The Crystal Structure of Cu$_3$Mo$_2$O$_9$

By Lars Kihlborg, Rolf Norrestam and Birgitta Olivecrona

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-104 05 Stockholm, Sweden

The copper(II) molybdate Cu$_3$Mo$_2$O$_9$ which was first prepared by Thomas, Herzog & McLachlan (1956) has unit-cell dimensions $a=7\cdot659$, $b=14\cdot613$, $c=6\cdot875$ Å. The space group is the acentric *Pna*2$_1$ with $Z=4$. The crystal structure has been determined from single-crystal diffractometer data by means of direct methods. Least-squares refinement resulted in a conventional $R=0\cdot070$. The structure, of a previously unknown type, contains almost regular MoO$_4$ tetrahedra, CuO$_6$ octahedra, distorted in two ways, and CuO$_5$ tetragonal pyramids. The copper-oxygen polyhedra share three or four edges among themselves to form a kind of aggregate infinite in the direction of the c axis. The MoO$_4$ tetrahedra are separate from one another, sharing corners with copper oxygen polyhedra only.

Introduction

A copper molybdenum oxide with the composition Cu$_3$Mo$_2$O$_9$ and orthorhombic symmetry was first reported by Thomas, Herzog & McLachlan (1956). They obtained the oxide as large, blue-black, needle-like crystals when molten mixtures of about 66 mole % CuO and 34 mole % MoO$_3$ were slowly cooled in an oxygen atmosphere. Unit-cell dimensions were $a=7\cdot78$, $b=14\cdot64$ and $c=6\cdot90$ Å and the space group was given incompletely as *Pna*. The phase was reported to give off oxygen reversibly at higher temperatures and thereby transform into the lower oxide 'Cu$_3$Mo$_2$O$_8$'.

Kohlmuller & Faurie (1967) investigated the phase diagram MoO$_3$–CuO and found that the phase Cu$_3$Mo$_2$O$_9$ decomposes peritectically at 870°C. The lengths of the b and c axes reported by these authors agree with the values of Thomas *et al.* but the a axis is given as 14·842 Å. A density $d_4^{24}=4\cdot67$ was observed.

In a thorough study of the same system under various pressures of oxygen Nassau & Shiever (1969) found that Cu$_3$Mo$_2$O$_9$ is stable only in a small temperature range, namely 835–865°C in oxygen (1 atm) and 812–840°C in air. They reported shiny black crystals of unit-cell dimensions $a=7\cdot64$ (±2), $b=14\cdot50$ (±3) and $c=6\cdot78$ (±2) Å and measured density 4·53 (±10) g.cm^{-3} at 60°C. The space group was said to be most probably *Pna*2$_1$ (without further comments).

Since an understanding of the mechanism of the oxygen evolution and uptake reported by Thomas *et al.* requires a knowledge of the crystal structures, the two phases involved were investigated at this institute. The present paper deals with the structure of the higher oxide. The study of the lower oxide, Cu$_{4-x}$Mo$_3$O$_{12}$, is presented in a separate paper (Katz, Kasenally & Kihlborg, 1971).

Experimental

Our first attempts to prepare Cu$_3$Mo$_2$O$_9$ according to the method of Thomas *et al.* were unsuccessful. Other methods, including hydrothermal synthesis, were also tried but gave no positive results. The appearance of the paper by Kohlmuller & Faurie (1967) led us to modify the procedure.

A thoroughly ground mixture of 3CuO+2MoO$_3$ was sealed in a silica tube containing air at reduced pressure. The tube was heated to 900°C; thereafter the temperature was lowered continuously to 865°C over a period of 7 days and kept at this temperature for 5 days. Then the tube was quenched in water. The resulting sample consisted of a rather fine crystalline black powder and a few aggregates of larger, mostly amber-coloured crystals. The powder pattern of the sample was very complex and could not be interpreted. Apparently the sample contained unidentified phases as main constituents.

