Tableau 3. *Distances* (Å) *dans le polyèdre de coordination du calcium*

Ca–O(1)	2,406 (5)	Ca–O(6^{iii})	2,482 (3)
Ca–O(4)	2,435 (5)	Ca–O(8)	2,484 (6)
Ca–O(3^{viii})	2,478 (3)	Ca–O(2)	2,511 (3)
Ca–O(5)	2,479 (3)	Ca–O(7^{viii})	2,533 (3)

Ca	O(2)	O(3^{viii})	O(4)	O(5)	O(6^{iii})	O(7^{viii})	O(8)
O(1)	3,242 (5)		3,121 (7)	3,007 (6)		2,867 (5)	
O(2)		2,858 (5)	2,855 (4)			3,077 (5)	
O(3^{viii})					2,869 (3)	3,095 (6)	3,279 (6)
O(4)				3,134 (8)	3,030 (7)		
O(5)					3,079 (7)		2,892 (8)
O(6^{iii})							3,292 (6)
O(7^{viii})							2,976 (7)

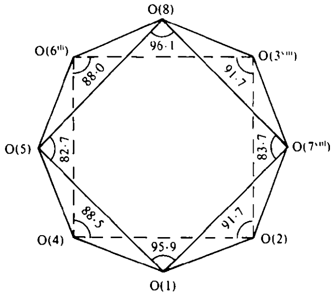

Fig. 3. Polyèdre de coordination du calcium. Les valeurs des angles sont affectées des écarts-type moyens 0,2°.

faces carrées de l'antiprisme, ont une longueur moyenne de 2,92 Å. Elles sont systématiquement et significativement plus courtes que les autres dispersées autour de la valeur 3,16 Å.

La cohésion de l'édifice cristallin est réalisée grâce à un ensemble de liaison hydrogène O—H···Cl et O—H···O (Fig. 1). Les premières interviennent entre les chaînes infinies d'octaèdres $CdCl_6$ et les polyèdres de coordination du calcium ou la molécule d'eau d'oxygène O(9) non coordiné au calcium. Les secondes se manifestent entre les groupements $Ca(H_2O)_8$, soit directement, soit par l'intermédiaire de la molécule d'eau O(9). L'une des liaisons O—H···O proposée (Fig. 1) intervient entre O(7) et O(7^{ii}); elle pose la question de la distance entre les deux atomes d'hydrogène équivalents qui doit être au moins de 2 Å (Baur, 1972). La réalisation de cette dernière condition est compatible avec l'existence de la liaison faible dans laquelle la distance H···O est d'environ 2,4 Å.

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Structure of Potassium Diaquatricuprooctadecatungstodiarsenate(III)(12−) Undecahydrate

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Abstract

$K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2].11H_2O$ is orthorhombic, space group *Pnma*, with $a = 30{\cdot}378\,(5)$, $b = 14{\cdot}985\,(3)$, $c = 19{\cdot}198\,(3)$ Å, $Z = 4$. The structure was determined from 4026 counter reflexions and refined to $R = 0{\cdot}049$. The complex consists of two α-*B* AsW_9O_{33} subunits joined by three Cu atoms, the coordination shells of which are different. Results are discussed with regard to the prominent part played by the As hetero-atom.

Introduction

The formation of polynuclear complexes between W and As or Sb in oxidation state III has been reported (Michelon, Hervé & Leyrie, 1980; Leyrie, Martin-Frère

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Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* W, As *and* Cu; $\times 10^4$ *for other atoms*) *and isotropic thermal parameters*

The e.s.d.'s in parentheses refer to last decimal places.

