The Crystal Structure of the Reduced Copper Molybdate
$Cu_{4-x}Mo_3O_{12}$ ($x \simeq 0.15$)

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The partially reduced copper molybdate that was studied is orthorhombic, space group $P2_12_12_1$ and has cell dimensions $a = 11\cdot034$ (± 2), $b = 17\cdot569$ (± 1) and $c = 5\cdot024$ (± 2) Å, in agreement with the values previously reported for '$Cu_3Mo_2O_8$'. Structure determination was based on visually estimated Weissenberg data (1098 independent reflexions). The structure was solved by a combination of Patterson and direct methods and was refined by the least-squares method to a conventional R index of $0\cdot10$. The structure is similar to that of $NaCo_{2\cdot31}Mo_3O_{12}$, with copper replacing both sodium and cobalt atoms. All molybdenum atoms are in fairly regular tetrahedral coordination. Two copper atoms are in 6-coordination within elongated octahedra. The third copper atom has five nearest neighbours at the corners of a square pyramid with a more distant oxygen atom completing a deformed triangular prism. Some copper atoms are in chains of face-sharing octahedra with short ($2\cdot51$ Å) Cu–Cu distances across the faces. Refinement of the site-occupancy factor for these copper atoms leads to an overall composition of $Cu_{3\cdot85}Mo_3O_{12}$, which is in reasonable agreement with preliminary phase analysis and density measurements. '$Cu_3Mo_2O_8$' was reported to participate in a reversible evolution and take-up of oxygen with $Cu_3Mo_2O_9$. As there is no simple relationship between the structures of these phases, this so-called 'breathing reaction' probably has a more complex mechanism.

Introduction

Thomas, Herzog & McLachlan (1956) reported on the crystallography of two compounds containing the oxides of copper and molybdenum for which they gave the formulae $Cu_3Mo_2O_9$ and $Cu_3Mo_2O_8$. They showed that $Cu_3Mo_2O_9$ lost oxygen reversibly and indicated the reaction to be $Cu_3Mo_2O_9 \rightleftharpoons Cu_3Mo_2O_8 + \frac{1}{2}O_2$. The change in *calculated* density in going from the higher oxide to the lower one, $4\cdot45$ g.cm^{-3} to $3\cdot48$ g.cm^{-3}, is so large, however, that one is forced to conclude that some error exists in the description of the compounds and their relationship to each other. Since a program on oxides of molybdenum and tungsten has been under way at this institute for some time it was decided to investigate these two compounds and their behaviour. This paper is devoted to the structure determination of the lower oxide.

Experimental

The compound was prepared by mixing appropriate amounts of Cu_2O, CuO and MoO_3 corresponding to the gross composition $Cu_3Mo_2O_8$. The three oxides were thoroughly ground and sealed in an evacuated quartz tube which was heated at 700°C for 40 hours. The black, crystalline product gave the powder pattern listed in Table 1 plus a few unidentified, fairly weak lines. Unit-cell dimensions obtained from this pattern

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Table 1. *Powder pattern*

Recorded on a Hägg–Guinier focusing camera with Cu $K\alpha_1$ ($\lambda = 1\cdot54051$ Å) radiation and KCl ($a = 6\cdot2919$ Å) as an internal standard. $\Delta = \sin^2 \theta_{obs} - \sin^2 \theta_{calc}$. The calculated values are based on the parameters given in Table 2, but the indexing has not been confirmed, particularly since the powder was not a single-phase (see text).

