Crystal Structures of Silver Dimolybdate, $Ag_2Mo_2O_7$, and Silver Ditungstate, $Ag_2W_2O_7$

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The crystal structures of $Ag_2Mo_2O_7$ (I) and $Ag_2W_2O_7$ (II) have been determined by single-crystal *X*-ray analysis. Both compounds crystallize in space group $P\bar{1}$, $Z = 2$, with for (I): $a = 6.095(3)$, $b = 7.501(3)$, $c = 7.681(3)$ Å, $\alpha = 110.4(1)$, $\beta = 93.3(1)$, $\gamma = 113.5(1)°$; and for (II): $a = 6.033(3)$, $b = 7.051(3)$, $c = 7.735(3)$ Å, $\alpha = 73.8(1)$, $\beta = 92.2(1)$, $\gamma = 104.7(1)°$. The structures were determined from diffractometer data by heavy-atom methods and refined to *R* 0.045 [(I), 1 208 observed reflections] and 0.047 [(II), 1 364 observed reflections]. The structures consist of infinite chains formed by blocks of four edge-shared octahedra joined by edge-sharing in (I), and by corner-sharing in (II), with the silver ions situated between the chains.

SEVERAL years ago Brown and Calvo[1] suggested that crystals with stoicheiometry $X_2Y_2O_7$ tended to belong to one of a small number of groups of related structures. A notable exception, however, was the dimolybdate $Na_2Mo_2O_7$. In this compound, unlike the corresponding dichromate which contained discrete $[Cr_2O_7]^{2-}$ anions, no $[Mo_2O_7]^{2-}$ anion existed. Instead the structure comprised infinite chains of linked MoO_4 tetrahedra and MoO_6 octahedra.[2,3] Recently there has been an increased interest in the univalent-metal dimolybdates and -tungstates, and structures so far reported appear to confirm the non-existence of the $[Mo_2O_7]^{2-}$ anion.

The chain structure in $Na_2Mo_2O_7$ ($Na_2W_2O_7$ is isostructural) (Figure 1a) may be compared (Figure 1b) with the somewhat different linkage of MoO_4 tetrahedra and MoO_6 octahedra in the chain structure recently reported for $K_2Mo_2O_7$.[4] The ammonium salt, $[NH_4]_2Mo_2O_7$, is isomorphous[5] with the potassium com-

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[1] I. D. Brown and C. Calvo, *J. Solid-State Chem.*, 1970, **1**, 173.

[2] I. Lindquist, *Acta Chem. Scand.*, 1950, **4**, 1066.

[3] M. Seleborg, *Acta Chem. Scand.*, 1967, **21**, 499.

[4] S. A. Magarill and R. F. Klevtsova, *Soviet Phys. Cryst.*, 1972, **16**, 645.

[5] I. Knöpnadel, H. Hartl, W.-D. Hunnius, and J. Fuchs, *Angew. Chem. Internat. Edn.*, 1974, **13**, 823.

pound, and while the structure of $Rb_2Mo_2O_7$ has yet to be determined it will almost certainly possess the same structure. Preliminary structural information for $Cs_2Mo_2O_7$ indicates that this compound could well possess a chain structure built of linked tetrahedra and octahedra.[6]

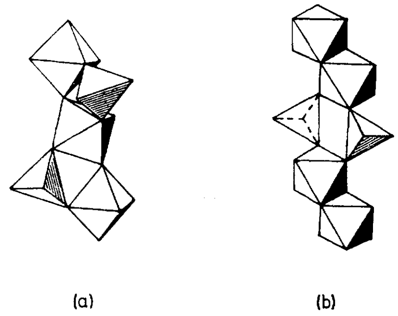

FIGURE 1 Idealized representations of the structures of (a) $Na_2Mo_2O_7$, and (b) of $K_2Mo_2O_7$ and $[NH_4]_2Mo_2O_7$

