Å and 0·003 rad (0·2°) in the final cycle, the r.m.s. average of the translations of the rigid bodies totaled over all the rings is 0·082 Å. The same average over the rotations is 0·029 rad (1·7°). A second measurement of the similarily between the observed and calculated structures is the r.m.s. displacement of the atoms. Since the phenyl rings were refined as rigid bodies, the comparison must be made between the final atomic coordinates of the calculated structure and the idealized coordinates based on Daly's work. The r.m.s. displacements between the atoms of the two structures are then 0·174, 0·117 and 0·195 Å, respectively, for the three phenyl rings. The phosphorus atom is translated by 0·147 Å, and the total r.m.s. displacement over all the atoms is 0·165 Å. These shifts are small; the experimental structure appears to be well reproduced.

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The Crystal Structure of Bi2(MoO4)3

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The crystal structure of $Bi_2(MoO_4)_3$ has been determined by Patterson and Fourier methods. Refinement was carried out by a block-matrix least-squares method, with 1902 Mo $K\alpha$ intensity data. The final R is 3·7%. The space group is $P2_1/c$ with lattice constants $a = 7·685$ (6), $b = 11·491$ (16), $c = 11·929$ (10) Å, $\beta = 115·40$ (2)°. There are four molecules per unit cell. Distorted tetrahedra of oxygen ions surround the molybdenum ions and occur in pairs. The bismuth ions have eight oxygen neighbours and the Bi–O distances can be divided into two distinct groups.

Introduction

During the last ten years, bismuth molybdates have been successfully applied as catalysts to the oxidation of propene and butene and the ammoxidation of propene, yielding respectively acrolein, butadiene and acrylonitrile. Although in the recent literature many efforts have been made to relate the activity and the selectivity of these mixed oxide catalysts to their physical and chemical characteristics, the crystal structures of some bismuth molybdates were still unknown or had not been determined with great accuracy. Therefore, as part of an investigation into the possible dependence of the catalytic properties of bismuth molybdates on the atomic arrangement in these catalysts, the crystal structure of $Bi_2(MoO_4)_3$ was determined.

Experimental

Very pure $Bi_2(MoO_4)_3$ was prepared by coprecipitation of bismuth nitrate with a very large excess of molybdic acid, as described by Batist, Bouwens & Schuit (1972). From the powder thus obtained, single crystals were grown by zone-melting in an open quartz-glass vessel.

The compound was analysed X-ray spectrographically from the intensity of the emitted Bi $L\alpha$ and Mo $K\alpha$ radiation. The ratio Bi:Mo was 2:2·85 between the limits 2:2·80 and 2:2·93. It was not possible to detect

a significant difference in composition between the single crystals and the powder from which they were prepared.

The linear absorption coefficient for Mo $K\alpha$, high because of the presence of Bi, was calculated as $\mu = 378$ cm^{-1}. In order to avoid tedious and time-consuming computation of large absorption corrections, a single crystal was ground to a sphere of radius $r = 0.16$ mm, $\mu r = 6.0$.

About 3000 independent reflexions were measured at the Philips Research Laboratories at Eindhoven, with the new computer-controlled 4-circle diffractometer PW 1100 using Mo $K\alpha$ radiation filtered with a graphite monochromator. From this data set 1902 reflexions with intensities greater than $3 \times$ the estimated standard deviation were selected.

Corrections were applied for Lorentz and polarization effects, and for X-ray absorption, calculated from the data in *International Tables for X-ray Crystallography* (1959) and secondary extinction. The last correction, however, was very small, the constant c, calculated according to Zachariasen (1963), being 10^{-7}.

Calculations were made with an EL X8 computer. Least-squares refinement was carried out with a program written by Rietveld (1966).

Determination of the structure

The relation between the structures of tetragonal $CaWO_4$, scheelite, $I4_1/a$ and monoclinic $Eu_2(WO_4)_3$, $C2/c$, was revealed by Templeton & Zalkin (1963). Scheelite can be considered as a stacking up of Ca^{2+} and WO_4^{2-} ions. In $Eu_2(WO_4)_3$ every three Ca^{2+} ions have been replaced by two Eu^{3+} ions and a vacancy. These vacancies are ordered in planes parallel to the a and b axes. The elementary cell of $Bi_2(MoO_4)_3$, as determined from powder data, $a = 7.685$, $b = 11.491$, $c = 11.929$ Å, $\beta = 115.40°$, has almost the same dimensions as that of $Eu_2(WO_4)_3$, $a = 7.676$, $b = 11.463$, $c = 11.396$ Å, $\beta = 109.63°$. The space group of $Bi_2(MoO_4)_3$, $P2_1/c$, determined from systematic absences, is a subgroup of $C2/c$. From inspection of the data set it was apparent that we could not be dealing with a distorted $Eu_2(WO_4)_4$ structure.

