THE CRYSTAL STRUCTURE OF MROSEITE, CaTeO₆(CO₃)

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ABSTRACT

Mroseite crystallizes orthorhombic, space group Pbca, lattice constants \(a = 6.988(15)\), \(b = 11.201(10)\), \(c = 10.566(10)\) Å, cell content \(8 \times \text{CaTeO}_6(\text{CO}_3)\). The structure was determined from x-ray intensities collected on an automatic Weissenberg-type diffractometer. Full-matrix least-squares refinement for the 807 observed reflections, with anisotropic temperature factors for Te and Ca, and isotropic temperature factors for C and O resulted in \(R = 0.066\).

The structure contains \(\text{CO}_3\) groups of the usual dimensions. Calcium is irregularly-coordinated by eight oxygens. Considering only Te-O bonds from 1.85 to 2.05 Å, tellurium forms \(\text{TeO}_4\) groups with the oxygens that are not bonded to carbon. These \(\text{TeO}_4\) groups consist of two \(\text{TeO}_3\) pyramids with a common O-O edge. Oxygen neighbours of the carbonate group with Te-O = 2.31 and 2.55 Å complete the coordination around tellurium.

RÉSUMÉ

La mroséite se cristallise en orthorhombique avec un groupe spatial \(\text{Pbca}\), des dimensions de maille \(a = 6.988(15)\), \(b = 11.201(10)\), \(c = 10.566(10)\) Å et un contenu de \(8 \times \text{CaTeO}_6(\text{CO}_3)\). La structure a été déterminée par les intensités des rayons-x amassées sur un diffractomètre automatique de type Weissenberg. Un résultat \(R = 0.066\) a été obtenu comme raffinage par la méthode des moindres carrés à matrice entière pour les 807 réflexions observées avec des facteurs de température anisotropiques pour Te et Ca et des facteurs de température isotropiques pour C et O.

La structure contient des groupes \(\text{CO}_3\) de dimensions habituelles. Le calcium est coordonné irrégulièrement par huit oxygènes. En considérant uniquement les liens Te-O de 1.85 à 2.05 Å, le tellurium forme des groupes \(\text{TeO}_4\) avec les oxygènes qui ne sont pas liés au carbone. Ces groupes \(\text{TeO}_4\) consistent de deux pyramides \(\text{TeO}_3\) avec une arête commune O-O. Les oxygènes voisins du groupe carbonate avec Te-O = 2.31 et 2.55 Å complètent la coordination autour du tellurium.

(Traduit par le journal)

INTRODUCTION

Mroseite, a new orthorhombic tellurite mineral from Moctezuma, Sonora, Mexico, was recently described by Mandarino et al. (1975). These authors analyzed the mineral and determined the x-ray crystallographic constants as follows: lattice constants \(a = 6.93, b = 11.16, c = 10.54\) Å, space group \(\text{Pbca}\); cell content \(8[\text{CaCO}_3\text{TeO}_3]\).

As one would expect mroseite to contain the usual \(\text{CO}_3\) group, the mineral belongs to the class of inorganic compounds that consist of a salt-like part and an oxide part, i.e., formal "double compounds". Therefore, it was of interest to determine the crystal structure to learn (1) if the oxygens of the \(\text{CO}_3\) group participate in the coordination around tellurium and (2) what kind of polymerization of tellurium-oxygen units occurs in this mineral.

EXPERIMENTAL, AND STRUCTURE DETERMINATION

Mroseite from the type locality was used for the structure determination. X-ray intensities were measured from a tiny, irregular crystal fragment \((\sim 100 \times 60 \times 60 \mu\text{m})\) on an automatic two-circle Weissenberg-type diffractometer with Mo radiation (Zr filter). The crystal was mounted with [100] parallel to the goniometer axis. The reflections of the zero through the 6th layer line with sine \(\theta/x < 0.70\) Å\(^{-1}\) were taken into consideration, except for the \(h00\) reflections which cannot be measured with this experimental procedure.