Single-crystals detached from the aggregates gave X-ray patterns consistent with the data of Thomas *et al.* for Cu$_3$Mo$_2$O$_9$. Both a transparent amber-coloured crystal and a black opaque crystal were checked and they gave identical patterns. This phenomenon of light and dark species giving identical X-ray patterns was recently encountered in a study of CuWO$_4$ (Kihlborg & Gebert, 1970) and is probably associated with slight deviations from stoichiometry. The transparent crystal was used for the data collection. It was a rod of length 0·116 mm (along c) and rectangular cross section 0·012 × 0·032 mm^2.

After preliminary rotation and Weissenberg photographs, the crystal was mounted on a Siemens A.E.D. automatic diffractometer. Intensities were recorded with Mo $K\alpha$ radiation for the reciprocal lattice points within one octant with $\theta<32°$. Then θ–2θ scans were made and the built-in '5-values technique' was used, so that each peak was scanned twice and the background was measured for the same period of time as required for the scanning. The scan interval was made up of the parts $\Delta\theta_-$ and $\Delta\theta_+$ on the negative and positive side of the peak, respectively, where $-\Delta\theta_-=0\cdot35+0\cdot20$ tgθ and $+\Delta\theta_+=0\cdot35+0\cdot40$ tgθ. Of the 1129 intensities measured, the 679 with $\sigma(I)/I<0\cdot5$ were

used in the calculations. Some pertinent crystallographic data are given in Table 1. Since no powder pattern of the phase was available unit-cell dimensions were measured with the diffractometer.

Table 1. Crystallographic data

Symmetry: orthorhombic, space group $Pna2_1$

Unit-cell dimensions:

$a = 7.659 \ (\pm 10)$ Å
$b = 14.613 \ (\pm 15)$
$c = 6.875 \ (\pm 10)$
$V = 769$ Å^3

Structure determination and refinement

A three-dimensional Patterson function revealed that most scattering material was concentrated close to two planes perpendicular to the c axis with a separation of $\Delta z = 0.5$.

The two space groups consistent with the symmetry and the systematic extinctions are $Pnam$ ($= Pnma$) and $Pna2_1$. By consideration of the point positions available for a cell content of 12 Cu and 8 Mo the first of these space groups could be rejected as being unlikely, if improbably short metal–metal distances were to be avoided. Efforts were therefore concentrated on finding a solution in the non-centrosymmetrical space group $Pna2_1$. All attempts to solve the structure by means of the Patterson function were fruitless. One reason for this is that the Harker section $P(uv\frac{1}{2})$ was severely dominated by non-Harker vectors because of the special feature mentioned in the preceding paragraph. Another reason seems to be the unfavourable scattering power of Cu compared to that of Mo: too close to permit the Mo–Mo vectors to be directly identifiable, and too different to allow the atoms to be treated as equal in the first approximation.

At this stage a set of computer programs written by one of the authors (R.N.) for phase determinations in non-centrosymmetrical cases was tested on this structure. These programs are based on the principle used in generating solutions of the triple relations between phases described by Karle & Karle (1966). The 200 highest E values ($|E| \geq 1.5$) were used to set up the equation system for the phase determination and to generate the best 700 triple relations ($|E_1 . E_2 . E_3| \geq 11.0$).

The phases of three reflexions specifying the origin could be chosen arbitrarily. It proved necessary to assign tentative phases to two additional reflexions in order to obtain solutions with a sufficient number of determined phases. This basic set of five reflexions is given in Table 2. If the phase $\pi/2$ is chosen for reflexion 591 to specify the origin it follows, based on the fact that the scattering material is concentrated near two planes (see above), that reflexions with l odd should have phases close to $\pm \pi/2$. These values were then assigned to A and B in the basic set (Table 2) in two permutations. Of the four possible permutations

only two needed to be considered since the other two were just the enantiomorphs. The solution with the smallest number of contradictions was selected and this gave phases for 157 of the 200 reflections used.

Table 2. Basic set used in the phase determination

h	k	l	E	Initial phase	Final phase
5	16	0	2.40	0	0.063
9	9	0	2.26	0	0.080
5	9	1	2.35	$+\pi/2$	1.542
6	5	5	2.53	A	-1.565
5	9	5	2.77	B	1.582

A Fourier calculation based on these 157 reflections gave the required number of distinct maxima corresponding to the metal atoms as well as a number of lower peaks at positions where oxygen atoms could be located. Least-squares refinement of the metal atom parameters reduced the (conventional) R value to 0.12, and a subsequent difference Fourier synthesis revealed the positions of all oxygen atoms.