I	d_{obs} (Å)	$\sin^2 \theta_{obs}$ ($\times 10^5$)	hkl	Δ ($\times 10^5$)
vw	8·80	766	020	−3
$vw-$	5·516	1950	200	+1
$vw-$	4·686	2702	220	−16
$vw-$	4·425	3030	111	0
$vw-$	4·363	3116	021	−3
vw	3·809	4089	031	+9
w	3·644	4469	211	−23
w	3·605	4565	131	−2
			310	−13
vs	3·416	5085	221	+17
w	3·336	5330	150	+37
w	3·302	5443	041	+17
vw	3·117	6106	330	−9
m	2·928	6918	311	−10
			060	−2
vw	2·832	7395	241	+20
			160	−12
vw	2·812	7504	321	0
			340	+43
vw	2·783	7660	151	+17
s	2·763	7773	400	−23
vs	2·645	8481	331	+15
w	2·582	8897	260	+28
$vw-$	2·541	9188	350	−3
w	2·527	9289	061	+19
s	2·511	9410	002	+9
w	2·466	9760	161	+3
$vw-$	2·398	10317	411	−22
$vw-$	2·360	10650	122	−7
$vw-$	2·333	10899	421	−16
			440	+27
$vw-$	2·072	13823	370	+19

(Table 2) are very nearly the same as those reported by Thomas *et al.* (1956) for '$Cu_3Mo_2O_8$'. The best density determination (from weight in air and chloroform) gave a value (Table 2) considerably higher than the density calculated for $Cu_3Mo_2O_8$.

Table 2. *Crystallographic data*

Symmetry: orthorhombic, space group $P2_12_12_1$

Unit-cell dimensions:

$a = 11 \cdot 034\ (\pm 2)$ Å
$b = 17 \cdot 569\ (\pm 1)$
$c = 5 \cdot 024\ (\pm 2)$
$V = 974 \cdot 0$ Å³

Unit-cell content: $4 \times Cu_{\sim 3 \cdot 85}Mo_3O_{12}$

Density: $D_{meas} = 5 \cdot 0$ g.cm⁻³
$D_{calc} = 4 \cdot 93$ g.cm⁻³

Later attempts to repeat the preparation of the phase in this simple way failed and yielded mixtures of other phases only. However, by heating mixtures of compositions $Cu_{3 \cdot 7-3 \cdot 8}Mo_3O_{12}$ in evacuated silica tubes to 800 °C and then lowering the temperature a few degrees per hour we obtained samples which, although microcrystalline, contained the desired phase as a main component. We believe that this reduced copper molybdate is stable only in a small region of the composition-temperature-pressure system.

The first preparation contained a few crystals large enough for single-crystal work. The selected crystal was prismatic with a length of 0·177 mm and a cross section (approximately a truncated square) of $0 \cdot 023 \times 0 \cdot 023$ mm². It gave X-ray photographs with perfectly sharp spots. Layer lines $hk0$–$hk4$ were recorded with a Weissenberg camera using Cu $K\alpha$ radiation and the multiple-film technique. Intensities were estimated visually by means of a calibrated scale and the subsequent data reduction included correction for absorption.

Structure determination

Systematic absences observed on the X-ray photographs were consistent with the space group $P2_12_12_1$ (No. 19), in agreement with the findings of Thomas *et al.* (1956). The only position in this space group has fourfold multiplicity. However, with four $Cu_3Mo_2O_8$ units per cell, the calculated density is very low, corresponding to a volume per oxygen atom of about 30 Å³. The corresponding value for $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968) is 21·6 Å³ and in most other oxide structures the oxygen volume is still lower. A more reasonable formula would be $Cu_4Mo_3O_{12}$. However, this formula would represent a change in the Cu:Mo ratio, so this lower oxide could not be involved in a simple way in a reversible evolution and take-up of oxygen with $Cu_3Mo_2O_9$. Structure determination was carried out without a commitment as to the exact content of the unit cell.

Several possible sets of three metal atoms were deduced from a three-dimensional Patterson synthesis.

Additional possible atom positions were determined from $hk0$ difference maps followed by least-squares refinement of the two-dimensional data. Metal atoms were all treated as Cu in the initial stages, but the best set of six atoms, even after assignment as copper and molybdenum, only lowered the (conventional) R index to 0·28. A difference map at this stage showed only one important peak, on or very near the screw axis at $x = \frac{1}{4}$, $y = 0$. This position had been tested earlier, but the refinement including this site had 'blown up'. The short, $c/2 = 2 \cdot 5$ Å, metal–metal distance along the screw axis also made this site seem unlikely.