$$B_{\mathrm{eq}} = \tfrac{4}{3} \textstyle\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}/B (Å^2)
W(1)	61653 (9)	12838 (25)	26231 (14)	1·07 (13)
W(2)	61039 (10)	1574 (21)	10957 (16)	1·09 (15)
W(3)	52015 (9)	12466 (22)	17183 (14)	0·95 (12)
W(4)	60264 (10)	13822 (23)	−5509 (15)	1·11 (14)
W(5)	51169 (14)	25000	395 (23)	1·07 (21)
W(6)	81694 (9)	12759 (24)	23701 (14)	1·15 (12)
W(7)	81177 (10)	1561 (21)	8455 (17)	1·20 (15)
W(8)	90550 (9)	12647 (23)	12784 (14)	1·00 (13)
W(9)	80466 (9)	13765 (23)	−8086 (15)	1·08 (13)
W(10)	89883 (14)	25000	−3977 (22)	1·13 (21)
As(1)	62369 (33)	25000	10332 (54)	0·78 (49)
As(2)	79862 (33)	25000	8136 (63)	1·06 (52)
Cu(1)	70761 (29)	9042 (56)	2043 (43)	1·13 (39)
Cu(2)	71720 (40)	25000	23280 (63)	1·24 (58)
O_a(1,2,3)	5939 (14)	1592 (30)	1475 (22)	0·8 (9)
O_a(4,4,5)	5907 (23)	2500	286 (35)	1·7 (15)
O_a(6,7,8)	8304 (15)	1644 (33)	1197 (25)	1·7 (10)
O_a(9,9,10)	8309 (22)	2500	−21 (36)	1·2 (14)
O_b(1,1)	6011 (21)	2500	2799 (31)	0·5 (12)
O_b(3,3)	5126 (22)	2500	1955 (34)	0·9 (14)
O_b(2,4)	5879 (13)	582 (19)	186 (20)	0·2 (8)
O_b(3,5)	5089 (13)	1614 (29)	752 (22)	0·6 (9)
O_b(6,6)	8361 (20)	2500	2573 (35)	1·0 (13)
O_b(8,8)	9115 (20)	2500	1488 (31)	0·4 (12)
O_b(7,9)	8245 (16)	494 (34)	−67 (26)	1·8 (10)
O_b(8,10)	9093 (14)	1605 (31)	307 (21)	0·9 (9)
O_c(1,2)	6201 (15)	221 (33)	2127 (22)	1·0 (9)
O_c(1,3)	5502 (11)	1137 (26)	2568 (20)	0·2 (8)
O_c(2,3)	5472 (15)	194 (34)	1312 (25)	1·5 (10)
O_c(4,4)	6041 (25)	2500	−1066 (39)	2·4 (16)
O_c(4,5)	5381 (13)	1626 (27)	−573 (19)	0·2 (8)
O_c(6,7)	8100 (16)	156 (35)	1859 (25)	1·9 (10)
O_c(6,8)	8817 (12)	1125 (30)	2180 (19)	0·2 (8)
O_c(7,8)	8779 (14)	200 (31)	1008 (23)	1·0 (9)
O_c(9,9)	7987 (25)	2500	−1282 (42)	2·6 (17)
O_c(9,10)	8679 (12)	1575 (25)	−926 (21)	0·2 (8)
O_d(1)	6239 (15)	885 (31)	3472 (22)	0·9 (9)
O_d(2)	6098 (14)	−970 (30)	953 (22)	0·9 (9)
O_d(3)	4693 (16)	879 (32)	1964 (23)	1·3 (10)
O_d(4)	6017 (20)	633 (42)	−1260 (30)	3·6 (13)
O_d(5)	4600 (28)	2500	−205 (42)	3·1 (18)
O_d(6)	8158 (15)	853 (33)	3197 (23)	1·3 (10)
O_d(7)	8102 (22)	−903 (47)	714 (36)	5·1 (16)
O_d(8)	9570 (17)	867 (37)	1395 (27)	2·6 (12)
O_d(9)	7952 (20)	622 (40)	−1492 (30)	3·4 (13)
O_d(10)	9497 (22)	2500	−737 (38)	1·4 (14)
O_d[1,Cu(2)]	6718 (17)	1612 (36)	2398 (28)	2·7 (12)
O_d[6,Cu(2)]	7624 (13)	1635 (28)	2201 (20)	0·2 (8)
O_d[2,Cu(1)]	6659 (15)	532 (33)	916 (25)	1·7 (10)
O_d[4,Cu(1)]	6609 (15)	1401 (34)	−304 (22)	1·4 (10)
O_d[7,Cu(1)]	7525 (13)	489 (28)	783 (21)	0·3 (8)
O_d[9,Cu(1)]	7528 (13)	1458 (31)	−422 (22)	0·7 (9)
K(1)	5000	5000	5000	4·6 (8)
K(2)	7985 (8)	7500	3668 (14)	2·1 (5)
K(3)	7158 (7)	5062 (13)	2103 (10)	2·8 (4)
K(4)	5842 (9)	7500	1600 (15)	2·8 (6)
K(5)	9277 (7)	5559 (14)	2425 (11)	3·4 (4)
K(6)	5022 (11)	7500	2996 (17)	4·2 (8)
K(7)	9159 (9)	2500	3149 (15)	2·7 (6)
K(8)	5151 (11)	2500	3444 (17)	4·3 (8)
K(9)	5847 (9)	4911 (21)	4581 (15)	6·6 (7)
O_w(1)	17 (21)	6397 (52)	3163 (35)	5·1 (16)
O_w(2)	8956 (21)	3668 (53)	4262 (34)	5·2 (16)
O_w(3)	7013 (15)	3892 (32)	4174 (25)	1·8 (10)
O_w(4)	5167 (33)	5621 (71)	3378 (49)	9·7 (28)
O_w(5)	5858 (27)	2500	−2426 (46)	3·4 (19)
O_w(6)	5936 (22)	6425 (50)	2696 (33)	4·9 (15)
O_w(7)	7974 (23)	4532 (51)	4577 (36)	5·5 (17)