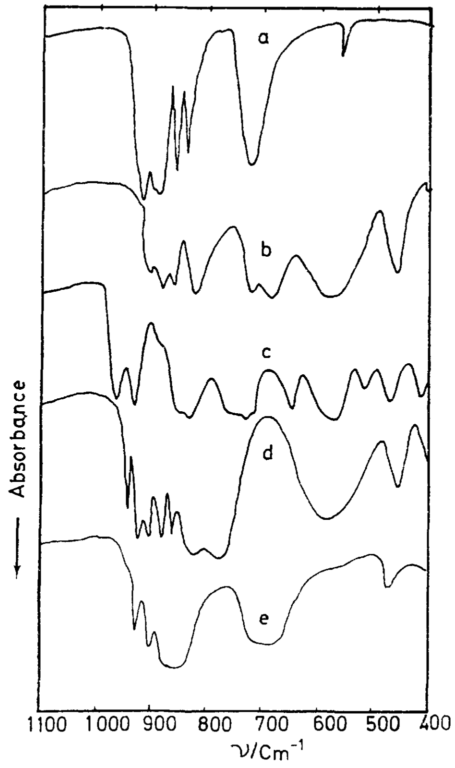

FIGURE 2 I.r. spectra of (a) $Ag_2Cr_2O_7$, (b) $Ag_2Mo_2O_7$, (c) $Ag_2W_2O_7$, (d) $Na_2Mo_2O_7$, and (e) $K_2Mo_2O_7$

Interestingly, $Li_2W_2O_7$ forms chains built entirely of WO_6 octahedra,[7,8] where the presence of the small, highly polarizing lithium ion apparently precludes the formation of WO_4 tetrahedra. A similar situation probably exists in $Li_2Mo_2O_7$, although the structure is still unknown.

From the i.r. spectra (Figure 2) it was apparent that the $Ag_2Mo_2O_7$ and $Ag_2W_2O_7$ structures were not identical, did not contain discrete $[Y_2O_7]^{2-}$ anions, and were not the same as the other two known dimolybdate chain structures. The near constancy of the *a* (prism) axial length (*ca.* 6 Å) which corresponds to a diagonal oxygen–oxygen distance of an edge-shared pair of MO_6 octahedra, and the M : O ratio of 2 : 7, suggested that both compounds would adopt chain structures built of edge-shared pairs of MO_6 octahedra in a manner probably not dissimilar to that found in $K_2Mo_4O_{13}$.[9]

We now report the crystal structures of the silver compounds, $Ag_2Mo_2O_7$ and $Ag_2W_2O_7$, which possess subtly different octahedral chain structures that bear a simple relationship to the $Li_2W_2O_7$ and other polymolybdate and -tungstate structures. A preliminary report has been published.[10]

EXPERIMENTAL

Silver dimolybdate was prepared by fusing silver molybdate and molybdenum trioxide (1 : 1 mole ratio) in a porcelain crucible, followed by slow cooling. The cooled melt was ground and refined at just below the melting point of this incongruently melting compound.

TABLE 1

Crystallographic data for silver dimolybdate (I) and silver ditungstate (II)

	(I)	(II)
Crystal habit	Prisms elongated on *a* axis	Prisms elongated on *a* axis
Colour	Pale yellow	Buff
M	519.6	695.4
Crystal system	Triclinic	Triclinic
a/Å	6.095(3)	6.033(3)
b/Å	7.501(3)	7.051(3)
c/Å	7.681(3)	7.735(3)
α/°	110.4(1)	73.8(1)
β/°	93.3(1)	92.2(1)
γ/°	113.5(1)	104.7(1)
U/Å³	293.72	305.53
Z	2	2
D_c/g cm⁻³	5.86	7.41
D_m/g cm⁻³	5.9(2)	—
Space group	$P\bar{1}$	$P\bar{1}$
μ(Mo-K_α)/cm⁻¹	104.3	449.0
Crystal dimensions/mm	0.25 × 0.05 × 0.05	0.06 × 0.03 × 0.03
F(000)	234	298
No. independent reflections	1 348	1 776
No. unobs. reflections $I/\sigma(I) \leqslant 3$	150	412
R Obs. reflections only	0.045	0.047
R' Obs. reflections only	0.071	0.062
R All reflections	0.049	0.061
R' All reflections	0.071	0.066

Silver ditungstate was prepared in an analogous fashion.

