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New Structure Determination of Murdochite, Cu_6PbO_8

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Abstract. $M_r = 716{\cdot}4$, cubic, space group $Fm3m$, $a = 9{\cdot}224\ (2)$ Å, $V = 784{\cdot}8\ (3)$ Å^3, $Z = 4$, $D_x = 6{\cdot}06$ Mg m^{-3}, $5{\cdot}9 \leq D_m \leq 6{\cdot}7$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 37{\cdot}55$ mm^{-1}, $T = 295$ K. Final $R = 0{\cdot}027$ for 255 unique observed reflections. The structure consists of $[PbO_8]$ cubes with Cu^{2+} ions spanning the 12 edges of the O_8 cubes building up a three-dimensional network to give a square-planar $[CuO_4]$ coordination. Halogen ions which occupy the interstices complete a (4 + 2) elongated $[CuO_4X_2]$ octahedron. The four Cu—O separations are 1·921 (1) Å and the Cu—X separations 3·261 (2) Å. Therefore, murdochite is not a representative of a compound with an undistorted octahedral copper coordination (dynamic Jahn–Teller effect) as proposed by Christ & Clark [*Am. Mineral.* (1955). **40**, 907–916]. This fact is consistent with thermoanalytical measurements. In view of the varying content of chloride and bromide in natural samples of murdochite its general formula may best be described as $Cu_6PbO_{8-x}(Cl,Br)_{2x}$, with $x \leq 0{\cdot}5$.

Introduction. From the observed stoichiometry $Cu_{6\cdot1}Pb_{0\cdot9}O_{8\cdot0}$ the idealized composition Cu_6PbO_8 was proposed (Fahey, 1955) for the rare mineral murdochite.

Based on 93 independent reflections from Weissenberg photographs a sodium chloride structure-type for $Cu_6Pb\square O_8$ with an ordered arrangement of the metal ions and vacant sites was proposed (Christ & Clark, 1955). This structure was refined to an R value of 0·17. Both metal ions show an octahedral coordination by six O atoms with M—O distances of 6 × 2·30 Å.

Since this structure contained an undistorted $[CuO_6]$ octahedron, it seemed possible that murdochite might represent a system showing a dynamic Jahn–Teller effect at room temperature. In this case, on cooling the compound cooperative long-range interactions between the copper(II) octahedra could be expected to become strong enough to cause a freezing of the dynamic to a static Jahn–Teller effect. Such phase transitions may be detected by differential scanning calorimetry (Dubler, Matthieu & Oswald, 1975). However, no phase transition occurred on cooling murdochite from room temperature to 90 K on a Perkin–Elmer differential scanning calorimeter DSC-2.

Moreover, the Cu—O distances of 2·30 Å in the proposed undistorted CuO_6 octahedron in murdochite are inconsistent with the well known crystal chemistry of copper(II) compounds. This can be demonstrated by a plot of the tetragonality T (defined as the mean in-plane bond length R_S divided by the mean out-of-plane bond length R_L) *versus* R_S and R_L using the data for different (4 + 2) distorted CuO_6 octahedra. If structures of non-chelated copper(II) compounds only are used for such a plot, a value of about 2·08 Å is predicted for Cu—O distances of an undistorted CuO_6 octahedron (Dubler, 1977).

Table 1. *Analytical data of murdochite, respective to various localities* (*Burke & Maaskant,* 1970)

	Tchah–Khuni, Iran	Hansonburg, New Mexico	Ideal composition for Cu_6PbO_8
CuO (%)	61·6	64·4	66·61
PbO_2 (%)	32·4	31·0	33·39
Cl (%)	4·6	3·0	—
Br (%)	1·5	1·5	—
Sum (%)	100·1	99·9	100·0
Cu/Pb	5·70	6·24	6·00

Using electron-microprobe analysis, Burke & Maaskant (1970) observed that natural murdochite contains significant amounts of chlorine and bromine. Table 1 gives a summary of the analytical data. The authors proposed that chloride and bromide ions could replace oxygen in the crystal lattice. With regard to the Cu/Pb variance they suggested the general formula $Pb_{1\pm x}Cu_{6\pm x}(O,Cl,Br)_8$ for murdochite.

In view of all these inconsistencies we have redetermined the crystal structure of murdochite.

Experimental. Winchell & Wenden (1969) obtained murdochite under hydrothermal conditions at 543 K as a by-product of the synthesis of diaboleïte, $Pb_2CuCl_2(OH)_4$, from solutions of $CuCl_2.2H_2O$ and $Pb(OH)_2$. Our attempts to reproduce these results, however, were not successful. The material for the investigation was kindly supplied by Dr P. Bariand (Paris) and Dr J. Ottemann (Heidelberg) who provided specimens of murdochite from the Hansonburg mining district and the Tchah–Khuni mine respectively.