Lattice constants were determined to be \(a = 6.988(15), b = 11.201(10), c = 10.566(10)\) Å (estimated errors in brackets), in good agreement with the values published by Mandarino et al. (1975). The space group \(\text{Pbca}\) given by the same authors was confirmed.

Of 936 crystallographically-independent reflections measured by the \(\omega\)-scan method, 807 with \(I_{\text{obs}} \geq 2\sigma(I)\) were treated as observed for all further calculations. The data were corrected for the Lorentz and polarization factors. Because of the small crystal size and the use of Mo radiation, no absorption correction was necessary.

A three-dimensional Patterson function yielded the tellurium position and a subsequent
Fourier summation gave the calcium and some of the oxygen positions. After a preliminary least-squares refinement of the Ca and Te coordinates, a three-dimensional Fourier synthesis clearly showed all the atoms of the unit cell.

After several cycles of isotropic least-squares refinement, $R = 0.08$ was reached. The comparison of $F_o$ and $F_e$ showed larger discrepancies for $\sim 5\%$ of the reflections, possibly caused by uncontrolled errors in the electronics. These were carefully remeasured. The structure was refined with the final controlled set of data for several full-matrix least-squares cycles. The carbon and oxygen temperature factors were refined isotropically, the calcium and tellurium temperature factors anisotropically. The final conventional $R$-value for the 807 observed reflections was 0.066; if the 129 non-observed reflections are included with $F_e = 0$, one obtains $R = 0.086$.

Table 1 gives the atomic coordinates and the thermal parameters. The comparison of $F_o$ and $F_e$, with $F_e$ based on the scattering curves for neutral atoms as listed in the International Tables, Vol. III (1962) is given in Table 2*.

*Table 2 has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

### Table 1. Fractional Coordinates and Temperature Factors

<table>
<thead>
<tr>
<th>0</th>
<th>y</th>
<th>z</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
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<tr>
<td>Ca</td>
<td>0.48009(49)</td>
<td>0.17222(25)</td>
<td>-0.00906(28)</td>
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<tr>
<td>Te</td>
<td>0.09155(16)</td>
<td>0.01761(7)</td>
<td>0.13362(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>C</td>
<td>0.2862(36)</td>
<td>0.2619(15)</td>
<td>0.2573(17)</td>
<td>1.7(3)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>O</td>
<td>0.3553(17)</td>
<td>0.3614(8)</td>
<td>0.2760(9)</td>
<td>0.8(2)</td>
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<tr>
<td>O</td>
<td>0.2953(18)</td>
<td>0.1962(9)</td>
<td>0.3523(10)</td>
<td>1.2(2)</td>
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<td>O</td>
<td>0.2136(17)</td>
<td>0.2266(8)</td>
<td>0.1396(10)</td>
<td>0.7(2)</td>
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<tr>
<td>O</td>
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<td>0.3915(10)</td>
<td>0.0270(10)</td>
<td>1.2(2)</td>
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<td>O</td>
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<td>0.0802(10)</td>
<td>1.0(2)</td>
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**DISCUSSION**

The projection of the crystal structure of mroseite parallel to [100] is given in Figure 1. The important inter-atomic distances and bond angles are summarized in Table 3.

As expected, the structure contains a carbonate group with the usual dimensions. The Ca atoms are coordinated by eight oxygens with Ca-O = 2.38-2.73Å; next-nearest neighbours are a carbon atom at 2.99Å and an oxygen atom at 3.38Å. The irregular CaO$_6$ polyhedra share three edges with each other and thereby form CaO$_{10}$ connections parallel to (001) (Fig 2). The shortest O-O distance in the CaO$_6$ polyhedron (2.20Å) is a common edge with a carbonate group. The next nearest O-O distance (2.60Å) is not, as one could expect, a common

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**Fig. 1.** Projection of the crystal structure of mroseite parallel [100]. Fractional coordinates are rounded to two decimals. To facilitate the recognition of important bonds, coordinates outside the unit cell are given for some atoms.
edge between two CaO₆ polyhedra, but rather a common edge between a CaO₆ polyhedron and the “TeO₅” coordination figure (including an oxygen with O-Te = 2.55 Å).