An independent, direct approach, based on symbolic addition was attempted on the $hk0$ data at this stage. Since the axial projections were all centrosymmetric but the space group was not, the method was not expected to work. However, enough signs were determined immediately and without ambiguity so that a Fourier projection could be calculated. The seven largest peaks included the six previously determined plus the site on the screw axis. These seven positions were tested in a least-squares calculation with a Cu atom at the screw axis held fixed, and the R index dropped from the six-atom value of 0·28 to 0·20; thus, there was no doubt that the seventh atom was correctly placed; the earlier difficulty apparently resulted from attempting to refine this position from $hk0$ data alone.

The z parameters for all but this extra copper atom, $Cu(X)$, were estimated from the Patterson maps and were refined from upper level data. The assumed z parameter for $Cu(X)$ could not be refined reliably in this way, however, since odd level data were insensitive to its position and agreement for even level data (except for $l = 0$) was somewhat worse with this atom included. A three-dimensional difference map based on 6 metal atoms showed the highest peak along the screw axis to be at about $z = 0 \cdot 1$, and another difference map based on all 7 metal atoms revealed the 12 oxygen positions.

Table 3. *Fractional atomic coordinates and isotropic temperature factors*

E.s.d.'s are given within parentheses.

	x	y	z	B
Cu(1)	0·4481 (3)	0·26966 (19)	0·7421 (12)	
Cu(2)	0·5941 (3)	0·21929 (20)	0·2696 (12)	
Cu(3)	0·2647 (4)	0·43472 (27)	0·7218 (12)	
Cu(X)	0·2498 (20)	0·9985 (10)	0·079 (22)	
Mo(1)	0·26796 (17)	0·19442 (10)	0·2393 (5)	0·28 (5)
Mo(2)	0·48814 (19)	0·39573 (11)	0·2193 (6)	0·54 (5)
Mo(3)	0·54558 (19)	0·09177 (11)	0·7979 (6)	0·41 (5)
O(1)	0·1435 (19)	0·2145 (11)	0·042 (5)	1·0 (3)
O(2)	0·4023 (17)	0·2047 (9)	0·047 (5)	0·4 (3)
O(3)	0·2593 (17)	0·1037 (10)	0·352 (5)	0·8 (3)
O(4)	0·2737 (18)	0·2594 (11)	0·505 (5)	1·0 (3)
O(5)	0·1298 (18)	0·3798 (11)	0·920 (5)	0·8 (3)
O(6)	0·0147 (16)	0·3252 (10)	0·426 (5)	0·5 (3)
O(7)	0·1390 (21)	0·4689 (12)	0·394 (5)	1·4 (4)
O(8)	0·4094 (17)	0·3638 (11)	0·932 (5)	0·8 (3)
O(9)	0·0300 (16)	0·1843 (10)	0·561 (5)	0·4 (3)
O(10)	0·3909 (23)	0·4481 (13)	0·392 (6)	2·0 (5)
O(11)	0·9148 (19)	0·4537 (11)	0·144 (5)	1·1 (4)
O(12)	0·6144 (21)	0·4520 (12)	0·150 (6)	1·6 (4)

Table 4. Anisotropic thermal parameters for the copper atoms

The β values refer to the temperature factor

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

$R(i)$, $i=1,3$, are the r.m.s. components of thermal displacement (in Å) along the principal axes of the ellipsoid of thermal vibration.

	$\beta_{11}\times10^4$	$\beta_{22}\times10^5$	$\beta_{33}\times10^3$	$\beta_{12}\times10^5$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$	$R(1)$	$R(2)$	$R(3)$
Cu(1)	7(3)	15 (11)	11 (3)	28 (15)	3 (9)	2 (5)	0·02	0·07	0·12
Cu(2)	9 (3)	4 (11)	15 (3)	−5 (16)	−7 (10)	3 (6)	0·02	0·07	0·14
Cu(3)	21 (5)	184 (21)	13 (4)	−113 (22)	4 (11)	33 (6)	0·04	0·12	0·20
Cu(X)	34 (6)	252 (33)	617 (78)	73 (35)	−348 (53)	−154 (37)	0·09	0·18	0·90

Table 5. Observed and calculated structure amplitudes

Reflexions marked with an asterisk were not used in the refinement.