Still the relation between $Bi_2(MoO_4)_3$ and $CaWO_4$, scheelite, was evident. Assuming that in $Bi_2(MoO_4)_3$ ordered cation vacancies occur, similar to the $Eu_2(WO_4)_3$ structure, but at different positions in the cell, these vacancies should occur on one of the following approximate positions:

(i)	4(e)	$x = \frac{3}{12}$	$y = \frac{3}{8}$	$z = \frac{3}{12}$
(ii)	4(e)	$x = \frac{7}{12}$	$y = \frac{1}{8}$	$z = \frac{5}{12}$
(iii)	4(e)	$x = \frac{11}{12}$	$y = \frac{1}{8}$	$z = \frac{1}{12}$

These values were obtained by subtracting $\frac{1}{4} . \frac{1}{4} . 0$ from the positions of Eu calculated by Templeton & Zalkin (1963). Alternatives (ii) and (iii) differ only in the choice of the origin. Calculating the vector set for both cases (i) and (ii) and comparing it with the Patterson function revealed clearly that (ii) was the correct choice. Alternative (i) would have yielded the same vacancy distribution as in $Eu_2(WO_4)_3$.

First the positional parameters of the metal ions were refined by successive Fourier syntheses, because initially least-squares refinement was unsuccesful. After four cycles six oxygen ions showed up and a complete model of the structure was obtained after three more cycles. From this point block matrix least-squares methods could take over. Anisotropic temperature factors were introduced for Bi and Mo and the oxygen ions were given individual isotropic temperature factors. Each time new variables were introduced the significance of the decrease of R was checked with Hamilton's (1965) tables, at a confidence level of 0.005. The final R on F value was 0.037 for 1902 independent reflexions, $I > 3$ times the standard deviation. R on I for these reflexions was 0.050.

From a difference Fourier synthesis no clear evidence of the presence of interstitial Bi could be found. Neither did it appear that the Mo locations were only partially filled. This could have been obscured however, by the use of too large temperature factors for the Mo ions. Least-squares refinement of the occupation numbers did not give results significantly contradictory to the stoichiometric model. Neither of the methods however, is a sensitive tool to prove the existence of small amounts of interstitial atoms or to decide whether or not a small number of vacancies occur, unless a very large set of extremely accurate intensity data is available.

The density, determined pycnometrically with carbon tetrachloride, was 5.97 g cm^{-3}, $D_x = 6.19$ g cm^{-3}. The deviation from the stoichiometric ratio Bi:Mo = 2:3 is caused by Mo vacancies. The ratio Bi:Mo, calculated from the density is Bi:Mo = 2:2.79, which is in good agreement with the results of the X-ray spec-

Table 1. *Atomic coordinates of* $Bi_2(MoO_4)_3$

The temperature parameters for Bi and Mo were calculated according to:
$$\exp[-(b_{11}h^2 + b_{12}hk + b_{13}kl + b_{22}k^2 + b_{23}kl + b_{33}l^2) \times 10^{-5}].$$
The temperature factor for the O ions is the common Debye–Waller factor.

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{22}	b_{33}
Bi(1)	0.25999 (8)	0.36188 (5)	0.25584 (5)	213 (10)	−6 (10)	118 (10)	100 (10)	−11 (10)	138 (10)
Bi(2)	0.90798 (10)	0.12976 (5)	0.08334 (6)	331 (10)	−66 (10)	217 (10)	103 (10)	−26 (10)	131 (10)
Mo(1)	0.0320 (2)	0.1114 (1)	0.4165 (1)	395 (20)	−40 (20)	140 (20)	74 (10)	11 (10)	126 (10)
Mo(2)	0.4218 (2)	0.1513 (1)	0.1089 (1)	168 (20)	−8 (20)	167 (20)	70 (10)	−16 (10)	198 (10)
Mo(3)	0.7341 (2)	0.3669 (1)	0.1952 (1)	229 (20)	−25 (20)	265 (20)	116 (10)	−35 (20)	240 (10)

Table 1 (cont.)

	x	y	z	B
O(1)	0·544 (2)	0·052 (1)	0·224 (1)	1·4 (2)
O(2)	0·936 (2)	0·054 (1)	0·256 (1)	0·9 (2)
O(3)	0·222 (2)	0·196 (1)	0·152 (1)	0·8 (2)
O(4)	0·864 (2)	0·208 (1)	0·412 (1)	1·1 (2)
O(5)	0·224 (2)	0·199 (1)	0·435 (1)	1·2 (2)
O(6)	0·620 (2)	0·205 (1)	0·072 (1)	1·1 (2)
O(7)	0·951 (2)	0·291 (1)	0·197 (1)	0·7 (2)
O(8)	0·507 (2)	0·316 (1)	0·198 (1)	1·2 (2)
O(9)	0·287 (2)	0·436 (1)	0·482 (1)	1·5 (2)
O(10)	0·128 (2)	0·448 (1)	0·082 (1)	0·8 (2)
O(11)	0·840 (2)	0·442 (1)	0·340 (1)	1·0 (2)
O(12)	0·692 (2)	0·468 (1)	0·084 (1)	1·9 (2)

trographical analysis. The atomic coordinates of $Bi_2(MoO_4)_3$ are given in Table 1.*