Hansonburg sample, black cube, two plane faces showing re-entrant angles, 0·09 × 0·11 × 0·09 mm, Gandolfi techniques, space group probably $Fm3m$ [systematic absences, hkl:$h + k, k + l, (l + h) = 2n + 1$; hhl:$(l + h) = 2n + 1$ ↻; $0kl$:$(k,l) = 2n + 1$ ↻] by

Weissenberg photographs ($hk0$, $hk1$, $hk2$, $hk3$ and $hk4$), $F(000) \cong 1358$, accurate cell dimensions from least-squares fit of 12 reflections, Picker FACS-I four-circle diffractometer, θ–2θ scan, $2 < 2\theta < 100°$, scan range 1·8° with allowance for α_1, α_2 dispersion, scan speed 1° min^{-1}, backgrounds counted at each end of scan for 20 s, 1723 total + three standard reflections, no significant variations, 258 independent, 255 with $I > 3\sigma(I)$; for absorption correction purposes (min. 7·58, max. 14·70) the crystal shape had to be idealized, corresponding maximum error about 10% on F^2; program system XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a CDC 6400/6500 computer at the ETH Zürich; atomic scattering factors of Pb^{4+}, Cu^{2+}, O^{2-}, Cl^- and Br^- computed according to Cromer & Mann (1968), function minimized in least-squares refinement $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma_F^2$.

Calculations were started in space group $Fm3m$. The positions of the heavy atoms could be deduced from a three-dimensional Patterson synthesis. The four Pb atoms lay in the special position 4(a) (0,0,0) and the 24 Cu atoms in the special position 24(d) $(\frac{1}{4},\frac{1}{4},0)$. Refinement of the individual thermal parameters of these heavy atoms yielded a conventional R value of 0·15. The positions of the Pb^{4+} ions agreed with those initially assumed by Christ & Clark (1955), whereas, in contrast to our results, these authors proposed a statistical distribution of the 24 Cu^{2+} over the 28 sites of the positions 24(d) and 4(b) $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. A difference Fourier map showed further peaks at the special positions 4(b) and 32(f). No peaks were found at the positions 8(c) and 24(e), where Christ & Clark (1955) had detected O atoms. The smaller peaks [position 32(f)] were assigned to the 32 O^{2-} in the unit cell.

In view of the varying chlorine and bromine content of murdochite from different localities (Table 1) we assumed that position 4(b) can be occupied statistically either by Cl or by Br atoms. The positioning of halogen atoms in 4(b) significantly improved the reliability indices of further refinements.

According to the analytical results of Burke & Maaskant (1970), refinements were started with a chloride:bromide atom ratio of 4·5:1. The total occupancy of the halogen site being $2x$, the occupancy of the oxygen position was constrained to $1 - \frac{x}{8}$. These constraints fulfil the requirements of electroneutrality of the compound as expressed by the formula $Cu_6PbO_{8-x}(Cl, Br)_{2x}$. Initial refinements with fixed temperature factors for the halogen atoms varying their occupancy factors and the constrained occupancy factor of the O atom resulted in a total occupancy factor $2x$ of about 1·0 for the halogen position. Starting values of 4·5:1 for the chloride:bromide ratio however resulted in oscillating, non-reasonable refinements. Best results were obtained with chloride:bromide ratios of about 1·8:1. The final refinement was carried out with a fixed value of $2x = 1·0$ varying the temperature parameters of all atoms, the x coordinate of the O atom and the occupancy factor of the Cl atom. The population parameters of the Br atom and of the oxygen position were constrained according to the requirements given above. Corrections for secondary extinction and for anomalous dispersion for Pb and Cu were also included. Final R values are $R = 0·027$ and $R_w = 0·026$.

The resulting occupancy of the oxygen position is 0·94; the content of a unit cell of murdochite therefore can be described as $Pb_4Cu_{24}O_{30}\square_2(Cl, Br)_4$. Keeping in mind the strong correlation between occupancy factors and thermal parameters of the halogen atoms in the refinements, however, we cannot exclude small deviations of the maximum amount of four halogen atoms per unit cell or of the chloride:bromide ratio of 1·8:1 by this crystal-structure determination. Attempts to replace $\frac{1}{12}$ of the Cu^{2+} ions on site 24 (d) by Pb^{4+} ions instead of assuming oxygen vacancies to obtain electroneutrality of the compound resulted in non-reasonable refinements of the structure and higher R values.

For comparison we also carried out least-squares refinements of our diffraction data of murdochite using the structure parameters of Christ & Clark (1955) as initial values. This resulted in a final R value of 0·129.

