JOURNAL OF SOLID STATE CHEMISTRY **44**, 156–161 (1982)

# The Crystal Structure of a Complex Cerium(III) Molybdate Containing a Dimolybdate Chain, $Ce_2(MoO_4)_2(Mo_2O_7)$

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Received February 15, 1982; in final form March 31, 1982

$Ce_2(MoO_4)_2(Mo_2O_7)$ crystallizes in the triclinic system with unit cell dimensions (from single-crystal data) $a = 11.903(8)$, $b = 7.509(5)$, $c = 7.385(5)$ Å, $\alpha = 94.33(8)$, $\beta = 97.41(8)$, $\gamma = 88.56(7)°$, and space group $P\bar{1}$, $z = 2$. The structure was solved using Patterson ("$P1$ method") and Fourier techniques. Of the 8065 unique reflections measured by counter techniques, 6314 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional $R$ of 0.035 ($R_w = 0.034$). The structure of $Ce_2(MoO_4)_2(Mo_2O_7)$ consists of dimolybdate chains of the $K_2Mo_2O_7$ and $(NH_4)_2Mo_2O_7$ type separated by isolated $MoO_4$ tetrahedra and cerium(III) polyhedra.

## Introduction

In two studies of reactions of cerium(III) or cerium(IV) oxide with molybdenum(VI) oxide several compounds, in addition to the well-known cerium(III) molybdate, were reported to form (*1*, *2*). Cerium(III) molybdate has been shown to be isostructural with lanthanum, praesodymium, and neodymium molybdates (*3*). The structure of lanthanum(III) molybdate has been reported (*4*).

The only other structure known in the cerium oxide–molybdenum oxide system, to our knowledge, is that of $Ce_6(MoO_4)_8(Mo_2O_7)$ reported from this laboratory (*5*). As a result of further examination of this system we report here the preparation and single-crystal structure determination of a compound with the empirical formula $Ce_2^{III}Mo_4^{VI}O_{15}$.

## Experimental

A red-brown acicular crystal (0.07 × 0.07 × 0.15 mm) was selected following the reaction of $CeO_2$ (Spec pure, Johnson Matthey Chemicals Ltd., U.K.) with $MoO_3$ (AnalaR B.D.H. Chemicals Ltd., U.K.) in the mole ratio 1 : 2 in an open silica tube at 700 ± 20°C for 24 hr. Silica is not essential for reaction as a small number of crystals were also subsequently obtained using a platinum crucible. The crystal was mounted on a silica capillary with clear epoxy resin ("Resiweld") and the crystal data were obtained using a Philips PW 1100 computer-controlled diffractometer in a manner described earlier (*6*).

*Crystal data.* $Ce_2Mo_4O_{15}$, $M = 904.0$, $a = 11.903(8)$, $b = 7.509(5)$, $c = 7.385(5)$ Å, $\alpha = 94.33(8)$, $\beta = 97.41(8)$, $\gamma = 88.56(7)°$. $U = 652.6$ Å$^3$, $D_c = 4.60$ g cm$^{-3}$ for z = 2, $F(000)$

0022-4596/82/110156-06$02.00/0

= 807.6. Sufficient material was not available for a pycnometric density measurement to be made. $\mu = 99.3\ \mathrm{cm}^{-1}$ for Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). Space group $P1$ or $P\bar{1}$; $P\bar{1}$ was confirmed by successful refinement.

### Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to $2\theta(\mathrm{Mo}K\alpha) = 80°$ using the $\theta$–$2\theta$ scan technique with a symmetric scan range of $\pm(1.5 + 0.30 \tan \theta)°$ in $2\theta$ from the calculated Bragg angle, at a scan rate of $0.04°\ \mathrm{sec}^{-1}$. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 8065 unique reflections measured 6314 were considered to be significantly above the background ($I \geq 3\sigma(I)$) and only these were used during the refinement. Three standard reflections, measured at 2-hr intervals, showed no significant variation in intensity.

The data were processed in a manner described recently (*6*). An absorption correction was applied to the data based on the indexed crystal faces $100$, $\bar{1}00$, $001$, $00\bar{1}$, $1\bar{1}0$, $\bar{1}10$, $110$, $\bar{1}\bar{1}0$, $010$, and $0\bar{1}0$. No extinction correction was applied but the 300 reflection was omitted in the final stages of refinement as being extinction affected. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (*7*). All calculations were carried out on the Monash University Burroughs B 6700 computer, and the major program used was SHELX (*8*).