Unit-cell parameters were obtained using a Philips PW 1100 computer-controlled *X*-ray diffractometer by least-squares refinement of the centred positions of nine reflections. Crystal data for the two compounds are compared in Table 1.

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[6] B. M. Gatehouse and P. Leverett, to be published.

[7] S. A. Magarill, R. F. Klevtsova, and V. V. Bakakin, *Soviet Phys. Cryst.*, 1973, **18**, 166.

[8] K. Okada, H. Morikawa, F. Marumo, and S. Iwai, *Acta Cryst.*, 1975, **B31**, 1451.

[9] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1971, 2107.

[10] B. M. Gatehouse, *J. Less-Common Metals*, 1974, **36**, 53.

Intensity Measurements.—Intensity data were collected on a Philips diffractometer by use of graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å). Three standard reflections, monitored every 2 h throughout data collection, showed no significant variations in intensity. The θ—2θ scan technique was used with a symmetric scan range of $\pm 1.3°$ in 2θ from the calculated scattering angle for (I) ($2\theta_{max.}$ 50°), and $\pm 0.90°$ for (II) ($2\theta_{max.}$ 60°). The scan rate in both cases was 0.05° s^{-1}. Intensity data were processed as described previously,[11] with the exception that 15 reflections for (I) were considered to be extinction-affected and were omitted in the final refinement stages, and an approximate absorption correction was applied to data for (II).

TABLE 2

Atomic position parameters ($\times$ 10^4) and isotropic thermal parameters

(*a*) For $Ag_2Mo_2O_7$, (I)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
Mo(1)	7 579(3)	2 716(2)	4 556(2)	*
Mo(2)	3 292(3)	3 298(2)	2 517(2)	*
Ag(1)	7 727(3)	2 625(3)	9 622(2)	*
Ag(2)	2 155(3)	2 216(3)	7 331(2)	*
O(1)	6 264(26)	151(22)	2 777(20)	0.9(2)
O(2)	1 593(25)	566(21)	1 684(19)	0.8(2)
O(3)	8 526(27)	2 393(23)	6 578(20)	1.0(2)
O(4)	4 912(23)	3 297(20)	5 300(17)	0.4(2)
O(5)	6 409(25)	3 672(21)	2 347(18)	0.7(2)
O(6)	767(23)	3 845(19)	3 954(17)	0.4(2)
O(7)	2 477(27)	4 015(23)	714(20)	0.9(2)

(*b*) For $Ag_2W_2O_7$ (II)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
W(1)	7 358(2)	7 052(2)	4 445(2)	†
W(2)	2 861(2)	7 294(2)	2 226(2)	†
Ag(1)	7 846(6)	7 143(6)	9 440(4)	†
Ag(2)	2 903(6)	7 220(5)	7 333(4)	†
O(1)	7 936(41)	6 139(36)	6 867(33)	1.2(4)
O(2)	3 964(40)	6 438(35)	4 949(31)	0.9(4)
O(3)	9 907(41)	6 687(36)	3 373(32)	1.2(4)
O(4)	5 838(40)	6 940(35)	2 046(31)	1.0(4)
O(5)	1 888(45)	6 959(40)	110(36)	1.6(4)
O(6)	7 932(42)	9 614(37)	4 122(33)	1.3(4)
O(7)	3 463(44)	9 902(38)	1 927(35)	1.4(4)

* Anisotropic thermal parameters of the form: $10^4 \times \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	49(5)	66(7)	85(7)	30(6)	28(5)	45(5)
Mo(2)	56(7)	80(7)	46(6)	37(6)	18(5)	18(5)
Ag(1)	243(9)	271(9)	118(7)	153(7)	88(6)	44(6)
Ag(2)	206(8)	234(8)	221(8)	164(7)	120(6)	137(6)

† Anisotropic thermal parameters

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	55(5)	98(6)	73(5)	18(4)	−14(4)	−18(4)
W(2)	67(5)	133(6)	40(5)	28(4)	−13(4)	−4(4)
Ag(1)	462(21)	523(22)	190(15)	341(18)	−87(14)	−168(15)
Ag(2)	465(21)	308(17)	147(13)	181(15)	31(13)	−72(12)

Structure Determination and Refinement.—In the least-squares calculations, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where w is the weight, $1/\sigma^2 F$, of each individual reflection. Scattering factors were taken from ref. 12. The major programs used during the refinement were modified versions of the full-matrix least-squares of Busing, Martin, and Levy,[13] the block-diagonal least-squares program of Shiono,[14] and the Fourier summation program of White.[15] All calculations were performed on the Monash University CDC 3200 computer.