Discussion of the structure

Both $Eu_2(WO_4)_3$ and $Bi_2(MoO_4)_3$ can be considered as scheelite structures with ordered cation vacancies. In the $Eu_2(WO_4)_3$ structure these vacancies lie in planes parallel to **a** and **b** [Fig. 1(a)]. In the case of $Bi_2(MoO_4)_3$ they are in a somewhat more complex way concentrated in planes parallel to **b** and **c** [Fig. 1(b)]. This was confirmed by the fact that (100) was an imperfect cleavage plane.

Each Mo ion is tetrahedrally surrounded by two oxygen neighbours at an average distance of 1·72 Å and two at ca. 1·87 Å. Moreover an oxygen ion occurs in the vicinity of each MoO_4 tetrahedron at a distance of ca. 2·2 Å (Table 2). If this coordination of Mo by O were considered to be fivefold, the coordination polyhedron would be an irregular trigonal bipyramid. Pairs of these polyhedra share edges. In $Eu_2(WO_4)_3$

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* A list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30164 (14 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

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part of the WO_4 tetrahedra occur in similar pairs, but in $Bi_2(MoO_4)_3$ all MoO_4 tetrahedra form Mo_2O_8 groups. Not all these groups have exactly the same shape. One of the types possesses a centre of symmetry while the other does not (Fig. 2).

Table 2. Interatomic distances (Å) in $Bi_2(MoO_4)_3$

Standard deviations are equal to 0·01 Å.

Mo(1)–O(4)	1·69	Mo(2)–O(1)	1·72	Mo(3)–O(12)	1·68
Mo(1)–O(5)	1·72	Mo(2)–O(9)	1·73	Mo(3)–O(11)	1·78
Mo(1)–O(2)	1·85	Mo(2)–O(6)	1·86	Mo(3)–O(8)	1·86
Mo(1)–O(10)	1·91	Mo(2)–O(3)	1·89	Mo(3)–O(7)	1·87
Mo(1)–O(10)	2·25	Mo(2)–O(8)	2·13	Mo(3)–O(6)	2·30

Bi(1)–O(10)	2·12	Bi(2)–O(2)	2·16
Bi(1)–O(3)	2·22	Bi(2)–O(7)	2·24
Bi(1)–O(7)	2·32	Bi(2)–O(3)	2·32
Bi(1)–O(8)	2·34	Bi(2)–O(6)	2·32
Bi(1)–O(1)	2·61	Bi(2)–O(9)	2·61
Bi(1)–O(2)	2·64	Bi(2)–O(4)	2·68
Bi(1)–O(9)	2·75	Bi(2)–O(11)	2·78
Bi(1)–O(5)	2·94	Bi(2)–O(11)	2·85

Although Bi has 8 oxygen neighbours, the Bi–O contacts are not all equivalent. From Table 2 it is apparent that the Bi–O distances can be divided into two groups, the first with distances between 2·12 and 2·35 Å and the second with very large distances ranging from 2·60 to 2·93 Å.

