



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 Bi_2MoO_6 , 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, $\mu = 698 \text{ cm}^{-1}$ for $\text{Mo } K\alpha$.

The difficulty of locating oxygen ions in the presence

of bismuth and molybdenum ions can be compared with that of finding the hydrogen atoms in an organic structure. It may be expected that quite good data are required to determine the oxygen positions in koechlinite without ambiguity.

Experimental

A single crystal of koechlinite, obtained from the Smithsonian Institution, Washington D.C. (cat. nr. B12489), was ground to a sphere of radius $r=0.0375$ mm. From this crystal all reflexions hkl and $hk\bar{l}$ were measured up to $\sin \theta/\lambda=0.72$, at the Philips Research Laboratories at Eindhoven, with the new automatic four-circle PW 1100 diffractometer, using Mo $K\alpha$ radiation filtered with a graphite monochromator.

The errors in the measurements were estimated by comparing the intensities of reflexions hkl and $hk\bar{l}$. The relative standard deviation was *ca.* 12% for intensities exceeding 0.3% of the strongest reflexion (Schulz & Huber, 1971; Schulz, 1971). The irregularities in the crystal shape were estimated under a microscope as 2% of the radius. From a graph presented by Jeffery & Rose (1964) the standard deviation in the intensities due to the non-ideality of the crystal shape was estimated to be *ca.* 12%, $\mu r=2.64$. The standard deviation calculated from azimuth-scan data around reflexions 002 and 060 was 11%. So it can be concluded that the errors in the intensity data are mainly due to the fluctuations in the radius of the spherical crystal.

The intensities of reflexions hkl and $hk\bar{l}$ were averaged. Corrections were applied for Lorentz and polarization factors and for absorption. Secondary extinction effects could not be detected. Least-squares refinements were carried out on an EL X8 computer, using a program written by Rietveld (1966).

The compound was analysed X-ray spectrographically. No deviation from the ideal ratio Bi:Mo=2:1, could be detected.

Determination of the structure

Inspection of the data set revealed that space group $Cmca$ could not be the correct one. The space group we determined was $Pca2_1$ (the a and c axes have been transposed). This space group does not contain an inversion centre. So the argument of Zemmann (1956), to exclude the possibility that molybdenum might be tetrahedrally surrounded by oxygen ions, does not hold. There are four molecular units per cell.

The systematically absent reflexions of space group $Pca2_1$, which were indeed not observed at a significant level, were removed from the data set, thus leaving 788 reflexions, observed and unobserved.

A model of the structure containing the metal ions at the positions found by Zemmann failed to refine directly with least-squares methods. The initial shifts were calculated from a Fourier synthesis. The metal ions were given individual isotropic temperature fac-

tors. Least-squares refinement of this model was quite straight forward now. After four cycles the oxygen positions showed up in a difference Fourier synthesis. After adding these oxygen ions to the model and assigning one isotropic temperature factor to all of them, refinement was continued. The final R on F value for 788 reflexions, observed and unobserved, was 0.087; the R on I for these reflexions was 0.059.

Individual isotropic temperature factors for the oxygen ions introduced at this stage had quite unrealistic values. Also the decrease in the R value after introducing them was far from being significant.

Space group $Pcam$ ($Pbcm$), although consistent with the observed systematic absences, is not the correct space group. The introduction of a mirror plane and an inversion centre is not justified by the data presented in Table 1. Refinement of the structure in space group $Cmca$ was unsuccessful. The temperature factors of the oxygen ions reached values greater than 5. As a result, the shifts in the positional parameters of the oxygen ions increased and after a few cycles of refinement, the R value increased rapidly.*

Table 1. Atomic coordinates of Bi_2MoO_6 , koechlinite

The temperature factors are the common Debye-Waller factors.

| | x | y | z | β |
|-------|-------------|------------|------------|-----------|
| Bi(1) | 0.5221 (6) | 0.4222 (4) | 0.9794 (7) | 0.63 (6) |
| Bi(2) | 0.4812 (6) | 0.0779 (4) | 0.9731 (5) | 0.54 (5) |
| Mo(1) | 0.0099 (10) | 0.2486 (5) | 0.0000 (0) | 0.47 (2) |
| O(1) | 0.039 (4) | 0.140 (2) | 0.099 (4) | 0.76 (11) |
| O(2) | 0.240 (9) | 0.999 (5) | 0.196 (9) | |
| O(3) | 0.25 (2) | 0.500 (5) | 0.26 (1) | |
| O(4) | 0.693 (4) | 0.236 (1) | 0.255 (5) | |
| O(5) | 0.214 (5) | 0.265 (1) | 0.350 (4) | |
| O(6) | 0.597 (5) | 0.358 (2) | 0.410 (4) | |