& Hervé, 1974; Tourné, Revel, Tourné & Vendrell, 1973; Leyrie & Hervé, 1978) and crystal structures of compounds including complete or incomplete α-*B* AsW_9O_{33} or SbW_9O_{33} as subunits have been described: $[NaSb_9W_{21}O_{86}]^{18-}$ (Fischer, Ricard & Weiss, 1976), $[NH_4As_4W_{40}O_{140}(CoH_2O)_2]^{23-}$ (Robert, Leyrie, Hervé & Jeannin, 1980), $[H_2AsW_{18}O_{60}]^{16-}$ (Jeannin & Martin-Frère, 1979) and $[As_2W_{21}O_{69}H_2O]^6$ (Jeannin & Martin-Frère, 1981). These studies showed the importance of the As or Sb lone pair of electrons in the polyoxotungstate formation path. Another example is the reaction between transition-metal ions of the first row and enneatungstoarsenate or -antimonate leading to complexes including three metals for two ennea units while enneatungstosilicates lead to compounds such as $[SiW_9O_{37}(FeOH_2)_3]^{7-}$ (Leyrie, 1980).

X-ray investigations are necessary to understand the relationships between the lone pair of electrons and the types of structure allowed. Thus the crystal structure of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2].11H_2O$ has been solved.

Experimental

Preparation of the compound

59·5 g of $Na_2WO_4.2H_2O$ and 2·6 g of $NaAsO_2$ were dissolved in 60 ml of boiling water and acidified by 60 ml of 6 *M* HCl. Then, 30 ml of 1 *M* $Cu(NO_3)_2$ were added; the pH was 7·5. The sodium salt of the complex crystallized on cooling. This salt was dissolved and precipitated by KCl five times to obtain a sodium-free salt. The potassium salt crystallized from aqueous solution at pH 7·5 at room temperature.

Crystal structure determination and refinement

The cell dimensions and space group were determined from oscillation and Weissenberg photographs. The systematic absences (0*kl* with $k + l = 2n + 1$ and *hk*0 with $h = 2n + 1$) indicate the centrosymmetric space group *Pnma* or the noncentrosymmetric $Pn2_1a$. Further centrosymmetry tests unambiguously assigned *Pnma*.

For data collection a green parallelepiped (0·0035 × 0·0069 × 0·046 mm) was mounted on an automatic Enraf–Nonius CAD-3 diffractometer. The cell dimensions were refined by least squares from the setting of 14 high-angle reflexions. The density calculated for half a polyanion per asymmetric unit (d_c = 4·097 Mg m^{-3}) agreed with that measured (d_m = 4·10 Mg m^{-3}). 4026 independent reflexions of one octant were collected at room temperature in the θ–2θ scan mode up to $2\theta_{\max}$ = 40° with Zr-filtered Mo $K\alpha$ radiation. The scan width takes into account the $K\alpha_1$–$K\alpha_2$ dispersion. Two standard reflexions were monitored every 50 reflexions and remained constant. A standard deviation $\sigma(I)$ calculated according to counting statistics for each reflexion allowed us to consider 1724 as observed with $I \geq 3\sigma(I)$. The other reflexions were omitted from further calculations. The intensities were corrected for Lorentz and polarization factors. Absorption corrections were necessary (μ = 26·24 mm^{-1}) (Wehe, Busing & Levy, 1962).