Note: During the course of this investigation, we received a preprint of an article by Cesari, Perego, Zazetta, Manara & Notari (1971), in which a description of the structure was given. Their paper does not mention the exact composition of their sample nor does it contain a list of atomic parameters.
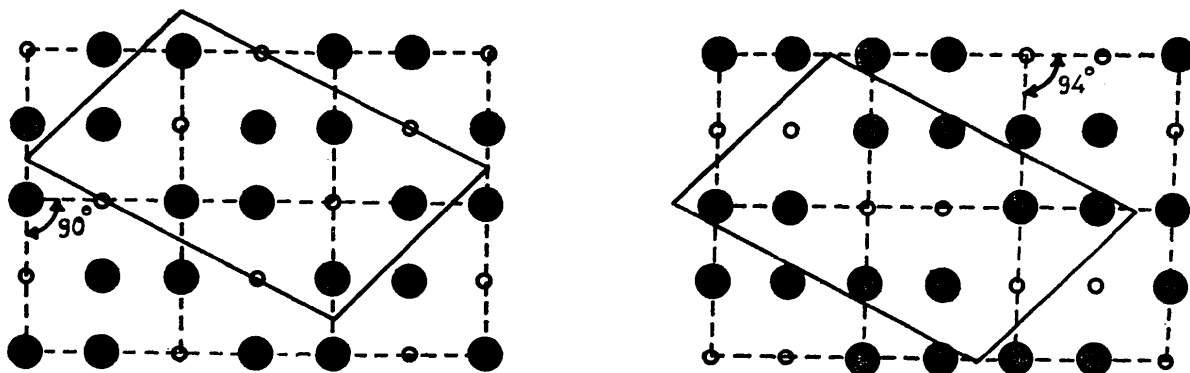
Fig. 1. (a) Projection along the b axis of the Eu sites in $Eu_2(WO_4)_3$. Large solid circles: occupied Eu sites. Small open circles: empty Eu sites. Broken lines: unit cells of $CaWO_4$. Solid lines: unit cell $Eu_2(WO_4)_3$. (b) Projection along the b axis of the Bi sites in $Bi_2(MoO_4)_3$. Large solid circles: occupied Bi sites. Small open circles: empty Bi sites. Broken lines: unit cells of $CaWO_4$. Solid lines: unit cell of $Bi_2(MoO_4)_3$.
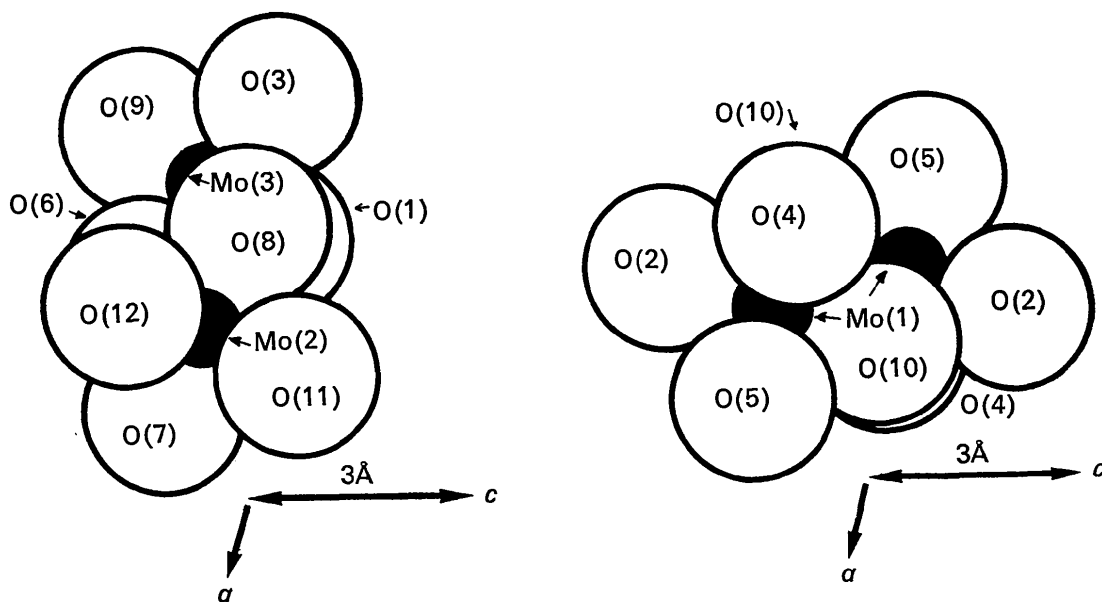
Fig. 2. (a) Projection along the b axis of the Mo_2O_8 groups formed by tetrahedra containing Mo(2) and Mo(3) (Table 1). (b) Projection along the b axis of the Mo_2O_8 groups formed by two tetrahedra containing Mo(1) (Table 1). These groups contain an inversion centre, while the others shown in (a) do not.

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Redetermination of the Structure of Bi2MoO6, Koechlinite

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The crystal structure of koechlinite has been redetermined by single-crystal X-ray analysis. The space group is $Pca2_1$, with cell dimensions: $a = 5.487$ (2); $b = 16.226$ (6); $c = 5.506$ (2) Å. There are four molecular units per unit cell. The structure was refined with block-matrix least-squares methods. The final R on F value was 8·7% for 788 independent reflexions, including the unobserved reflexions. Molybdenum is octahedrally surrounded by six oxygen ions. These octahedra share four corners with neighbouring octahedra in one plane. The other two apex ions points towards a BiO layer of the type that occurs, for example, in BiOCl.

Introduction

In a recent article Batist, Bouwens & Schuit (1968) state that the activity of bismuth molybdates as oxidation catalysts is related to the presence of corner-sharing MoO octahedra. This hypothesis was based on a model of the koechlinite structure as determined by

Zemann (1956). The intensity data Zemann used for his calculations were collected from a rather irregular and poorly defined specimen. The calculated absorption corrections may therefore be expected to be inaccurate because of the large linear absorption coefficient, $\mu = 698$ cm^{-1} for Mo $K\alpha$.

The difficulty of locating oxygen ions in the presence