Refinement of positions and isotropic thermal parameters for all 14 atoms resulted in the parameters listed in Table 3 and gave an R value of 0.070. Refinement with anisotropic thermal parameters for the metal atoms gave a better R value, 0.056 (all reflexions included), but the temperature factor became negative for all three copper atoms and one molybdenum atom. Since the space group is polar, the z coordinate for one of the atoms, Mo(1), was held fixed at $z = \frac{1}{2}$.

Table 3. Fractional atomic coordinates and isotropic temperature factors

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

	x	y	z	B
Cu(1)	0.9944 (12)	0.9949 (5)	0.243 (2)	0.35 (6)
Cu(2)	0.1611 (4)	0.1402 (2)	0.994 (2)	0.63 (5)
Cu(3)	0.2049 (4)	0.4361 (2)	0.491 (2)	0.66 (6)
Mo(1)	0.2625 (3)	0.16606 (15)	$\frac{1}{2}$	0.47 (4)
Mo(2)	0.1513 (3)	0.38533 (15)	0.000 (2)	0.48 (4)
O(1)	0.0892 (26)	0.0147 (13)	0.985 (14)	0.7 (3)
O(2)	0.1945 (27)	0.2685 (14)	0.010 (8)	1.4 (5)
O(3)	0.4306 (35)	0.0937 (16)	0.977 (8)	2.0 (6)
O(4)	0.2417 (40)	0.4294 (22)	0.210 (4)	-0.1 (4)
O(5)	0.1195 (39)	0.1288 (19)	0.297 (4)	0.4 (5)
O(6)	0.2988 (27)	0.2804 (14)	0.485 (10)	1.2 (4)
O(7)	0.4695 (29)	0.1090 (14)	0.494 (10)	1.6 (4)
O(8)	0.1590 (39)	0.1375 (21)	0.718 (5)	0.6 (5)
O(9)	0.2520 (70)	0.4429 (30)	0.792 (7)	2.4 (1.1)

Although lower R values are usually obtained with diffractometer-collected data there are no indications of serious systematic errors or incorrectly located atoms. The highest maxima in a final three-dimensional full-difference synthesis are about half the magnitude of the lowest oxygen peaks. The temperature factors for the metal atoms do not differ appreciably and are quite reasonable; for the oxygen atoms they are rather divergent with fairly high standard errors.

The fact that the interatomic distances are quite

normal (see below) supports the correctness of the structure.

Calculation details

All calculations were performed on IBM 1800 and IBM 360/75 computers.

Program *SIP* for producing a diffractometer steering tape and program *SIMSA* for evaluating the output tape were written by R. Norrestam. Lorentz polarization and absorption corrections were performed by program *DATAPH* (Coppens, Leiserowitz & Rabinovich, 1965, modified by P. Coppens & W. C. Hamilton, U.S.A., and I. Carlbom, Sweden). Structure factor and Fourier calculations were performed by program *DRF* (A. Zalkin, U.S.A., modified by R. Liminga & J.-O. Lundgren, Sweden, by O. Lindgren, Sweden, and by A. G. Nord & B. G. Brandt, Sweden).

Program *FAME* (R. B. K. Dewar & A. L. Stone, U.S.A., modified by R. Karlsson, Sweden) was used for calculating Wilson plot and *E* values. Phase-determination program were *TRISS* for generating triple-phase relations and *NONCE* for the automatic solution of triple-phase relations (R. Norrestam).

Three least-squares programs in *World List of Crystallographic Computer Programs* (1966) were used: block-diagonal matrix program *SFLS* (No. 6023, modified by B. G. Brandt, Sweden) and full-matrix programs *LALS* (No. 384, modified by A. Zalkin, U.S.A., J.-O. Lundgren, R. Liminga & C.-I. Bränden, Sweden, by O. Lindgren, Sweden, and by B. G. Brandt, Sweden) and *LINUS* (No. 360, modified by W. C. Hamilton & J. A. Ibers, U.S.A., and by I. Carlbom, Sweden). Interatomic distances and bond angles were computed by program *DISTAN* (A. Zalkin, U.S.A., modified by A. G. Nord & B. G. Brandt, Sweden).