The structure was solved from a Patterson map which gave the positions of the W atoms. Successive Fourier syntheses and full-matrix least-squares refinement allowed us to locate all the other atoms. In the last cycles the W, As and Cu atoms were refined anisotropically and a weighting scheme of the form $w = (84{\cdot}34 - 0{\cdot}5204F_o)^{-1}$ was introduced. The secondary-extinction parameter g was refined to 0·406 × 10^{-8}. The final $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0·049 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ = 0·061. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Real and imaginary parts of the anomalous scattering were introduced for W, As and Cu. The final atomic coordinates are listed in Table 1.*

Results and discussion

Description of the structure

O atoms are referred to as O_a,O_b,O_c,O_d (Robert, Tézé, Hervé & Jeannin, 1980) and the formulae of the compounds shortened to AsW_9, AsW_{18} and As_2W_{21}. The atomic numbering is shown in Fig. 1. The overall structure can be described as two identical α-B AsW_9O_{33} subunits joined by three Cu atoms. This assemblage is similar to $[As_2W_{21}O_{69}H_2O]^{6-}$ for which Cu is replaced by W and the subunits are near to those previously reported for AsW_{18}, As_2W_{21} and As_4W_{40}. The polyoxotungstate shows a crystallographic mirror plane [including As(1), As(2) and Cu(2)] which divides the two AsW_9 subunits; thus, the asymmetric unit is made up of two independent half AsW_9 subunits.

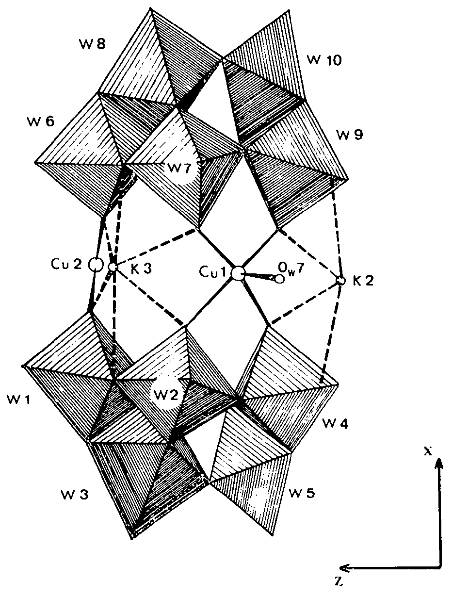

Fig. 1. The $[As_2W_{18}O_{66}Cu_3(H_2O)_2]^{12-}$ anion viewed along **b**.

The α-B AsW_9O_{33} subunit

The subunit consists of a Keggin-type assemblage of three W_3O_{13} groups around the As atom. As has a pyramidal environment of O atoms and the lone pair of electrons is directed towards the opening of the subunit. Such an assemblage around the hetero-atom has been referred to as α-B type (Hervé & Tézé, 1977). There are no particular variations between the two sets of values related to the equivalent bond distances (Table 2) for the two independent half units of the asymmetric unit, except for As(1), As(2), for W(5)—O_a(4,4,5) and for W(10)—O_a(9,9,10). The mean values for W—O_a (2·35), W—O_b (1·94), W—O_c (1·95) and W—O_d (1·70 Å) are within the usual range for such compounds. The W—O_d(Cu) mean value (1·81 Å) is midway between W—O_b and W—O_d distances. Likewise, each W atom has an octahedral environment of O atoms with a tetragonal distortion along the $O_a\cdots O_d$ direction due to the multiple-bond character of W—O_d and lies on the side of O_d. The O_a—W—O_d mean angle is 170°. Bond angles around As atoms (Table 3) are similar but the equivalent bond distances As—O_a are reversed from one subunit to the other.