Both structures were solved by Patterson methods and refined by Fourier and full-matrix least-squares techniques. At the stage when it became obvious that the heavy atoms were vibrating anisotropically the refinement was continued by use of block-diagonal least-squares methods as, with the limited computer store available, this allowed simultaneous refinement of positional, anisotropic, and isotropic thermal parameters together with a scale factor. Refinement was considered to be complete when all shifts were $<0.2\sigma$.

A final difference synthesis revealed no significant maxima or minima.

Final positional and vibrational parameters are listed in Table 2 with their estimated standard deviations derived from the inverse least-squares matrix. Final observed and calculated structure factors are given in Supplementary Publication No. SUP 21668 (8 pp., 1 microfiche).*

RESULTS

Structure Description.—Both compounds possess chain structures produced by different modes of linking of a basic unit of four octahedra. The unit consists of edge-shared pairs of octahedra, two such pairs sharing three edges to produce a centrosymmetric block of four octahedra. The hypothetical unit, M_4O_{16}, has been shown to be common to a variety of structures.[10]

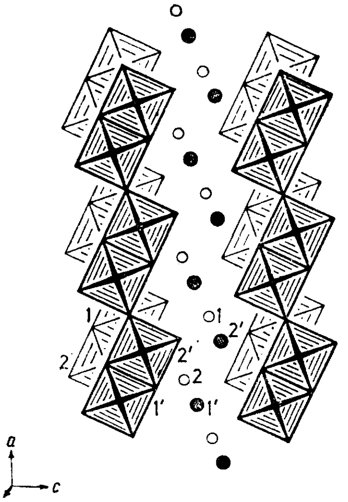

FIGURE 3 Idealized drawing of the structure of $Ag_2Mo_2O_7$. Open and hatched circles represent Ag^+ ions at two different levels

In $Ag_2Mo_2O_7$ these units are linked by a common edge (Figure 3); in $Ag_2W_2O_7$ the same units are linked by two common corners (Figure 4). Thus the stoicheiometry of

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* See Notice to Authors No. 7 in *J.C.S. Dalton* 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies).

[11] G. D. Fallon and B. M. Gatehouse, *J.C.S. Dalton*, 1975, 1344.

[12] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1975, **18**, 104.

[13] W. R. Busing, K. O. Martin, and H. A. Levy, 1962, Program ORFLS, Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[14] R. Shiono, 1968, S.F. Block-diagonal least-squares refinement program, University of Pittsburgh.

[15] J. C. B. White, 1965, Melbourne University Fourier Program, MUFR3. See J. S. Rollett, in 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, Oxford, 1961, p. 87.

the two compounds is the same. The chains formed by linking of the units described above extend infinitely through the structure with the silver ions packed between adjacent chains. The structures are illustrated in idealized form in Figures 3 and 4.

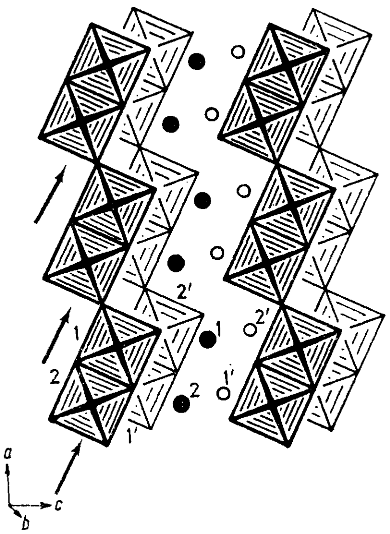

FIGURE 4 Idealized drawing of the structure of $Ag_2W_2O_7$. Open and hatched circles represent Ag^+ ions at two different levels

The simple inter-relationship between these two structures is apparent if the upper zig-zag layer of WO_6 octahedra and the associated silver ions of $Ag_2W_2O_7$ are shifted a distance of one octahedron, in the direction of the arrows shown in Figure 4, with respect to the lower layer of octahedra and silver ions, in which case the $Ag_2Mo_2O_7$ structure (Figure 3) is produced.