Positional coordinates and vibrational parameters are listed in Table 2.* The resulting thermal values are rather small in murdochite. This may be due to problems with the correction for absorption effects within the irregular-shaped data crystal.

Discussion. The structure of murdochite can be described as follows: edges of $[PbO_8]$ cubes are spanned by Cu^{2+} ions building up a three-dimensional network to give a square-planar CuO_4 arrangement. Halogen ions complete a (4 + 2) elongated $CuO_4(Cl, Br)_2$ octahedron. Figs. 1 and 2 show the arrangement of

Table 2. *Positional and thermal parameters of murdochite*

Standard deviations of the last digit calculated in the final least-squares refinement are given in parentheses.

	Position	x	y	z	Occupancy	U(Å^2 × 10^2)
Pb	4(a)	0·0	0·0	0·0	1·0	0·65 (1)
Cu	24(d)	0·25	0·25	0·0	1·0	0·47 (3)*
O	32(f)	0·1429 (2)	0·1429 (2)	0·1429 (2)	0·94	0·55 (3)*
Cl	4(b)	0·5	0·5	0·5	0·64 (2)	4·8 (9)
Br	4(b)	0·5	0·5	0·5	0·36	2·0 (3)

* Isotropic thermal parameters are those calculated before anisotropic refinement.

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* Lists of structure amplitudes and anisotropic thermal parameters for Cu and O have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38129 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

PbO_8 and CuO_4X_2 polyhedra within the structure. The stereochemistry of the copper and the lead coordination polyhedra is represented in Figs. 3 and 4. Metal–metal distances are: Cu—Cu = 3·261 (2), Cu—Pb = 3·261 (2) and Pb—Pb = 6·522 (2) Å.

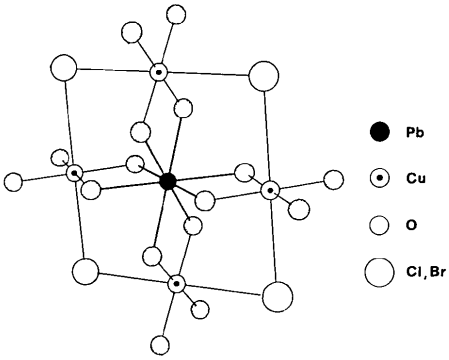

Fig. 1. Partial view of the structure of murdochite.

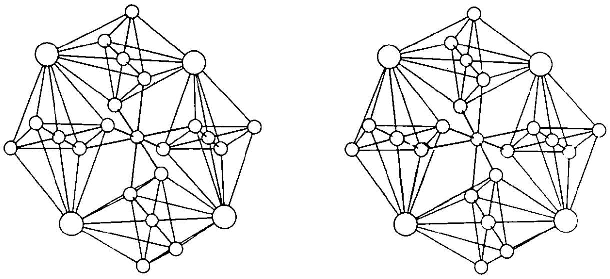

Fig. 2. Stereodrawing illustrating the linking of PbO_8 cubes and CuO_4X_2 octahedra.

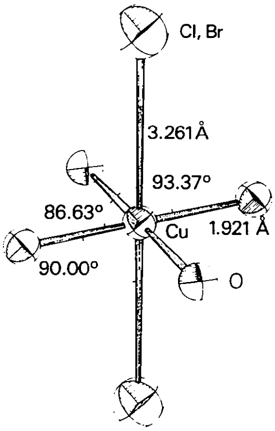

Fig. 3. Geometry of the CuO_4X_2 octahedron in murdochite. E.s.d.'s: Cu—O 0·001, Cu—X 0·002 Å, bond angles 0·04°.

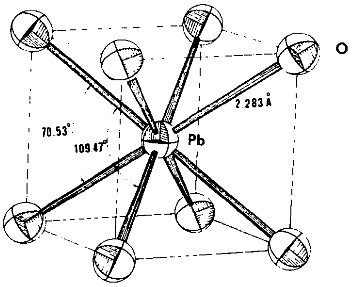

Fig. 4. Geometry of the PbO_8 cubes in murdochite. E.s.d.'s: Pb—O 0·001 Å, bond angles 0·006°.

The Cu—O distances of 4 × 1·921 (1) Å in the CuO_4X_2 octahedron are rather short compared with similar compounds (Dubler, Korber & Oswald, 1973) but in good agreement with the magnetic properties of murdochite: above room temperature the Curie–Weiss law is satisfied with $\theta = -700 \pm 50$ K. The effective magnetic moment per Cu^{2+} ion was found to be $1 \cdot 75 \pm 0 \cdot 02$ BM ($1\text{ BM} = 9 \cdot 27 \times 10^{-24}$ JT^{-1}), which is very near the value for complete orbital quenching (Edwards, 1955).