[Table of observed (F_O) and calculated (F_C) structure amplitudes, arranged in columns headed H K L FO FC.]

An isotropic three-dimensional block-diagonal refinement with the 7 metal atoms and 12 oxygens reduced R to 0·16; with the copper atoms anisotropic, full-matrix refinement reduced R to 0·12. In this anisotropic refinement, Cu(X) showed very anisotropic behaviour, with extremely large vibration amplitude (of

the order of 1 Å) in the z direction. This, of course, is many times larger than usual values and could be simulated by a column of scattering matter of varying density in the z direction. Refinement of a site-occupancy factor for $Cu(X)$ gave values around 0·85. The least-squares results, then, correspond to an incompletely filled position with extremely anisotropic motion. This would also be consistent with atomic motion along z or with some randomness in position along z. We tried to replace atom $Cu(X)$ by two half copper atoms at $z = 0.07 \pm 0.04$ which would correspond to an ambiguity in the location. Simultaneous refinement of these two positions was not possible, however, because correlations between the parameters were too high.

A Fourier difference map along $\frac{1}{4}, 0, z$ shows two maxima, one at $z = 0.1$ (height 16·6 e.Å^{-3}) and a second peak not much lower (13·8 e.Å^{-3}) at $z = 0.36$. An attempt to refine a partial copper atom in this second position resulted in a drop of its occupancy factor from the initial value of 0·4 to below 0·1 within a few cycles. This second peak is therefore probably only a series-termination effect.

The set of parameters obtained with copper atoms anisotropically refined is listed in Tables 3 and 4. Observed and calculated structure amplitudes are given in Table 5.

Calculation details

Computers of type TRASK, IBM 360 & IBM 1800 were used for the calculations. Refinement of cell parameters from powder patterns and single-crystal absorption correction were made with programs written by P.-E. Werner (Nos. 6019 & 6027 in *World List of Crystallographic Computer Programs*, 1966). Structure factor and Fourier calculations were made partly with program *DRF** and programs *STORK* (L.-O. Larsson & L.-O. Hagman, Sweden) and *SFEXP-SIG*1 (R. Karlsson, Sweden). Program *FAME** was used for calculating Wilson plot and *E*-values. Three least-squares programs in *World List of Crystallographic Computer Programs* (1966) were used at different stages of the calculations, namely the block-diagonal matrix program *SFLS** (No. 6023) and full-matrix programs *LALS** and *LINUS** (Nos. 384 and 360, respectively). Interatomic distances and bond angles were computed with program *DISTAN.** Thermal ellipsoid calculations were made with program *ORTEP* (No. 388 in *World List*, modified by I. Carlbom, Sweden).

The HFS scattering factors given by Hanson, Herman, Lea & Skillman (1964) were used and the real parts of the dispersion correction (Cromer, 1965) were applied to these curves. The least-squares programs minimized the function $w(|F_o| - |F_c|)^2$ and the weights were calculated according to the Hughes expression: $w = |F_o|^{-2}$ if $|F_o| > A$ and $w = A^{-2}$ if $|F_o| < A$. Value $A = 48$ was found suitable in the present case. The

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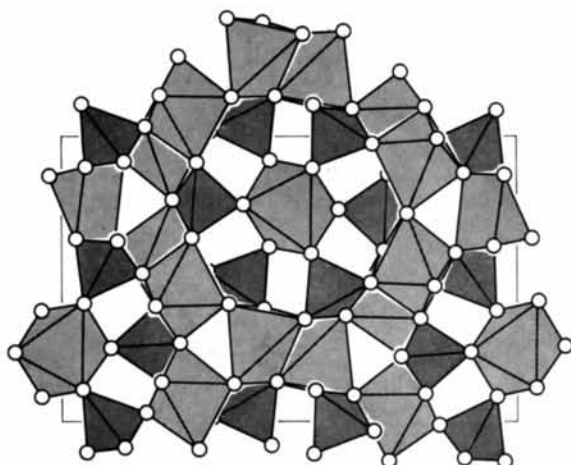* The names of the authors are given in the preceding paper (Kihlborg, Norrestam & Olivecrona, 1971).