### Structure Solution and Refinement

The solution to the structure was obtained by the "$P1$" method described by Abrahams (*9*) and used here in the determination of other triclinic structures, e.g., $Ag_6Mo_{10}O_{33}$ (*10*) and H–$Li_2Mo_4O_{13}$ (*11*). Following the location of 12 heavy atoms in $P1$, refinement of positional and isotropic thermal parameters enabled the distinction of cerium from molybdenum. The correlation between the atomic parameters of pairs of atoms enabled the location of the center of inversion and refinement gave a conventional $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.12$. Fifteen oxygen atom positions were located in the subsequent difference Fourier synthesis; full-matrix least-squares refinement using isotropic thermal parameters gave $R = 0.06$ with no significant features remaining in the difference Fourier synthesis. The empirical formula was thus established as $Ce_2^{III}Mo_4^{VI}O_{15}$.

Final refinement of all parameters (anisotropic thermal parameters for all atoms) re-

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES (Ce, Mo × $10^5$, OTHERS × $10^4$)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Ce(1) | 22,346(2) | 39,772(3) | 27,321(3) | 87(1) |
| Ce(2) | 77,724(2) | 90,283(3) | 18,052(3) | 74(1) |
| Mo(1) | 12,841(3) | 92,026(5) | 27,272(5) | 82(1) |
| Mo(2) | 87,342(3) | 42,381(5) | 21,934(5) | 82(1) |
| Mo(3) | 52,594(3) | 24,800(5) | 6,838(5) | 87(1) |
| Mo(4) | 52,892(3) | 67,202(5) | 40,444(5) | 88(1) |
| O(1) | −161(3) | 8,938(6) | 2,027(6) | 216(10) |
| O(2) | 1,503(4) | 10,074(6) | 5,013(6) | 264(12) |
| O(3) | 1,965(3) | 7,114(5) | 2,474(6) | 224(12) |
| O(4) | 1,859(3) | 10,846(4) | 1,439(5) | 134(9) |
| O(5) | 10,186(3) | 3,945(6) | 2,162(6) | 216(10) |
| O(6) | 8,491(4) | 5,099(6) | 4,381(5) | 256(12) |
| O(7) | 8,102(3) | 2,153(5) | 1,607(7) | 220(11) |
| O(8) | 8,192(3) | 5,893(4) | 633(5) | 127(7) |
| O(9) | 5,874(3) | 4,264(5) | 2,042(5) | 156(8) |
| O(10) | 5,922(3) | 469(4) | 1,331(5) | 134(8) |
| O(11) | 3,797(3) | 2,570(4) | 845(5) | 141(8) |
| O(12) | 5,512(3) | 2,826(5) | −1,656(5) | 176(9) |
| O(13) | 4,675(4) | 8,327(5) | 5,307(6) | 234(11) |
| O(14) | 6,624(3) | 7,605(5) | 3,850(6) | 187(9) |
| O(15) | 5,937(3) | 5,187(4) | 5,877(4) | 187(6) |

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$

sulted in $R = 0.035$ and $wR = [\Sigma w^{1/2}(|F_0| - |F_c|)/\Sigma w^{1/2}F_0] = 0.034$, $w = (\sigma^2(F))^{-1}$. Final parameters with their estimated standard deviations are presented in Table I.[1]

## Description and Discussion of the Structure

The $Ce_2Mo_4O_{15}$ structure, with the origin as chosen, may be described in general terms as having discrete $MoO_4$ tetrahedra at $x \approx \frac{1}{8}$, separated from a dimolybdate chain at $x \approx \frac{1}{2}$ (parallel to the $z$ direction) and by cerium(III) polyhedra at $x \approx \frac{1}{4}$, as shown in Fig. 1. The dimolybdate chain, shown in Fig. 2, consists of edge-shared pairs of $MoO_6$ octahedra bridged by two $MoO_4$ tetrahedra. The two tetrahedra are corner-shared to adjacent oxygen atoms of an octahedron; the chain so formed is similar to that found in $K_2Mo_2O_7$ (*12*) and $(NH_4)_2Mo_2O_7$ (*13*), but not to those found in $Na_2Mo_2O_7$ (*14*) and $K_2Mo_2O_7 \cdot 2H_2O$ (*15*). Interchain and intrachain oxygen–oxygen contacts are very similar so that layers of chains may be considered as sheets of approximately close-packed oxygen ions with octahedral and tetrahedral sites occupied in a regular manner within the confines of the chains (Table II). The sheets are separated by cerium polyhedra and $MoO_4^{2-}$ tetrahedra (see Fig. 1).