The numbering schemes used, and the packing of the chains in the unit cells are illustrated stereoscopically in Figure 5. Selected interatomic bond lengths and angles are listed in Table 3. The distortions present in the MO_6 octahedra are particularly apparent in $Ag_2Mo_2O_7$, in particular, the characteristic two short, two intermediate, and two long Mo–O bond lengths commented upon previously.[9] In $Ag_2Mo_2O_7$ the silver-ion co-ordination is considered to be irregular six-fold (distorted octahedral) for both Ag(1) and Ag(2), whereas for $Ag_2W_2O_7$ it is somewhat more irregular, being five-co-ordinate for both Ag(1) and Ag(2) if a maximum Ag–O bond length of 3.0 Å is taken.

DISCUSSION

During the past few years the alkali-metal molybdates and tungstates have been extensively studied,[3-10] and with results for the present two structures it is now possible to rationalize the possible structures which will almost certainly exist in the Ag_2MoO_4–MoO_3 and the Ag_2WO_4–WO_3 systems. In a study of these two systems Kohlmuller and Faurie [16] and Faurie [17] reported the existence of the phases $Ag_2M_2O_7$ and $Ag_2M_4O_{13}$. This was contrary to our findings when the structure of

TABLE 3

Selected interatomic distances (Å) and angles (°)

(*a*) For $Ag_2Mo_2O_7$(I)

(MoO_6) octahedra		Ag–O polyhedra	
Mo(1)–O(3)	1.75(2)	Ag(1)–O(5) [b]	2.28(2)
Mo(1)–O(1)	1.74(1)	Ag(1)–O(3)	2.38(2)
Mo(1)–O(4)	1.91(2)	Ag(1)–O(2′) [c]	2.46(2)
Mo(1)–O(6) [a]	1.94(2)	Ag(1)–O(1′) [c]	2.53(2)
Mo(1)–O(6′)	2.17(2)	Ag(1)–O(7) [d]	2.62(3)
Mo(1)–O(5)	2.24(2)	Ag(1)–O(7′)	2.67(3)
Mo(2)–O(2)	1.73(1)	Ag(2)–O(1′) [c]	2.32(2)
Mo(2)–O(7)	1.76(2)	Ag(2)–O(3) [e]	2.32(2)
Mo(2)–O(5)	1.83(2)	Ag(2)–O(7) [b]	2.43(3)
Mo(2)–O(6)	2.03(2)	Ag(2)–O(4)	2.45(3)
Mo(2)–O(4′)	2.26(2)	Ag(2)–O(5′)	2.76(3)
Mo(2)–O(4)	2.30(2)	Ag(2)–O(2′) [f]	2.76(3)
Angles O–Mo–O			
O(3)–Mo(1)–O(5)	169.8(7)	O(2)–Mo(2)–O(4′)	156.3(7)
O(1)–Mo(1)–O(6′)	162.9(7)	O(7)–Mo(2)–O(4)	165.2(7)
O(4)–Mo(1)–O(6) [a]	145.1(7)	O(5)–Mo(2)–O(6)	153.1(7)
Mo · · · Mo across a shared edge			
Mo(1) · · · Mo(2)	3.223(3)	Mo(1) · · · Mo(2′)	3.315(3)
Mo(1) · · · Mo(1′) [a]	3.314(3)	Mo(2) · · · Mo(2′)	3.667(3)
Shared-edge O · · · O			
O(6) · · · O(6′) [e]	2.45(2)	O(4) · · · O(5)	2.56(2)
O(6) · · · O(4′)	2.51(2)	O(4) · · · O(4′)	2.71(2)
Closest cation · · · cation			
Ag(1) · · · Ag(1′) [d]	3.347(3)	Ag(1) · · · Ag(2)	3.582(3)
Ag(1) · · · Ag(2) [a]	3.362(3)		