Fig. 1. Structure of $Cu_{4-x}Mo_3O_{12}$ visualized in terms of MoO_4 tetrahedra, CuO_6 octahedra and CuO_5 square pyramids and viewed along the c axis. The b axis is horizontal.
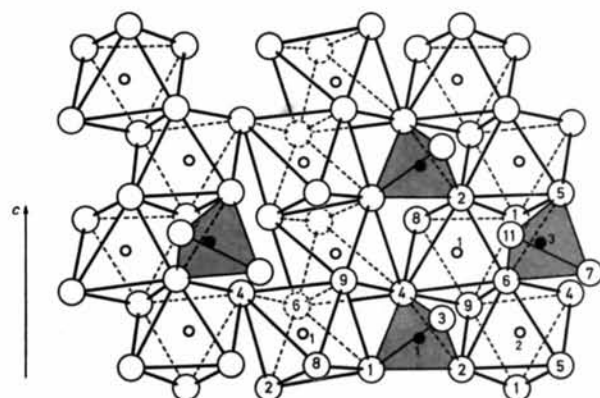

Fig. 2. Interconnexion of the coordination octahedra around $Cu(1)$ and $Cu(2)$, seen perpendicular to the plane defined by the metal atoms in the zigzag string to the right. A few MoO_4 tetrahedra connected to the octahedra are also shown (shaded).

weight analysis obtained in the final refinement cycle is given in Table 6.

Table 6. *Weight analysis*

$\Delta = ||F_o| - |F_c||$, $w =$ weighting factor, $N =$ number of independent reflexions. The $w\Delta^2$ values have been normalized.

F_o	N	$\overline{w\Delta^2}$	$\sin\theta \times 10^4$	N	$\overline{w\Delta^2}$
0·0– 25·6	98	0·43	0–4642	119	1·38
25·6– 36·8	105	0·83	4642–5848	136	0·80
36·8– 44·8	104	0·88	5848–6694	120	1·02
44·8– 55·3	107	1·42	6694–7368	131	1·19
55·3– 63·9	108	1·28	7368–7937	110	0·93
63·9– 73·8	107	1·12	7937–8434	103	0·62
73·8– 85·1	108	1·02	8434–8879	95	0·55
85·1– 98·3	106	0·93	8879–9283	97	0·60
98·3–122·6	107	1·11	9283–9655	107	1·48
122·6–254·4	108	0·92	9655–9999	40	1·80

During refinement it became evident that the strongest reflexions suffered from extinction: $|F_o|$ was consistently smaller than $|F_c|$; therefore, the 29 reflections with highest intensity were not used in the final calculations. These reflexions are indicated by an asterisk in Table 5. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ not including these strong reflexions was 0·10.

Description

The structure is best described in terms of MoO_4 tetrahedra, CuO_6 octahedra and CuO_5 square pyramids. The way it is built up from these elements is illustrated in Fig. 1. Octahedra around Cu(1) and Cu(2) share edges, forming zigzag chains along [001] (Fig. 2). The same type of chains occurs for example in $CuWO_4$ with a di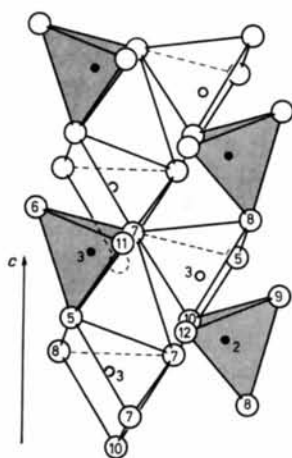storted wolframite-type structure (Kihlborg & Gebert, 1970). The chains are coupled to like chains through common corners, thus forming puckered layers of octahedra at about $y = \frac{1}{4}$ and $\frac{3}{4}$. A part of such a layer is depicted in Fig. 2.