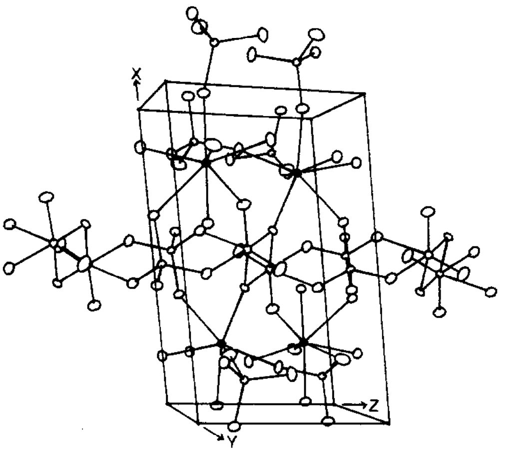

FIG. 1. Unit cell contents of $Ce_2(MoO_4)_2(Mo_2O_7)$ showing the metal–oxygen bonds. Cerium atoms are shown as small solid circles, molybdenum atoms as small open circles.

The cerium atoms, Ce(1) and Ce(2), are irregular seven- and eight-coordinate, respectively, with Ce(1) approximating monocapped trigonal prismatic coordination and Ce(2) dodecahedral coordination.

The Mo–O and Ce–O distances are listed in Table III. The Mo–O distances within the discrete tetrahedra range from 1.739 to 1.812 (mean 1.764) Å, in the bridging tetrahedron the range is from 1.730 to 1.831 (mean 1.770) Å, and in the octahedron from 1.680 to 2.422 (mean 1.968) Å. The discrete

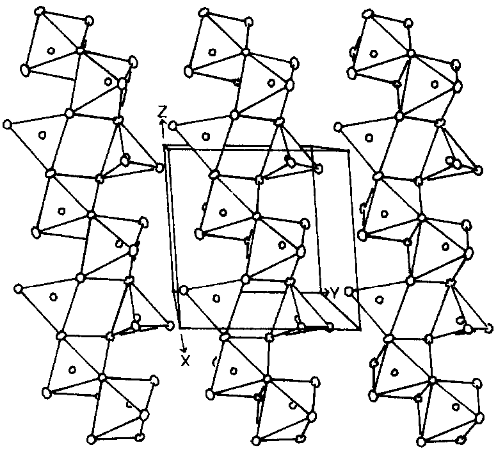

FIG. 2. The dimolybdate chains in $Ce_2(MoO_4)_2(Mo_2O_7)$ are shown in relation to one another and to the unit cell. Coincidentally the chains in the figure form stereoscopic pairs!

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[1] For a table of observed and calculated structure factors see NAPS document No. 03962 for 36 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 for up in 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE II

INTERCHAIN AND INTRACHAIN O . . . . . O DISTANCES (Å)

| | | | |
|---|---|---|---|
| | Tetrahedron | | |
| O(9)–O(11) | 2.818(5) | O(10)–O(11) | 2.945(5) |
| –O(12) | 2.843(5) | –O(12) | 2.917(5) |
| –O(10) | 2.859(5) | O(11)–O(12) | 2.944(5) |
| | Octahedron | | |
| O(9)–O(12) | 2.715(5) | O(13)–O(14) | 2.707(6) |
| –O(15′) | 2.810(5) | –O(12) | 2.752(6) |
| –O(15) | 2.856(5) | –O(15) | 2.792(5) |
| –O(14) | 2.858(5) | –O(15′) | 2.800(5) |
| O(14)–O(15) | 2.647(5) | O(15′)–O(15) | 2.441(6) |
| –O(12) | 2.846(5) | –O(12) | 2.737(5) |
| | Interchain | | |
| O(10)–O(11) | 2.729(5) | O(11)–O(8) | 2.741(5) |
| –O(13) | 2.751(5) | –O(4) | 2.772(5) |
| –O(10) | 2.818(6) | –O(15) | 2.831(5) |
| –O(7) | 2.892(5) | | |
| O(13)–O(13) | 2.735(8) | | |

tetrahedra may be compared with those in $Ce_6(MoO_4)_8(Mo_2O_7)$ (*5*), where the Mo–O distances are between 1.72 and 1.85 (mean 1.77) Å. The bridging tetrahedra in $Na_2Mo_2O_7$ (*14*), $K_2Mo_2O_7$ (*12*), and $(NH_4)_2Mo_2O_7$ (*13*) have Mo–O distances that fall within the range 1.71 to 1.82 Å with a mean distance of 1.76 Å, very similar to those observed here.