The HFS scattering factors given by Hanson, Herman, Lea & Skillman (1964) were used with the dispersion corrections calculated by Cromer (1965). The least-squares programs minimize the function $w(|F_o| - |F_c|)^2$ and the weights are calculated according to the expression $w = (\sigma_F^2 + k|F_o|^2)^{-1}$, where σ_F is the estimated standard deviation based on counting statistics and k is an empirical constant for which the value $k = 0.0033$ was found suitable. The weight analysis obtained in the final cycle of refinement is given in Table 4.

Table 4. *Weight analysis*

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

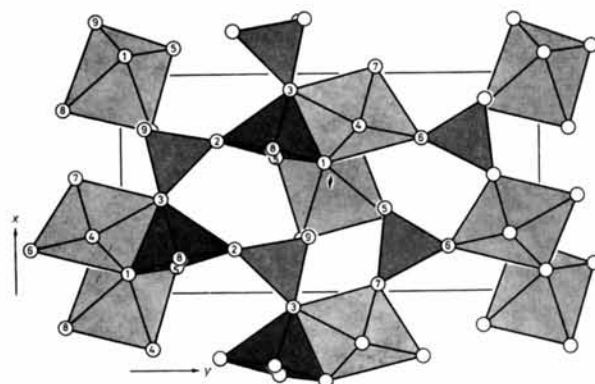| F_o	N	$\overline{w\Delta^2}$	$\sin \theta$ ($\times 10^4$)	N	$\overline{w\Delta^2}$
0·0– 37·6	67	1·02	0–2506	119	1·07
37·6– 43·3	68	0·94	2506–3158	101	0·88
43·3– 50·7	68	1·83	3158–3615	98	1·07
50·7– 59·5	68	0·97	3615–3979	77	0·83
59·5– 69·6	68	0·89	3979–4286	76	0·89
69·6– 81·3	68	0·84	4286–4555	65	1·01
81·3– 94·5	68	0·89	4555–4795	36	1·05
94·5–110·4	68	0·85	4795–5013	44	0·81
110·4–145·2	68	0·81	5013–5214	29	1·75
145·2–432·4	49	0·91	5214–5400	15	1·04

Fig. 1. Structure of $Cu_3Mo_2O_9$ viewed along the *c* axis. Only the coordination polyhedra around the metal atoms at $z \simeq 0$ and $\frac{1}{4}$ are shown. Other half of structure is related to this part by the screw axes parallel to *z*, one of which is indicated. The octahedra (light grey) with O(1) as central apex contain Cu(1), those with O(4) at the top contain Cu(3). The square pyramids (dark grey) contain Cu(2). The two tetrahedra (triangles in this projection) shown to the left contain Mo(2), those to the right Mo(1).

The strongest reflexions suffered from extinction, evident by $|F_o|$ being consistently smaller than $|F_c|$. An extinction-correction factor was introduced as a refinable parameter in *LINUS*. When *LALS* was used the 19 strongest reflexions were excluded from the refinement. The difference between the results obtained with these two procedures is negligible. Observed and calculated structure amplitudes are listed in Table 5. In this table the reflexions not used in the *LALS* refinement (although corrected for extinction here) are marked by an asterisk.

Description

Each molybdenum atom is surrounded by four oxygen atoms at the corners of an almost regular tetrahedron. The coordination around the copper atoms Cu(1) and Cu(3) is distorted octahedral while Cu(2) has only five oxygen neighbours at the corners of a distorted square pyramid.

