Acta Cryst. (1956). 9, 316

The crystallography of two compounds containing the oxides of copper and molybdenum.

By Ivor D. Thomas,* Arno Herzog† and Dan McLachlan, Jr.,‡ *University of Utah, Salt Lake City, Utah, U.S.A.*

(*Received* 10 *October* 1955)

The purpose of this communication is to report the unit-cell dimensions and space groups of two compounds, $Cu_3Mo_2O_9$ and $Cu_3Mo_2O_8$.

When mixtures of cupric nitrate and ammonium molybdate are heated, the gases escape to leave the oxides of the metals. Further heating causes compounds of the oxides to be formed. When the heating is continued through the melting points, an evolution of oxygen takes place in quantities which are a function of the composition, as shown in Fig. 1.

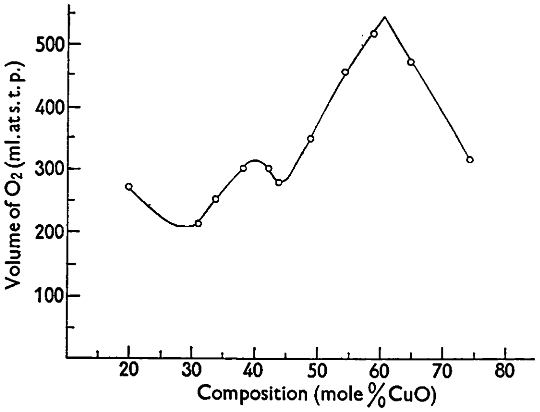

Fig. 1. The evolution of oxygen as a function of composition. The temperatures of the samples at the time of oxygen evolution were used in this work in order to standardize the gas volumes but are not recorded or discussed in this paper.

The reversibility of the oxygen evolution is indicated in Fig. 2, where the sample is taken through two heating and cooling cycles. By very careful chemical procedures it was shown that the following chemical reaction takes place:

$$Cu_3Mo_2O_9 \rightleftharpoons Cu_3Mo_2O_8 + \tfrac{1}{2}O_2 \,.$$

When molten mixtures of approximately 66 mole% CuO are slowly cooled in an oxygen atmosphere, beautiful blue-black needle-like crystals of $Cu_3Mo_2O_9$ are formed about 1 cm. long and ½ mm. thick. Cooling in the absence of oxygen produces agglomerated crystals of $Cu_3Mo_2O_8$ having poorly defined shapes.

Single-crystal X-ray data, confirmed by powder data, give the following crystallographic information:

	Higher oxide	Lower oxide
Space group	*Pna*	$P2_12_12_1$
a (Å)	7·78	11·02
b (Å)	14·64	17·58
c (Å)	6·90	5·03
Cell volume (Å^3)	785·91	974·46
Calculated density (g.cm.$^{-3}$)	4·454	3·4802

For references to other systems which give off oxygen as a function of temperature and composition, the following authors are cited: Prandtl & Meerschhause, 1907, 1908; Flood, Krog & Sörum, 1946; Tropov & Borisento, 1950; Thomas, 1951.

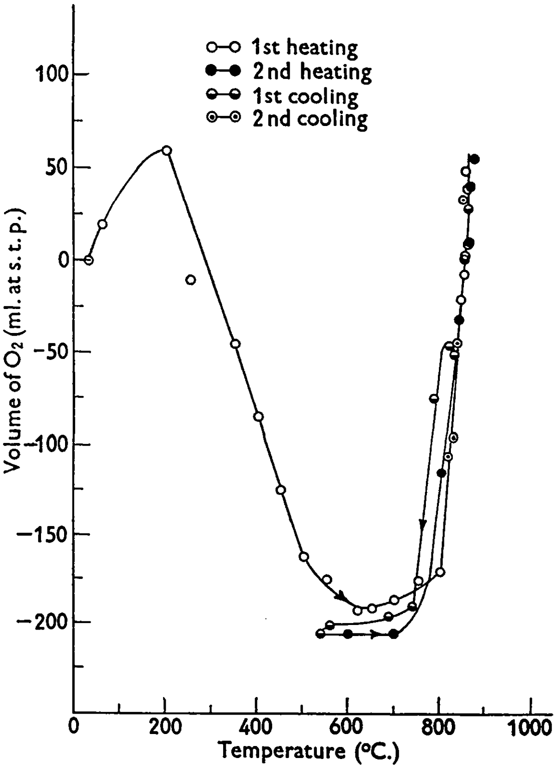

Fig. 2. The evolution and take-up of oxygen as a function of temperature.