Discussion of the structure

Koechlinite can be considered as a stacking of planes alternately containing respectively $(BiO^+)_{2N}$ and $(MoO_4^{2-})_N$. These planes are perpendicular to the y direction. The arrangement as a whole is strongly related to the $LiBi_3O_4Cl_2$ structure and its isotypes, in which $(LiBi_3O_4)^{2+}$ forms an arrangement similar to that of BiO^+ in $BiOCl$ (*Structure Reports for 1947-1948*, 1951). In the $LiBi_3O_4Cl_2$ structure more complex ions like CO_3^{2-} can take the place of the halogen ions. To compensate for the extra negative charge, Li^+ must be replaced by Bi^{3+} . This compound, $Bi_2O_2CO_3$, is known as the mineral bismutite (*Structure Reports*). In $La_2O_2MoO_4$, La^{3+} takes the place of Bi^{3+} and the halogen ions have been replaced by separate MoO_4^{2-} tetrahedra.

In the koechlinite structure, however, the $(MoO_4^{2-})_N$ layer is built up by deformed MoO octahedra, sharing

* A table of structure factors has been deposited at the National Lending Library, England as Supplementary Publication No. SUP 30165 (9 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

four corners, [two O(4) and two O(5), Table 1], with neighbouring MoO octahedra in the same plane perpendicular to the y direction. The Mo–O distances in such a plane can be divided in two classes, the first with bond lengths of *ca.* 1.75 Å and the second with bond lengths of *ca.* 2.24 Å. The other two apex ions of the MoO octahedra, [O(1) and O(6), Table 1], point towards a $(\text{BiO}^+)_{2N}$ layer, one above and one below. These Mo–O bonds have intermediate lengths, 1.85 Å and 1.93 Å respectively (Table 2).

As all the bismuth ions have been shifted towards smaller a coordinates relatively to the oxygen ions in the BiO planes, [O(2) and O(3), Table 1], the Bi–O distances in that plane can be divided in two groups,

distances shorter than 2.3 Å and distances exceeding that value (Table 2). Each bismuth ion shares two more oxygen ions at approximate distances of 2.33 Å and 2.66 Å, [O(6) and O(1), Table 1] with two neighbouring MoO octahedra.

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Table 2. *Interatomic distances in koechlinite*

| | | | |
|------------|----------|------------|----------|
| Bi(1)–O(3) | 2.50 (8) | Bi(2)–O(1) | 2.72 (2) |
| Bi(1)–O(3) | 2.15 (8) | Bi(2)–O(1) | 2.29 (2) |
| Bi(1)–O(3) | 2.29 (8) | Bi(2)–O(2) | 2.21 (6) |
| Bi(1)–O(3) | 2.36 (7) | Bi(2)–O(2) | 2.50 (6) |
| Bi(1)–O(6) | 2.62 (3) | Bi(2)–O(2) | 2.33 (6) |
| Bi(1)–O(6) | 2.37 (3) | Bi(2)–O(2) | 2.25 (6) |
| Mo(1)–O(1) | 1.86 (3) | | |
| Mo(1)–O(4) | 2.24 (2) | | |
| Mo(1)–O(4) | 1.76 (2) | | |
| Mo(1)–O(5) | 2.24 (2) | | |
| Mo(1)–O(5) | 1.75 (3) | | |
| Mo(1)–O(6) | 1.93 (3) | | |

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The Crystal Structure of $(-)_589$ -Tris-(1,3-diaminopropane)cobalt(III) Chloride Monohydrate, $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$

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Crystals of $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ are monoclinic with space group $P2_1$. The cell dimensions are: $a = 12.871$ (6), $b = 7.545$ (2), $c = 9.360$ (6) Å and $\beta = 91.17$ (6)°, with two formula units in the unit cell. The structure was refined by anisotropic block-diagonal least-squares methods to an R value of 0.033 for 2806 observed reflexions collected by the diffractometer method. The structure is isotopic with its bromide analogue. The complex ion has an approximate threefold axis of rotation. The absolute configuration is A . The three six-membered chelate rings have the chair conformation. In one of the chelate rings the carbon atoms exhibit much greater thermal motion relative to those in the other chelate rings, suggesting a change in conformation in solution.

Introduction

Six-membered chelate rings have been a subject of extensive study on coordination compounds by the method of strain-energy minimization. Calculated values of conformational energy, however, are different

according to the choice of potential function (Geue & Snow, 1971; Gollogly & Hawkins, 1972; Niketić & Woldbye, 1973). Thus we have to rely primarily on the results of structure determination. The tris-(1,3-diaminopropane)cobalt(III) ion represents a prototype of a tris(bidentate) complex with three saturated six-membered chelate rings. The geometry of this complex ion was determined by crystal-structure analysis of $(-)_589$ - $[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ (Nomura, Marumo & Sai-

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