The square pyramids around Cu(3) are located around one set of screw axes at $y = 0$ and $\frac{1}{2}$ and they share corners with each other (Fig. 3) and with octahedra of two neighbouring 'layers'. As seen in Fig. 1 the polyhedra around Cu(1), Cu(2) and Cu(3) thus form a three-dimensional, pseudohexagonal network with wide tunnels running in the **c** direction. The MoO_4 tetrahedra line these tunnels, sharing three of their corners with the framework, with the fourth apex pointing towards the middle (Fig. 1). This results in octahedral sites in the middle of the tunnels at the levels $z \simeq 0$ and $\frac{1}{2}$ and these are the location of Cu(X). These coordination octahedra share faces along [001] forming columns within which the separation of copper atoms is remarkably short. The Cu(X) position is only partially occupied, however. Note that the MoO_4 tetrahedra are not linked directly to each other but are distributed fairly evenly throughout the structure. A stereo view of the structure along [001] is given in Fig. 4.

Disregarding some differences in coordination and symmetry the present structure is the same as that of $NaCo_{2·31}Mo_3O_{12}$, a fact that is discussed below.

Fig. 3. Interconnexion of the square pyramids around Cu(3) and some of the MoO_6 tetrahedra linked to these polyhedra. The **c** axis is slightly inclined to the plane of the paper.
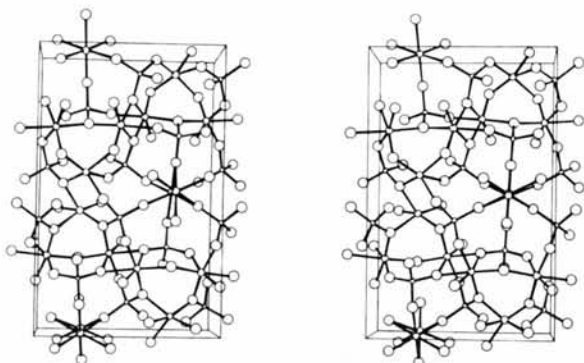

Fig. 4. A stereo view of the structure along [001]. Lower left back corner is $0, 0, \frac{1}{2}$ with respect to the coordinates given in Table 3, a axis horizontal. Large circles are oxygen atoms, small circles in four-coordination are molybdenums, and small circles in five- and six-coordination are copper atoms. (Photo prepared by University of Connecticut Photographic Laboratory.)

Coordination and bond distances

Important interatomic distances are listed in Table 7, which shows that the coordination around Cu(1) and Cu(2) is quite similar: four shorter equatorial Cu–O bonds and two longer ones, approximately perpendicular to these. This $4+2$ coordination is very common for divalent copper and is due to the Jahn–Teller distortion. Average lengths of the short and long bonds are 1·985 and 2·355 Å, respectively. These values are quite normal (Abrahams, Bernstein & Jamieson, 1968) and agree well with the corresponding distances in $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968) and $CuWO_4$ (Kihlborg & Gebert, 1970).

The coordination for Cu(3) has been described above as fivefold, square pyramidal. The five bonds fall within the range 2·04–2·28 Å (mean value 2·182 Å) and it is evident from Fig. 5 that the coordination figure is not quite regular. There is, however, a sixth oxygen atom at a distance of 2·81 Å which might be considered as belonging to the coordination sphere of Cu(3). The polyhedron is then changed into a triangular prism, an unusual coordination for copper. Bond lengths are significantly longer than for Cu(1) and Cu(2); the mean value of the four shortest Cu(3)–O distances is 2·156 (*cf.* above). Also, the bond lengths are considerably longer than in $CuMoO_4$ where the corresponding averages for the 5-coordinated copper are 2·010 (all five bonds) and 1·928 Å (four shortest) (Abrahams, Bernstein & Jamieson, 1968).

The six Cu–O distances around Cu(X) are even longer; the average is 2·24 Å. The two opposite, very

short Cu–Cu distances across the shared faces are the remarkable feature in this coordination, however.