The authors wish to thank D. J. Hugh Hamilton, Head, Utah Engineering Experiment Station, and Dr John R. Lewis, Head, Department of Metallurgical Engineering, for facilities and grants which made this investigation possible. We also wish to thank the Monsanto Chemical Company for a fellowship which made a portion of this work possible.

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* Now at Hanford Works, General Electric Company, Richland, Washington, U.S.A.

† Now at Research and Engineering Division, Monsanto Chemical Company, Dayton 7, Ohio, U.S.A. Mr Herzog was supported in this work by a fellowship from the Monsanto Chemical Company.

‡ Now at the Stanford Research Institute, Menlo Park, California, U.S.A.

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Acta Cryst. (1956). **9**, 317

The determination of absolute configuration by the use of an internal reference asymmetric centre.

By A. McL. MATHIESON, *Chemical Physics Section, Division of Industrial Chemistry, C.S.I.R.O., Box 4331, G.P.O., Melbourne, Australia*

(*Received* 21 *October* 1955)

Bijvoet, Peerdeman & van Bommel (1951*a*) have shown how X-ray analysis can determine absolute configuration by using the anomalous scattering of X-rays near an absorption edge. In particular, the absolute configurations of D(+)-tartaric acid (Bijvoet, Peerdeman & van Bommel, 1951*b*; van Bommel, 1953) and of D(−)-*iso*leucine (Trommel & Bijvoet, 1954) have been determined. Hence, all compounds which can be related chemically to tartaric acid or *iso*leucine are determined with respect to their optical behaviour.

For moderately complex organic compounds (20–50 atoms excluding hydrogen) of unknown or only partially known structure (Mathieson, 1955), it may not always be practicable to satisfy the experimental conditions required in respect of X-radiation (Bijvoet *et al.*, 1951*a*) or intensity measurement (Peterson, 1955). With such large molecules, a more direct method of determining the absolute configuration would be to introduce an additional but *known*† asymmetric centre in the form of a derivative. Then X-ray analysis of this diastereoisomer, e.g. $(-)X.\mathrm{L}(-)A^*$, where X is the compound of unknown configuration and A^* is the compound or radical of known configuration, would permit definition of the absolute configurations of the asymmetric centres in the large molecule, X, by reference to the known asymmetric group A^*.

As an indication of the very small amount of additional crystallographic effort involved in the application of this method, we may illustrate by reference to earlier analyses of moderately complex molecules. In the determination of the structure of lanostenol, $C_{30}H_{52}O$ (Fridrichsons & Mathieson, 1953), the iodoacetate derivative was used to provide the 'heavy atom'. As a result, only the *relative* configurations of the asymmetric centres in lanostenol could be deduced from this analysis. If, instead, one lanostenyl iodochloroacetate diastereoisomer,

$$\text{e.g. } (+) \text{ or } (-)\ \mathrm{ICl}\overset{*}{\mathrm{C}}\mathrm{HCOOC}_{30}\mathrm{H}_{51},$$

had been analysed, the absolute configuration would have been achieved with only one more atom involved in all calculations. Also, in the X-ray analysis of *iso*cryptopleurine methiodide (Fridrichsons & Mathieson, 1954, 1955) the replacement of the methyl group attached to the nitrogen atom by an asymmetric radical,

$$\text{e.g. D or L } \mathrm{C_2H_5(CH_3)}\overset{*}{\mathrm{C}}\mathrm{H},$$

would have yielded the absolute configurations of the other asymmetric centres.

This method of introducing a known asymmetric centre as an internal reference has several practical advantages: (1) it does not require special radiations; (2) it has wide application since the reference asymmetric centre can be introduced in the most convenient form either as part of a simple derivative or where possible as solvent of crystallization; (3) only one crystal and one set of crystal data are needed; and (4) the additional computation involved is small.

The proposed method therefore provides an elegant technique whereby not only the structure but also the absolute configuration of a compound of unknown structure can be attained in one step. It is hoped to test this method in the near future.

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* Defined by reference to tartaric acid or *iso*leucine.

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