Cu *atoms bridging the* AsW_9O_{33} *subunits*

Cu atoms bridge the two AsW_9 subunits by sharing with each other two O atoms of two different W_3O_{13} groups. Cu(2) is four-coordinated by both subunits and is in a square-planar environment: Cu(2) lies in the plane defined by the four O atoms: O_d[1,Cu(2)], O_d[6,Cu(2)] and those related by symmetry. The two

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36044 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å)

W(1)–O_a(1,2,3)	2·35 (4)	W(6)–O_a(6,7,8)	2·35 (5)
W(1)–O_b(1,1)	1·91 (2)	W(6)–O_b(6,6)	1·96 (2)
W(1)–O_c(1,2)	1·86 (5)	W(6)–O_c(6,7)	1·96 (5)
W(1)–O_c(1,3)	2·03 (4)	W(6)–O_c(6,8)	2·01 (4)
W(1)–O_d(1)	1·75 (4)	W(6)–O_d(6)	1·71 (4)
W(1)–O_d|1,Cu(2)|	1·80 (5)	W(6)–O_d|6,Cu(2)|	1·77 (4)
W(2)–O_a(1,2,3)	2·32 (4)	W(7)–O_a(6,7,8)	2·40 (5)
W(2)–O_b(2,4)	1·98 (4)	W(7)–O_b(7,9)	1·86 (5)
W(2)–O_c(1,2)	2·00 (4)	W(7)–O_c(6,7)	1·95 (5)
W(2) O_c(2,3)	1·95 (5)	W(7)–O_c(7,8)	2·03 (4)
W(2)–O_d(2)	1·71 (5)	W(7)–O_d(7)	1·61 (7)
W(2)–O_d|2,Cu(1)|	1·81 (5)	W(7)–O_d|7,Cu(1)|	1·87 (4)
W(3)–O_a(1,2,3)	2·35 (4)	W(8)–O_a(6,7,8)	2·36 (5)
W(3)–O_b(3,3)	1·95 (2)	W(8)–O_b(8,8)	1·90 (1)
W(3)–O_b(3,5)	1·97 (4)	W(8)–O_b(8,10)	1·94 (4)
W(3)–O_c(1,3)	1·88 (4)	W(8)–O_c(6,8)	1·89 (4)
W(3)–O_c(2,3)	1·94 (5)	W(8)–O_c(7,8)	1·88 (5)
W(3)–O_d(3)	1·71 (5)	W(8)–O_d(8)	1·69 (5)
W(4)–O_a(4,4,5)	2·35 (5)	W(9)–O_a(9,9,10)	2·40 (5)
W(4)–O_b(2,4)	1·91 (4)	W(9)–O_b(7,9)	2·03 (5)
W(4)–O_c(4,4)	1·95 (4)	W(9)–O_c(9,9)	1·92 (4)
W(4)–O_c(4,5)	1·99 (4)	W(9)–O_c(9,10)	1·96 (4)
W(4)–O_d(4)	1·76 (6)	W(9)–O_d(9)	1·76 (6)
W(4)–O_d|4,Cu(1)|	1·83 (5)	W(9)–O_d|9,Cu(1)|	1·75 (4)
W(5)–O_a(4,4,5)	2·45 (7)	W(10)–O_a(9,9,10)	2·19 (7)
W(5)–O_b(3,5)	1·91 (4)	W(10)–O_b(8,10)	1·93 (4)
W(5)–O_c(4,5)	1·93 (4)	W(10)–O_c(9,10)	1·96 (4)
W(5)–O_d(5)	1·64 (8)	W(10)–O_d(10)	1·68 (7)
As(1)–O_a(1,2,3)	1·84 (4)	As(2)–O_a(6,7,8)	1·77 (5)
As(1)–O_a(4,4,5)	1·75 (7)	As(2)–O_a(9,9,10)	1·88 (7)
Cu(1)–O_d|2,Cu(1)|	1·95 (5)	Cu(1)–O_d|7,Cu(1)|	1·87 (4)
Cu(1)–O_d|4,Cu(1)|	1·88 (5)	Cu(1)–O_d|9,Cu(1)|	2·00 (4)
Cu(1)–O_w(7)	2·39 (8)		
Cu(2)–O_d|1,Cu(2)|	1·92 (5)	Cu(2)–O_d|6,Cu(2)|	1·90 (4)