All three MoO_4 tetrahedra are fairly regular with all O–Mo–O angles falling within the range 104–117°. The average of the Mo–O bonds lengths, 1·756 Å, is also quite normal (see for instance Abrahams, Bernstein & Jamieson, 1968) and the difference in the coordination around the three molybdenum atoms is insignificant. Three bonds are remarkably short, namely Mo(1)–O(3), Mo(2)–O(10) and Mo(3)–O(11), falling within the range 1·677 ± 0·017 Å. This range should be compared with the value 1·671 (± 8) Å found in MoO_3 (Kihlborg, 1963) for an oxygen atom bonded only to one molybdenum atom, which should thus represent a double-bond length. This means that the oxygen atoms O(3), O(10) and O(11) are tightly bonded to the molybdenum atoms and should have little bonding power left for Cu(X), Cu(3) and Cu(X), respectively.

Atoms O(3) and O(11) constitute four of the six anions around Cu(X). The two remaining ones are formed by O(12). Bond Mo(2)–O(12) is close to the average Mo–O bond length. If this bond then is assigned a formal bond number of 6/4 = 1·5, each O(12) would have a bond strength of 0·5 left for Cu(X). The sum of the strengths of the bonds to Cu(X) would then be 1, if no contribution is assumed from O(3) and O(1).

All oxygen atoms are linked to one Mo atom and two Cu atoms if the long O(10)–Cu(3) distance and all O–Cu(X) links are included. The O–O separations are longer than 2·73 Å except for O(6)–O(9) which is only 2·57 (± 2) Å. This latter distance corresponds to one of the shared edges in the wolframite-type strings of CuO_6
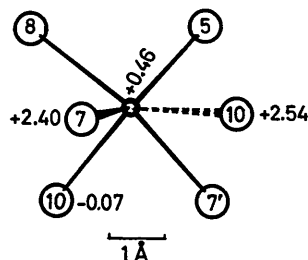

Fig. 5. Coordination around Cu(3) projected on to a plane defined by the oxygen atoms 8, 5 and 7'. The levels in Å of the rest of the atoms above (+) or below (−) this plane are indicated in the figure.

octahedra. The other shared edge is not particularly short, O(1)–O(2) 2·86 (± 3) Å. The same phenomenon was observed in $CuWO_4$.

Discussion

As mentioned before, this structure turned out similar to that of a sodium cobalt molybdate, $NaCo_{2\cdot31}Mo_3O_{12}$ (Ibers & Smith, 1964). In Megaw's terminology (Katz & Megaw, 1967), if we refer to the structure of $NaCo_{2\cdot31}Mo_3O_{12}$ as the 'aristotype', the structure of $Cu_{3\cdot8}Mo_3O_{12}$ may be called a 'hettotype', since it is of lower symmetry but topologically similar. The space group for $NaCo_{2\cdot31}Mo_3O_{12}$ is $Pnma$. Positions corresponding to Cu(1) and Cu(2) are thereby equivalent and are partially occupied by cobalt atoms (occupancy factor 0·7). Also the site of Cu(X) corresponds to a cobalt position, likewise partially occupied. It was mentioned before that the coordination polyhedron

Table 7. Selected interatomic distances

The standard deviations in the last digits are in parentheses.

Cu(1)–O(9)	1·946 (23) Å		Cu(X)–O(12)	2·08 (7) Å
–O(8)	1·956 (21)		–O(3)	2·13 (6)
–O(2)	1·975 (23)		–O(12')	2·18 (7)
–O(6)	2·007 (19)		–O(11)	2·30 (6)
–O(4)	2·271 (22)		–O(3')	2·30 (7)
–O(1)	2·429 (23)		–O(11')	2·42 (7)
–Cu(2)	3·002 (12)		–Cu(X)(2×)	2·513 (12)
–Cu(2')	3·225 (13)			
Cu(2)–O(6)	1·928 (24)		Mo(1)–O(3)	1·694 (19) Å
–O(9)	2·023 (19)		–O(1)	1·731 (23)
–O(5)	2·023 (21)		–O(4)	1·778 (21)
–O(1)	2·024 (26)		–O(2)	1·778 (21)
–O(4)	2·313 (22)			
–O(2)	2·408 (21)		Mo(2)–O(10)	1·660 (27)
–Cu(1)	3·002 (12)		–O(12)	1·743 (23)
–Cu(1')	3·225 (13)		–O(8)	1·777 (24)
–Cu(3)	3·296 (6)		–O(9)	1·846 (20)
Cu(3)–O(5)	2·035 (22)		Mo(3)–O(11)	1·676 (21)
–O(10)	2·176 (31)		–O(5)	1·766 (24)
–O(7)	2·177 (23)		–O(7)	1·768 (24)
–O(7')	2·237 (27)		–O(6)	1·873 (20)
–O(8)	2·284 (21)			
–O(10')	2·814 (25)			
–O(4)	3·269 (21)			
–Cu(2)	3·296 (6)			
–Cu(3)(2×)	3·417 (11)			