The structure is visualized in terms of these coordination polyhedra in Fig. 1. The octahedra around Cu(1) share corners [O(1)] with equivalent octahedra, symmetry-related by the screw axis, to form a string running in the direction of the *c* axis and centered around $(0,0,z)$ and $(\frac{1}{2},\frac{1}{2},z)$. The Cu(3) octahedra each share two edges with the octahedra of this string to form a zigzag ribbon (Fig. 2). The other polyhedra are linked to these ribbons, the Cu(2) pyramids by edge-sharing with three neighbouring octahedra of the ribbon, and the molybdenum tetrahedra by corner-sharing. Along the *z* direction, the Cu(2) pyramids alternate with Mo(1) tetrahedra and the Cu(3) octahedra alternate with Mo(2) tetrahedra; thus, Cu(1) octahedra share four edges and the other two copper polyhedra share three

Table 5. *Observed and calculated structure amplitudes*

edges with other copper–oxygen polyhedra, to form a kind of aggregate infinite in the direction of the *c* axis. These aggregates are interconnected perpendicularly to *c* through corner-sharing between molybdenum tetrahedra and copper polyhedra.

This structure is believed unique. The other Cu(II) molybdate, whose structure is known, is $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968). It is also built up of both CuO_6 octahedra and CuO_5 square pyramids in addition to MoO_4 tetrahedra, but the arrangement is entirely different. There, six copper–oxygen polyhedra share edges to form spiral-shaped chain fragments, interconnected by MoO_4 tetrahedra.

Coordination and interatomic distances

The Mo–O distances, given in Table 6, are quite normal. The average values are 1·771 and 1·756 Å for Mo(1) and Mo(2), respectively, and can be compared with corresponding values for several other molybdates listed by Abrahams, Bernstein & Jamieson (1968), falling within the range 1·750–1·772 Å. In $Cu_{4-x}Mo_3O_{12}$ the corresponding mean value is 1·756 Å (Katz, Kasenally & Kihlborg, 1971). The O–Mo–O angles range from 104 to 114° and the O–O distances along the tetrahedral edges are all between 2·74 and 2·99 Å so that the MoO_4 tetrahedra are almost regular.

Table 6. *Interatomic distances*

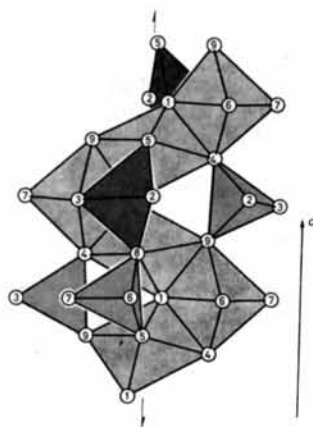|				
Cu(1)–O(1)	1·79 (9) Å		Cu(3)–O(7)	1·92 (2) Å
–O(1')	1·93 (9)		–O(1)	1·95 (2)
–O(9)	2·11 (5)		–O(4)	1·96 (3)
–O(5)	2·21 (3)		–O(9)	2·10 (5)
–O(4)	2·24 (3)		–O(6)	2·39 (2)
–O(8)	2·27 (3)		–O(3)	2·53 (2)
–Cu(2)	2·878 (14)		–Cu(1)	2·973 (14)
–Cu(3)	2·973 (14)		–Cu(1')	3·006 (14)
–Cu(3')	3·006 (14)		–Cu(2)	3·153 (5)
–Cu(2')	3·013 (14)			
Cu(2)–O(2)	1·90 (2)		Mo(1)–O(6)	1·69 (2)
–O(8)	1·90 (3)		–O(8)	1·74 (3)
–O(1)	1·92 (2)		–O(7)	1·79 (2)
–O(5)	2·12 (3)		–O(5)	1·86 (3)
–O(3)	2·18 (3)			
–Cu(1)	2·878 (14)		Mo(2)–O(3)	1·72 (3)
–Cu(1')	3·013 (14)		–O(4)	1·73 (3)
–Cu(3)	3·153 (5)		–O(2)	1·74 (2)
			–O(9)	1·83 (5)

Fig. 2. Part of the structure seen perpendicular to a plane defined by the *c* axis and Cu(3) [situated in the octahedra behind O(6) and O(3)]. The zigzag ribbon of octahedra is clearly visible and some of the CuO_5 pyramids and MoO_4 tetrahedra coupled to this are also shown. As in Fig. 1 the square pyramids are shaded darkest.

The coordination around Cu(1) is rather unusual with respect to the deformation of the CuO_6 octahedron. Usually one encounters the typical Jahn–Teller

distortion with four closer 'equatorial' bonds and two longer 'polar' bonds, and this normal type is found in the present structure around Cu(3). The distortion is reversed for Cu(1), however, as the two opposite 'polar' bonds are the shortest. The standard deviations for these distances are very large, however.