In each of the molybdenum tetrahedra one Mo–O distance is notably greater than the other three. O(4) and O(8), bonded to Mo(1) and Mo(2), respectively, are both considered to be part of the Ce(1) and Ce(2) polyhedra, whereas the other oxygen atoms of the Mo(1) and Mo(2) tetrahedra have only one other contact and that is to one of the cerium atoms. O(12) bridges the Mo(3) tetrahedron and the Mo(4) octahedron resulting in the long contact to Mo(3). O(9) also bridges Mo(3) and Mo(4) but its long contact is to the octahedron. Similar tetrahedral distortions occur in $Ce(MoO_4)_8(Mo_2O_7)$ for similar oxygen situations (*5*).

The wide range of Mo–O distances within the octahedron (Mo(4)) reflects the off-center position of the molybdenum atom rather than the distortion of the octahedron of oxygen atoms. This can be seen from the three equatorial least-squares planes, each containing four oxygen atoms, calculated for the octahedron and the approximately equal distances of the remaining oxygen atoms above and below these planes (Table IV). The octahedron edge lengths are given

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| | | | |
|---|---|---|---|
| Mo(1)–O(1) | 1.743(4) | Mo(2)–O(5) | 1.739(4) |
| –O(2) | 1.753(4) | –O(6) | 1.750(4) |
| –O(3) | 1.755(4) | –O(7) | 1.754(3) |
| –O(4) | 1.812(3) | –O(8) | 1.809(3) |
| Mo(3)–O(9) | 1.730(3) | Mo(4)–O(13) | 1.680(4) |
| –O(10) | 1.756(4) | –O(14) | 1.765(3) |
| –O(11) | 1.760(3) | –O(15) | 1.916(3) |
| –O(12) | 1.830(4) | –O(12) | 1.944(4) |
| | | –O(15) | 2.079(3) |
| | | –O(9) | 2.421(4) |
| Ce(1)–O(15) | 2.363(3) | Ce(2)–O(7) | 2.407(4) |
| –O(3) | 2.388(4) | –O(10) | 2.425(3) |
| –O(5) | 2.421(4) | –O(1) | 2.444(4) |
| –O(6) | 2.449(4) | –O(2) | 2.447(4) |
| –O(8) | 2.481(4) | –O(14) | 2.478(4) |
| –O(4) | 2.499(3) | –O(4) | 2.500(4) |
| –O(11) | 2.620(4) | –O(8) | 2.507(3) |
| Ce(1) . . . O(14) | 3.019(4) | –O(11) | 2.752(3) |
| . . . O(2) | 3.666(5) | Ce(2) . . . O(6) | 3.655(5) |
| Mo(3) . . . Mo(4) | 3.562(1) | Mo(4) . . . Mo(4) | 3.167(1) |

TABLE IV

EQUATIONS FOR MEAN PLANES AND DEVIATIONS (Å) OF ATOMS FROM THESE PLANES. EACH PLANE IS REPRESENTED BY AN EQUATION OF THE TYPE $Ax + By + Cz + D = 0$

| | | | |
|---|---|---|---|
| Plane 1 | O(12), O(14), O(15), O(15′) | | |
| *A* 0.4353 | *B* −0.6977 | *C* −0.5689 | *D* 2.0860 |
| Mo(4) −0.3355(4) | O(9) 2.074(4) | O(13) −2.012(4) | |
| Plane 2 | O(9), O(12), O(13), O(15) | | |
| *A* 0.8444 | *B* 0.5330 | *C* −0.0538 | *D* −7.3142 |
| Mo(4) 0.1985(4) | O(14) 1.937(4) | O(15) −1.839(3) | |
| Plane 3 | O(9), O(13), O(14), O(15′) | | |
| *A* −0.3644 | *B* 0.4623 | *C* −0.8084 | *D* 2.3995 |
| Mo(4) 0.0438(4) | O(12) 1.932(4) | O(15) −1.822(3) | |

in Table II; the shortest distance is the shared edge, O(15)–O(15) 2.441(6) Å, resulting from the Mo–Mo repulsion (Mo(4)–Mo(4) 3.167(1) Å) that draws the two oxygen atoms toward one another. The O(15)–Mo(4)–O(15′) angle is 75.2(1)°.