Primes denote the centrosymmetrically related atom at $\bar{x}$, $\bar{y}$, $\bar{z}$. Letters indicate the neighbouring unit cell in which the atom lies as follows:

a	+ 0 0	*d*	+ 0 +
b	0 0 +	*e*	− 0 0
c	0 − 0	*f*	− − 0

(*b*) For $Ag_2W_2O_7$, (II)

(WO_6) octahedra		Ag–O polyhedra	
W(1)–O(6)	1.70(2)	Ag(1)–O(1)	2.31(3)
W(1)–O(1)	1.86(2)	Ag(1)–O(4) [b]	2.35(2)
W(1)–O(3)	1.88(3)	Ag(1)–O(7′) [c]	2.37(3)
W(1)–O(2)	2.01(2)	Ag(1)–O(5)	2.50(3)
W(1)–O(4)	2.06(2)	Ag(1)–O(5′)	2.86(3)
W(1)–O(2′)	2.30(2)	Ag(1)–O(3) [b]	3.22(2)
W(2)–O(7)	1.73(2)	Ag(2)–O(5) [b]	2.21(3)
W(2)–O(5)	1.78(3)	Ag(2)–O(2)	2.23(3)
W(2)–O(4)	1.89(2)	Ag(2)–O(6′) [c]	2.37(2)
W(2)–O(3) [a]	1.92(2)	Ag(2)–O(7′) [c]	2.75(2)
W(2)–O(2)	2.16(2)	Ag(2)–O(1) [a]	2.93(2)
W(2)–O(1′)	2.25(2)	Ag(2)–O(3′)	3.03(2)
		Ag(2)–O(4′)	3.12(3)
Angle O–W–O			
O(6)–W(1)–O(2′)	171.2(10)	O(7)–W(2)–O(1′)	169.9(10)
O(1)–W(1)–O(4)	157.4(10)	O(5)–W(2)–O(2)	157.2(10)
O(3)–W(1)–O(2)	152.0(10)	O(4)–W(2)–O(3) [a]	153.8(10)
W · · · W edge-shared			
W(1) · · · W(2)	3.174(2)	W(1) · · · W(1′)	3.441(2)
W(1) · · · W(2′)	3.391(2)		
W · · · W across shared corner			
W(1) · · · W(2) [e]	3.744(2)		
Shared-edge O · · · O		Closest cation · · · cation	
O(2) · · · O(4)	2.46(3)	Ag(1) · · · Ag(2′) [b]	3.223(4)
O(1) · · · O(2′)	2.62(4)	Ag(1) · · · Ag(2)	3.352(5)
O(2) · · · O(2′)	2.62(4)	Ag(1) · · · Ag(2) [e]	3.499(5)

Primes denote the centrosymmetrically related atom at $\bar{x}$, $\bar{y}$, $\bar{z}$. Letters indicate the neighbouring unit cell in which the atom lies, as follows:

a	− 0 0	*d*	+ 0 +
b	0 0 +	*e*	+ 0 0
c	0 + 0		

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[16] R. Kohlmuller and J. P. Faurie, *Bull. Soc. chim. France*, 1968, **11**, 4379.

[17] J. P. Faurie, *Bull. Soc. chim. France*, 1971, **4**, 1170.

$Ag_6Mo_{10}O_{33}$ was determined,[18] and no evidence for the formation of the tri- or tetra-molybdate (as in the alkali-metal system [9,19]) was found.

Clearly the di-molybdate and -tungstate of silver are stable phases; however, as in the Ag_2MoO_4–MoO_3 system, no tetratungstate appears to exist, and the only other compound observed is a yellow orthorhombic material with the unit-cell dimensions given in Table 4.