Cu(1) atoms are in a distorted square-pyramidal environment. Cu(1) lies 0·12 Å out of the mean basal plane defined by O_d|2,Cu(1)|, O_d|4,Cu(1)|, O_d|7,Cu(1)| and O_d|9,Cu(1)| on the side of the water molecule O_w(7) which occupies the fifth coordination position at a distance of 2·39 Å from Cu(1) in a direction perpendicular to the basal plane. Moreover, a weak equatorial distortion is observed with two bond lengths relative to *trans* O atoms shorter than the two others by about 0·1 Å. Bond lengths and angles around the Cu atoms are listed in Tables 2 and 3.

Potassium coordination

Three K^+ ions must be distinguished: K(2), K(3) and that related by symmetry. They interact with one O_c and two O_d(Cu) atoms of each AsW_9 subunit (the mean value K–O is 2·89 Å); they lie at about 2 Å outside the plane defined by the O_d(Cu) atoms, so they fill the holes between Cu atoms. For K(3) a seventh coordination position is occupied by O_d(9) belonging to another polyoxotungstate. For the other K^+ ion, there are no particular characteristics; the coordination varies from six to eight and is ensured more by O atoms of the polyoxotungstates than by water molecules |except for K(6)|. K^+ ions interact with O atoms of two or three different polyoxotungstates |except for K(2) and K(6)|.

Discussion

The most surprising characteristics of the solved structure are that the AsW_9 subunits do not face each other exactly and that Cu atoms are not equivalent.

The homologous W atoms and the two As atoms of the two subunits are equidistant from the Cu plane, so there is no overall deformation perpendicular to this plane; but the projection of their location in this plane shows a one-sided shift of about 0·27 Å for As, 0·3 Å for homologous W sharing O atoms with Cu and of 0·5 Å for the others (Table 4). So, an AsW_9 subunit has undergone a glide, with respect to the other, in a direction parallel to the intersection of the Cu plane and the mirror plane. This glide means that the coordination sites of the Cu atoms became differentiated and it can be seen that O atoms linked to Cu(2) have undergone the same shift as the W atoms they coordinate, while O atoms linked to Cu(1) have undergone a smaller shift. These remarks suggest a scheme for the Cu complexation (Fig. 2). When Cu atoms are linked, if two AsW_9 units were drawn together to ensure suitable bond lengths for stable Cu oxo complexes (the usual mean value is 2 Å) with three equivalent Cu atoms and D_{3h} symmetry for the compound, the lone pairs of the As atoms would face each other and repulsion would occur. Consequently, the limited shift observed between the two subunits

Table 3. *Bond angles* (°) *around* As *and* Cu *atoms*

O_a(4,4,5)–As(1)–O_a(1,2,3)	96 (2)	O_w(7)–Cu(1)–O_d|2,Cu(1)|	94 (2)
O_a(1,2,3)–As(1)–O_a(1,2,3)′	95 (3)	O_w(7)–Cu(1)–O_d|4,Cu(1)|	92 (2)
O_a(9,9,10)–As(2)–O_a(6,7,8)	94 (2)	O_w(7)–Cu(1)–O_d|7,Cu(1)|	93 (2)
O_a(6,7,8)–As(2)–O_a(6,7,8)′	93 (3)	O_w(7)–Cu(1)–O_d|9,Cu(1)|	96 (2)
O_d|2,Cu(1)|–Cu(1)–O_d|4,Cu(1)|	89 (2)	O_d|1,Cu(2)|–Cu(2)–O_d|6,Cu(2)|	93 (2)
O_d|2,Cu(1)|–Cu(1)–O_d|7,Cu(1)|	88 (2)	O_d|1,Cu(2)|–Cu(2)–O_d|1,Cu(2)|′	88 (3)
O_d|2,Cu(1)|–Cu(1)–O_d|9,Cu(1)|	170 (2)	O_d|1,Cu(2)|–Cu(2)–O_d|6,Cu(2)|′	177 (2)
O_d|4,Cu(1)|–Cu(1)–O_d|7,Cu(1)|	174 (2)	O_d|6,Cu(2)|–Cu(2)–O_d|6,Cu(2)|′	86 (3)
O_d|4,Cu(1)|–Cu(1)–O_d|9,Cu(1)|	92 (2)		
O_d|7,Cu(1)|–Cu(1)–O_d|9,Cu(1)|	90 (2)		

