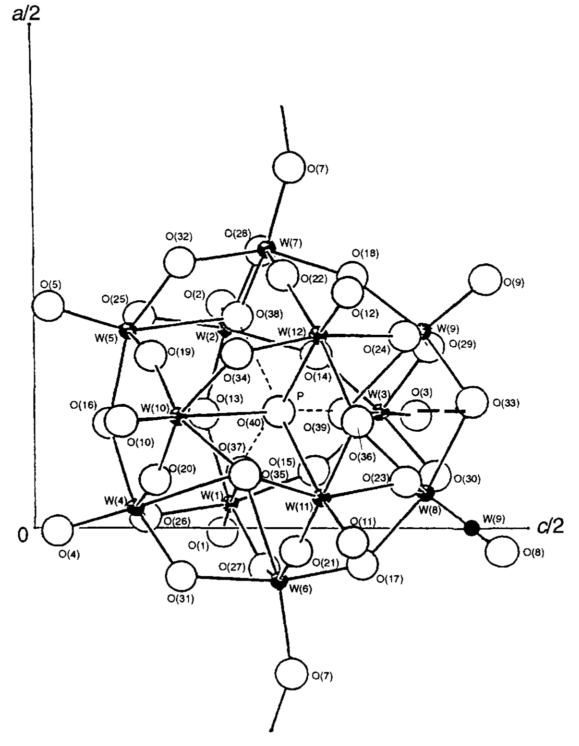

Fig. 2 View of the structure of one Keggin chain unit of compound **1** along the *b* axis, showing the atom numbering used in Table 2

At the centre of the Keggin molecule the average P–O bond length is 1.52 Å (individual standard errors 0.06 Å, range 1.37–1.67 Å); the average As–O length is 1.65 Å (range 1.50–1.83 Å). In $H_3PW_{12}O_{40}\cdot 5H_2O$ the P–O distance is 1.531(1) Å;[10] a typical average As–O distance is found in $Ca_2Pb_3(AsO_4)_3Cl$ (hedyphane, apatite structure) to be 1.69 (range 1.66–1.73 Å).[12]

Details of the W–O–Co link are obscured by the disorder with the Co–O–W orientation, but it is clearly unsymmetrical: W(6)–O(7) (61% Co) 2.00(5), W(7)–O(7) (39% Co) 1.84(5) Å, for **1**. The angle at O(7) is 156(1)° for **1**, 162(2)° for **2**. In the chain manganese complex[7] this link is also disordered (the oxygen link appears to lie on a two-fold axis in *I*2/*m*). Those authors[7] were unable to prepare the cobalt(II) complex by electrolysis of the aqueous polytungstate–thiofulvalene solution.

The general arrangement of the Keggin chains is illustrated in

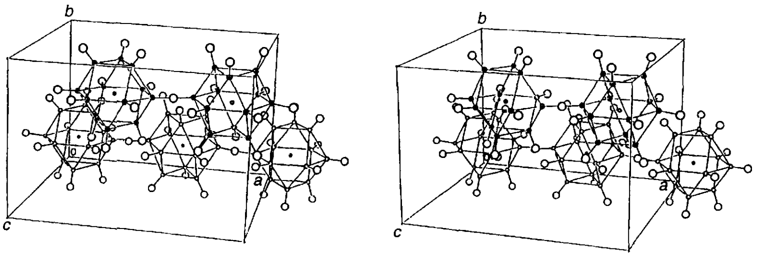

Fig. 3 Stereoscopic view of the unit cell containing two Keggin chains. Only the terminal oxygen atoms are shown, external to the W_{12} polyhedron. The orientation is the same as in Fig. 1

Table 3 Average and range of tungsten–oxygen bond lengths (Å) for four types of oxygen links in the Keggin molecule in compounds **1** and **2**

Type A [terminal, excluding W(6), W(7); n = 10]
1 1.73(7), 1.62–1.84
2 1.70(9), 1.55–1.86
Ref. 10. 1.7041(11)

Type B (2 W bonds, triplet link; n = 24)
1 1.93(11), 1.71–2.16
2 1.89(19), 1.73–2.29
Ref. 10. 1.9094(7)

Type C (2 W bonds, cross-link; n = 24)
1 1.92(8), 1.71–2.14
2 1.94(14), 1.71–2.20
Ref. 10. 1.9029(6)

Type D (4 W, P bonds; n = 12)
1 2.45(10), 2.32–2.47
2 2.33(9), 2.30–2.50
Ref. 10. 2.4993(10)

b-axis projection in Fig. 2 to show the atom numbering, and in oblique stereoview in Fig. 3 The five N atoms (not shown) are associated with the surface of the Keggin groups, some [N(1), N(2), N(4)] apparently forming hydrogen bonds with external O atoms. (Certain of these may actually be water molecules.) The appearance of ghosts with the W atoms at constant displacement along the polar z axis suggests the presence of disorder which may be related to lamellar twinning (merohedral) on the (001) plane with a small shift in the z direction. The cross-twins may arise by shifting the chain links from 180° in the crystal to another terminal O atom in the twin; this may account for the contact twins which have (110) faces in common, and with prism axes (b) subtending an angle of 126° (Fig. 1).

Conclusion

The refinement of these crystal structures has been hampered by three types of disorder: (1) Co–W disorder at the link, which degrades the details of this region; (2) disorder which appears as a ghost of the structure displaced 0.15 Å along the polar z axis (doubled by the a-glide plane), and which has only been modelled for the W atoms (this disorder may be the result of merohedral twinning on 001); and (3) the probability of considerable orientational disorder of the intermolecular triethylammonium cations. The existence revealed here of the chain-linked Keggin molecules, which presumably are associated with and promoted by monosubstitution of one terminal WO group by a hydrated transition-metal group $M^{II}(H_2O)$ (Co or Mn), adds another facet to the extreme versatility of structure in polyoxometalate molecular chemistry.[13]

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