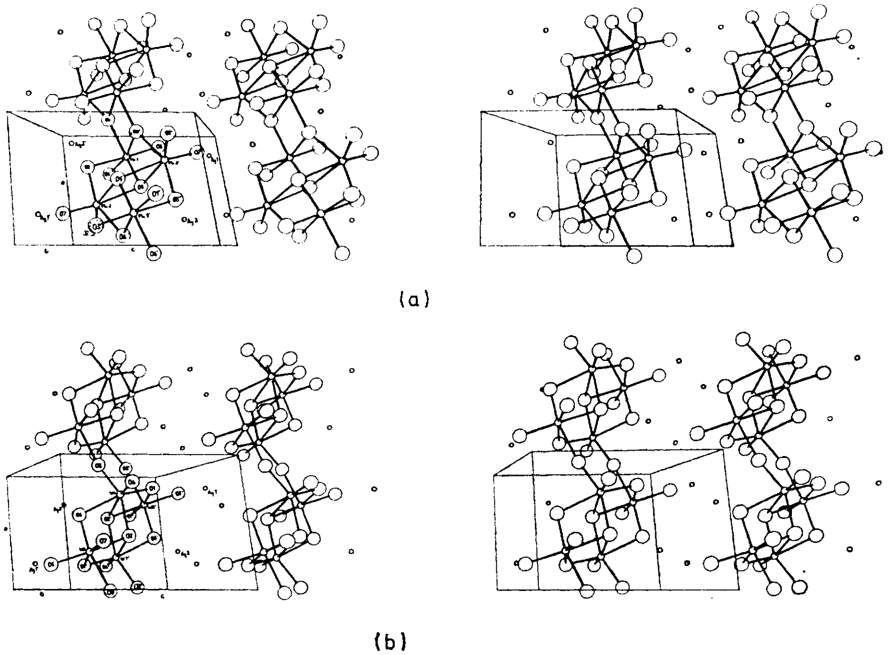

FIGURE 5 The packing of the chains and the silver ions in the structures of (a) $Ag_2Mo_2O_7$ and (b) $Ag_2W_2O_7$

TABLE 4

Unit-cell dimensions

	Ag_2MoO_4 Cubic	Ag_2WO_4 Orthorhombic	$Ag_6W_{10}O_{33}$ (?) Orthorhombic
a/Å	9.31	10.85	7.31
b/Å		12.05	7.56 (3.8 × 2)
c/Å		5.91	12.68
U/Å^3	806.95	772.23	700.74
Space group	$Fd3m$	$Immm$	$C222_1$

From the known structures of other silver compounds, for which the volume per oxygen is constant at *ca.* 21.0 Å^3, it is predicted that the unit cell will contain 32 or 33 oxygen atoms, indicating the probable formulae $Ag_6W_{10}O_{33}$ or $Ag_2W_5O_{16}$ ($Z = 2$). In addition, the pronounced 3.8 Å sub-cell in the b axis direction would suggest a predominantly octahedral co-ordination in the structure.

In considering the structures of tetra-tungstates and -molybdates reported to date, it is indeed surprising that $K_2W_4O_{13}$ (ref. 20) is not more closely related to $Na_2W_4O_{13}$ (ref. 21) and $K_2Mo_4O_{13}$.[9] The latter compound has a block of four octahedra which is very similar to that occurring in $Ag_2Mo_2O_7$ and $Ag_2W_2O_7$, and $Na_2W_4O_{13}$ has sheets with one layer or section of octahedra as for $K_2Mo_4O_{13}$. One of the intersecting chains in $Na_6Mo_{10}O_{33}$ [10] is of the same type as in $K_2Mo_4O_{13}$ and the other of the type found in $Ag_6Mo_{10}O_{33}$.[18] These relationships suggest a re-examination of the K_2WO_4–WO_3 system.

Interestingly, although the spinel structure of Ag_2MoO_4 is well known,[18,22] and, in general, a simple univalent metal molybdate and its analogous tungstate will be isostructural, this does not appear to be the case for Ag_2WO_4. Firstly, the i.r. spectrum shows no strong absorption corresponding to tetrahedral co-ordination of tungsten (as observed in all other simple tungstates),[23] and secondly the unit cell, in spite of having a volume very similar to that of Ag_2MoO_4, is orthorhombic [24] (see Table 4). A recent report [25] dealing with phase relations in the Na_2WO_4–Na_2MoO_4 systems, gives unit cell dimensions for α-Na_2MoO_4, which are similar to those listed in Table 4 for Ag_2WO_4. However, it appears that α-Na_2MoO_4 has a distorted spinel structure, which is not the case for Ag_2WO_4.

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