Table 4. *Distances of some atoms to the copper plane and shift in this plane for homologous atoms*

	Distance (Å)	Shift (Å)		Distance (Å)	Shift (Å)
As(1)	2·66 (1)	0·27 (2)	W(5)	5·914 (4)	0·50 (1)
As(2)	2·68 (1)		W(10)	5·876 (4)	
W(1)	3·091 (3)	0·31 (1)	$\mathrm{O}_d\vert 1,\mathrm{Cu}(2)\vert$	1·39 (5)	0·30 (7)
W(6)	3·016 (3)		$\mathrm{O}_d\vert 6,\mathrm{Cu}(2)\vert$	1·39 (4)	
W(2)	3·068 (3)	0·34 (1)	$\mathrm{O}_d\vert 2,\mathrm{Cu}(1)\vert$	1·36 (5)	0·19 (6)
W(7)	3·068 (3)		$\mathrm{O}_d\vert 7,\mathrm{Cu}(1)\vert$	1·28 (4)	
W(4)	3·077 (3)	0·31 (1)	$\mathrm{O}_d\vert 4,\mathrm{Cu}(1)\vert$	1·35 (5)	0·17 (7)
W(9)	3·079 (3)		$\mathrm{O}_d\vert 9,\mathrm{Cu}(1)\vert$	1·46 (4)	
W(3)	5·887 (3)	0·51 (1)			
W(8)	5·849 (3)				

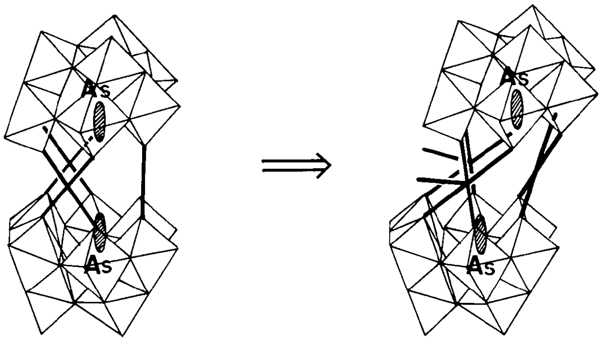

Fig. 2. Schematic representation of the subunit glide which accommodates both As lone-pair repulsion and Cu coordination. For clarity the shift has been enhanced.

must not only decrease sufficiently the repulsion between the lone pairs, but also preserve convenient Cu—O bond lengths to keep the complex stable. In that way, the coordinated O atoms of Cu(1) undergo a smaller shift than those of Cu(2): the glide direction makes an angle of 60° with the perpendicular to the basal plane of the Cu(1) square pyramid but it is perpendicular to the Cu(2) square plane; so, the glide moves away two *trans* O atoms and brings closer the two others for Cu(1) that cannot be restricted, while *trans* O atoms remain equidistant for Cu(2). This explains the presence of equatorial distortion around Cu(1) and its absence around Cu(2). It is surprising that the Cu coordination shells are different. This difference is not due to crystal packing because there is a large space available for a water molecule near Cu(2), but final difference syntheses showed no appreciable residual density. This is probably related to the equatorial distortion of Cu(1). These remarks imply that this situation must remain in aqueous solution. A different coordination type for metals in such compounds is also met for $[As_2W_{21}O_{69}H_2O]^{6-}$ (Jeannin & Martin-Frère, 1981) for which two W atoms are five-coordinated and one six-coordinated. But, for this latter complex no glide is observed due to statistical disorder in the crystal.

Conclusion

This study confirms the prominent part played by the nature of the hetero-atom in polyoxotungstate formation which was observed previously. In the present compound, the As lone pair prevents the *α-B* AsW_9O_{33} unit from adding three metals as for *α*- or *β-A* $[SiW_9O_{34}]^{9-}$ but assigns two units to be bridged with a shift through three Cu atoms that become differentiated.

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