The distribution of the five nearest neighbours around tellurium corresponds to the known stereochemical behaviour of Te(IV) towards oxygen as summarized by Zemann (1971) and confirmed and extended by Pertlik & Zemann (1971), Lindqvist (1973), Meunier (1974) and Galy et al. (1975). The coordination around tellurium consists of three nearer oxygens that are non-bonded to carbon, and of two more-distant oxygens of the carbonate groups. The three nearer neighbours build a trigonal pyramid with the tellurium. Two such TeO₅ pyramids have an edge in common. If the longer Te-O bonds are neglected, a finite Te₂TeO₅ group results (Fig. 3). The Te-Te distance in this “TeO₅ group” measures only 3.11 Å; this is, to the best of our knowledge, the shortest distance yet observed between two Te(IV). The

Te-O distance of 2.31 Å undoubtedly represents a weak bond, and the Te-O distance of 2.55 Å indicates, in our opinion, more than a pure van der Waals interaction.

It is interesting to compare the tellurium-

FIG. 2. Slice of the structure of mroseite projected parallel [001]. Fractional coordinates are rounded to two decimals. The slice comprises atoms between z = ⅓ and z = ⅔.

FIG. 3. “TeO₅ group” of mroseite projected on the plane defined by the oxygen atoms O(4) and O(5). In addition, the carbonate-oxygen O(1) is drawn.
The coordination around tellurium in mroseite is in some respects transitional between those in TeO₄•HNO₃ and in TeO₂(HPO₄). In the first compound, the oxygens of the HNO₃ group do not participate in the coordination around tellurium (shortest distance of a nitrate-oxygen to Te: 2.80 Å); in mroseite, the shortest distance of a carbonate-oxygen to tellurium (2.31 Å) indicates a weak bond; in TeO₂(HPO₄), however, the shortest bond of a phosphate-oxygen to tellurium measures only 2.12 Å (Mayer 1975) and represents, therefore, a rather strong bond.

The results of valence-bond summations after Donnay & Allmann (1970) and after Brown & Shannon (1973) and Brown (1975) are given in Table 4. The method of Donnay & Allmann gives somewhat less-satisfactory results, partly — in our opinion — the consequence of their somewhat arbitrary choice of \( L_{\text{max}}(\text{Te-O}) = 2.35 \) Å. But even a larger \( L_{\text{max}} \) for Te-O would, for example, not eliminate the difference in the valence-bond sums at O(4) and O(5); also, the summation after Brown & Shannon and Brown with no \( L_{\text{max}} \) gives different sums at O(4) and O(5).

ACKNOWLEDGEMENTS

Computer programs by Fischer, Kupčík, v. Mertens, Suesse and Tillmanns were used for the conversion of x-ray intensities into Fᵢ’s and for the computation of bond distances and bond angles. The least-squares refinements were carried out with the program ORFLS by Busing & Lévy (modified by Durovič and Fischer). Computer facilities were generously provided by “Interfakultaeres Rechenzentrum des Universitäten Wien”.

Our sincere thanks go to Dr. J. A. Mandarino, Royal Ontario Museum, for the sample of mroseite and for information on his work prior to publication, and to Dr. H. Mayer, Vienna, for his information on TeO₂(HPO₄). Mrs. Cathryn Jelinek kindly read the manuscript.

REFERENCES


Galy, J., Meunier, G., Andersson, S. & Åström, A. (1975): Stéréochimie des éléments coprinent des pairs non liés: Ge(II), As(III), Se(IV), Br(V), Sn(II), Sb(III), Te(IV), I(V), Xe(VI), Ti(II), Pb(II), et Bi(III) (oxydes, fluorures et oxyfluorures). J. Solid State Chem. 13, 142-159.


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TABLE 4. VALENCE BOND SUMS IN MROSEITE

<table>
<thead>
<tr>
<th>Z(4)</th>
<th>Z(5)</th>
<th>Z(6)</th>
<th>Z(7)</th>
<th>Z(8)</th>
<th>Z(9)</th>
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<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Standard deviations as derived from the standard deviations of interatomic distances are given in brackets.

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