around Cu(3) could be regarded as a distorted triangular prism if a remote oxygen atom was included. In the sodium cobalt molybdate the corresponding coordination figure is a fairly regular trigonal prism enclosing sodium.

One of the most interesting features in both structures is the column of octahedra sharing faces within which the metal–metal distances are remarkably short [Cu–Cu, 2·513 ($\pm$12) Å and Co–Co, 2·623 ($\pm$3) Å]. In both cases the refinements indicate partial occupancy and highly anisotropic thermal vibration with maximum amplitude along the column axes. In the present case the amplitude is so large that its interpretation in terms of thermal vibration must be questioned.

Although the Cu(X)–Cu(X) distances are shorter than the bond lengths, 2·556 Å, in metallic copper, it is not an unknown feature and even a closer approach of copper atoms is known. Thus, a value of 2·418 ($\pm$2) Å was reported for $CuCN.NH_3$ by Cromer, Larson & Roof (1965) and 2·45 Å has been observed in two organic complexes of copper(I) (Brown & Dunitz, 1961; Corfield & Shearer, 1966). Further examples of compounds with Cu–Cu bonds are presented in a review by Baird (1968). Infinite columns of face-sharing octahedra with short M–M distances occur in $BaNiO_3$ (Lander, 1951). In the present structure, as in the sodium cobalt molybdate, the columns are not necessarily infinite because of the partial occupancy.

It is not possible without further evidence from other types of measurement to assign definite oxidation states to all the metal atoms. Only hexavalent molybdenum is known in tetrahedral coordination, so the molybdenum atoms can, with some confidence, be assigned the oxidation number 6. The deviation from regular octahedral environment observed for Cu(1) and Cu(2) is common for divalent copper and as the arrangement of these coordination polyhedra is the same as that found in $CuWO_4$ it seems most likely that both these atoms are in oxidation state +2. Although Cu(3) corresponds to Na in the sodium cobalt molybdate, its square-pyramidal coordination has counterparts in several compounds of divalent copper, for example in $CuMoO_4$. As mentioned before, however, the five bonds are significantly longer in the present compound than in $CuMoO_4$. This might indicate an oxidation state below +2. A wide variety of mixed valence compounds of copper is known and has recently been reviewed by Robin & Day (1967).

If the above assumptions about the valences of Mo, Cu(1) and Cu(2) are correct, the oxidation states of Cu(3) and Cu(X) are necessarily interrelated, so that each Cu(X) atom given an oxidation number above zero requires a Cu(3) atom being reduced below +2.

Low-valent Cu(X) is not improbable in view of the strong Mo–O bonds around Cu(X), and would leave valence electrons free to participate in Cu–Cu bonds, possibly delocalized, along the column axes. The rough estimation of formal bond numbers points to an oxidation number of +1. Absent or weak bonding forces between Cu(X) and the surrounding oxygen atoms would explain why the oxygen atoms, as indicated by their normal B values, are not affected much by the partial filling of the Cu(X) positions or by the high thermal vibration or disorder along the strings. Obviously there is a strong need for measurements of the electric and magnetic properties of this phase. This requires, however, that it can be reproducibly prepared in pure form. This problem will be further investigated.

The crystal structure of $Cu_3Mo_2O_9$ has also been determined (Kihlborg, Norrestam & Olivecrona, 1971). No simple relationship exists between that structure and the present one, so the 'breathing reaction' reported by Thomas et al. (1956) must have a complex mechanism.

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