Atom Cu(2) is definitely 5-coordinated; the five oxygen atoms are within 2·18 Å while the sixth next nearest oxygen is 3·6 Å away. The coordination, distorted square pyramidal, as indicated in Fig. 3, is not unusual for divalent copper and is present for example in $CuMoO_4$. The four basal Cu–O bonds are slightly longer than in $CuMoO_4$, the averages being 1·956 and 1·928 Å, respectively, while the apical bond, 2·17 Å, is considerably shorter than that in $CuMoO_4$, which is 2·341 Å.

The oxygen atoms have different bonding patterns. Atom O(1) is bonded to four copper atoms, but O(2), O(6) and O(7) are bonded to one molybdenum and one copper atom, while the remaining five oxygen atoms are each linked to one molybdenum and two copper atoms. No oxygen–oxygen approach is closer than 2·61 Å.

Conclusions

No obvious relationship exists between the present structure and that of the reduced molybdate $Cu_{4-x}Mo_3O_{12}$ ($x \approx 0·15$) (Katz, Kasenally & Kihlborg, 1971) though they contain the same types of coordination polyhedra. This is interesting since the crystallographic data for $Cu_{4-x}Mo_3O_{12}$ are identical with those for '$Cu_3Mo_2O_8$' reported by Thomas, Herzog & McLachlan (1956) to take part in a reversible evolution and up-take of oxygen with the present phase. The difference in the structures seems to exclude such a reaction with the molybdates in the solid state.

The crystal structures of five molybdates and tungstates of copper are now known. These are $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968), $Cu_3Mo_2O_9$, $Cu_{4-x}Mo_3O_{12}$ ($x \approx 0·15$), $CuWO_4$ (Kihlborg & Gebert, 1970) and Cu_3WO_6 (Gebert & Kihlborg, 1969). It is remarkable that these structures appear quite unrelated to each other. Although there are structural elements of wolframite type in $Cu_{4-x}Mo_3O_{12}$ there is no further similarity with the wolframite-type structure of $CuWO_4$.

Molybdenum is consistently tetrahedrally coordinated while tungsten occurs 6-coordinated within slightly distorted octahedra. This difference is found in other cases with these elements in the hexavalent state. A
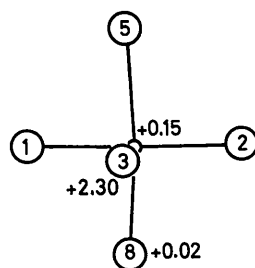

Fig. 3. Coordination around Cu(2) projected on to a plane defined by O(1), O(2) and O(5). Heights in Å of the other atoms above this plane are indicated.

tendency in the same direction can be observed in the trioxides. Although in both MoO_3 and WO_3 the metal atoms can be regarded as octahedrally coordinated, the distortion is much greater in the case of MoO_3 and is such as to justify a description in terms of tetrahedral coordination (Kihlborg, 1963).

References

ABRAHAMS, S. C., BERNSTEIN, J. L. & JAMIESON, P. B. (1968). *J. Chem. Phys.* **48**, 2619.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

GEBERT, E. & KIHLBORG, L. (1969). *Acta Chem. Scand.* **23**, 221.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.

KATZ, L., KASENALLY, A. & KIHLBORG, L. (1971). *Acta Cryst.* **B27**, 2071.

KIHLBORG, L. (1963). *Ark. Kemi* **21**, 357.

KIHLBORG, L. & GEBERT, E. (1970). *Acta Cryst.* **B26**, 1020.

KOHLMULLER, R. & FAURIE, J.-P. (1967). *C. R. Acad. Sci., Paris,* **C267**, 1751.

NASSAU, K. & SHIEVER, J. W. (1969). *J. Amer. Ceram. Soc.* **52**, 36.

THOMAS, I. D., HERZOG, A. & McLACHLAN, D. JR (1956). *Acta Cryst.* **9**, 316.

World List of Crystallographic Computer Programs (1966). 2nd ed., IUCr. Programs 360, 384 & 6023.