Equations for the formation, from $CeO_2$ and $MoO_3$, of the three compounds now known in the $Ce_2O_3 : MoO_3$ system can be written as follows

$$6CeO_2 + 9MoO_3 \rightarrow 3Ce_2(MoO_4)_3 + 1\tfrac{1}{2}O_2,$$

$$6CeO_2 + 10MoO_3 \rightarrow Ce_6Mo_{10}O_{39} + 1\tfrac{1}{2}O_2,$$

$$6CeO_2 + 12MoO_3 \rightarrow 3Ce_2Mo_4O_{15} + 1\tfrac{1}{2}O_2.$$

It can be seen that cerium(IV) is reduced to cerium(III) by oxide ($O^{2-}$) ions in the presence of $MoO_3$ at elevated temperatures. A further compound has been observed in this system with unit cell dimensions $a \approx 11.33$, $b \approx 17.05$, $c \approx 14.05$ Å, $\beta \approx 90.6°$. The only crystals obtained so far have proved to be twinned, and while it is possible that this compound is formed from the $6CeO_2 : 11MoO_3$ reaction, giving $Ce_6Mo_{11}O_{42}$, confirmation must await further analysis. Attempts will also be made to prepare and characterize a cerium(IV) molybdate.

**APPENDIX: Anisotropic Temperature Factors of the Form $\exp[-2\pi^2 (U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$ ($\times 10^4$)**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ce(1) | 63(1) | 83(1) | 107(1) | −27(1) | 5(1) | 0(1) |
| Ce(2) | 64(1) | 66(1) | 92(1) | −5(1) | 14(1) | −2(1) |
| Mo(1) | 74(1) | 82(1) | 90(1) | −5(1) | 13(1) | −16(1) |
| Mo(2) | 67(1) | 83(1) | 93(1) | 0(1) | 7(1) | 7(1) |
| Mo(3) | 70(1) | 85(1) | 108(1) | 7(1) | 20(1) | 21(1) |
| Mo(4) | 93(1) | 82(1) | 91(1) | 10(1) | 16(1) | −22(1) |
| O(1) | 106(13) | 292(19) | 242(19) | −67(15) | 37(13) | −34(13) |
| O(2) | 253(19) | 392(24) | 139(16) | −75(16) | 28(14) | −97(17) |
| O(3) | 220(17) | 110(13) | 356(23) | 41(14) | 77(16) | 26(12) |
| O(4) | 180(14) | 71(11) | 151(14) | 5(10) | 29(12) | 12(10) |
| O(5) | 105(13) | 282(19) | 257(19) | −12(16) | 23(13) | −1(13) |
| O(6) | 241(18) | 402(24) | 116(15) | −43(15) | 44(14) | 69(17) |
| O(7) | 184(16) | 95(13) | 370(23) | 22(14) | −17(16) | −37(11) |
| O(8) | 169(14) | 80(11) | 130(13) | 13(10) | 13(11) | 8(10) |
| O(9) | 139(13) | 145(13) | 191(16) | 10(12) | 45(12) | −8(11) |
| O(10) | 107(12) | 121(12) | 172(15) | 17(11) | 9(11) | 40(10) |
| O(11) | 106(12) | 136(13) | 181(15) | −25(11) | 39(11) | 8(10) |
| O(12) | 185(15) | 214(16) | 143(15) | 61(13) | 52(12) | 36(12) |
| O(13) | 311(20) | 147(15) | 261(20) | −29(14) | 130(17) | −3(14) |
| O(14) | 150(14) | 153(14) | 273(19) | 30(13) | 70(13) | −57(11) |
| O(15) | 83(11) | 128(12) | 105(12) | 12(10) | −18(10) | −34(9) |

## Acknowledgment

This work forms part of a project supported by the Australian Research Grants Committee.

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