Examples of structural studies which definitely establish coordination numbers greater than six for Pb^{IV} are few in number, and all involve coordination wholly or largely by pairs of O atoms in chelating ligands (Wells, 1975). Usually an octahedral environment is found for Pb^{4+} as in PbO_2 (6 × 2·18 Å) or Pb_3O_4 (6 × 2·14 Å). The longer Pb—O distances of 8 × 2·28 Å found for murdochite are entirely consistent with the greater steric demands of eightfold coordination over sixfold coordination.

The O^{2-} ion is nearly tetrahedrally surrounded by one Pb^{4+} and three Cu^{2+} ions with bonding angles of 101·42 (1) and 116·18 (2)°. The halogen ions are surrounded by twelve Cu^{2+} ions at a distance of 3·261 (2) Å, forming a four-capped cube.

As a consequence of this new structure determination of murdochite an extension of its original formula Cu_6PbO_8 into $Cu_{6\pm x}Pb_{1\pm x}(O, Cl, Br)_8$ as proposed by Burke & Maaskant (1970) is inadequate, since the halogen ions occupy positions which are structurally independent of the oxygen position. The formula $Cu_6PbO_{8-x}(Cl, Br)_{2x}$ with $x \leq 0 \cdot 5$ given in this paper takes into consideration our structural results.

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Room-Temperature Structure of Carbon Monoxide at 2·7 and 3·6 GPa

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Abstract. A single crystal of CO was grown at room temperature in a high-pressure Merrill–Bassett diamond cell and examined by X-ray diffraction at 2·7 and 3·6 GPa. At 4·2 GPa the sample appeared to undergo a photochemical change induced by the weak laser light used to make ruby fluorescence pressure measurements. The unit cell is hexagonal, space group $P6_3/mmc$, with two molecules per unit cell, which is the same as that of β-CO near the triple point. At $P = 2·7$ GPa the lattice constants are $a = 3·615$ (1) and $c = 5·880$ (1) Å, and at 3·6 GPa they are $a = 3·532$ (1) and $c = 5·744$ (2) Å, giving molar volumes very near to those for β-N_2 under similar conditions. The final R_w, refined from ten observations, is 0·103 for a model with molecules tilted 49° from the c axis, statistically disordered, and randomly polarized. Calculations using a Gordon–Kim electron-gas model show that the $P6_3/mmc$ structure with randomly polarized CO molecules should have a minimum energy at a tilt angle of 50°, while polarized molecules give 48°. The melting pressure of CO at room temperature is about 2·6 GPa and is considerably lower than published measurements would indicate.

Introduction. Recent experimental and theoretical studies of molecular crystals have been aimed at a detailed understanding of intermolecular potentials, which determine the way physical properties vary with pressure and temperature. Using improved models and more powerful computing techniques, we can now predict with some success the crystal structures and phase diagrams of a few simple molecules (LeSar & Gordon, 1982).

N_2 and CO constitute a useful pair of molecules for separate study because they show many striking similarities, especially at low pressure (Raich & Mills, 1971). The two molecules are isoelectronic, have the same molecular size and weight, and condense into liquids with almost identical molar volumes. Liquid CO and N_2 freeze at triple points of 68·15 and 63·14 K, respectively, giving a disordered hexagonal solid, the β phase, which on further cooling transforms into an ordered cubic structure, the α phase. The crystallographic transition occurs at 61·6 K for CO and 35·6 K for N_2 and is driven primarily by electric quadrupole–quadrupole interactions.

For many years a controversy brewed over whether the molecules in α-N_2 are centrosymmetric in space group $Pa3$ (Ruhemann, 1932; Bolz, Boyd, Mauer & Peiser, 1959; Hörl & Marton, 1961; Schuch & Mills, 1970; Venables, 1970; Kjems & Dolling, 1975) or whether they are slightly shifted along the cube diagonals giving space group $P2_13$ (Vegard, 1929; Jordan, Smith, Streib & Lipscomb, 1964; Brookeman, McEnnan & Scott, 1971; LaPlaca & Hamilton, 1972; Wachtel, 1972). A definitive electron-diffraction study, however, by Venables & English (1974) shows that twinning of the (111) planes in the $Pa3$ structure can explain much of the evidence that led previously to the assignment of space group $P2_13$.

There is also dispute about the exact nature of the disorder in β-N_2. Streib, Jordan & Lipscomb (1962) reported the space group to be $P6_3/mmc$ with molecules precessing around the c axis at an angle of about 55°, whereas Press & Hüller (1978) favor a spherically disordered model from a careful reanalysis of X-ray, NQR, and theoretical work.

The structure determinations of α-CO are likewise conflicting (Lipscomb, 1964). From X-ray measurements, Krupskii, Prokhvatilov, Erenburg & Yantsevich (1973) found the $Pa3$ space group, while Vegard (1930)

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