

The Crystal Structure of a Complex Cerium(III) Molybdate; $Ce_6(MoO_4)_8(Mo_2O_7)$

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Received August 8, 1977; in revised form December 13, 1977

$Ce_6Mo_{10}O_{39}$ crystallizes in the triclinic system with unit-cell dimensions (from single-crystal data) $a = 10.148(5)$ Å, $b = 18.764(6)$ Å, $c = 9.566(5)$ Å, $\alpha = 103.12(7)^\circ$, $\beta = 78.07(7)^\circ$, $\gamma = 107.69(7)^\circ$, and space group $P\bar{1}$, $z = 2$. The structure was solved using direct methods with 3113 countermeasured reflections (MoK α radiation), and refined using Fourier and least-squares techniques to a conventional R of 0.039 ($\omega R = 0.047$). $Ce_6Mo_{10}O_{39}$ has a structure that consists of isolated MoO_4 tetrahedra together with one corner-shared pair of tetrahedra, linked to irregular eight-coordinate Ce(III) polyhedra. The average Mo-O distance of 1.77 Å, and average Ce-O distance of 2.52 Å are in good agreement with previously reported values.

Introduction

Rare earth molybdates and tungstates have received considerable attention in view of their potentially interesting physical properties. The trivalent rare earth molybdates provide a number of materials with fluorescent, piezoelectric, ferroelectric, and ferroelastic properties, for example (1). The structures of relatively few cerium molybdates are known compared with those of other lanthanide molybdates, and no cerium(IV) molybdate structures have been characterized.

The unit-cell dimensions and space group of a compound believed to be $Ce(MoO_4)_2$ were reported (2) and an interest in polymolybdates in general (3) prompted this study in which the structure of $Ce_6^{III}Mo_{10}^{VI}O_{39}$ is reported.

A brief preliminary report has been published elsewhere (4).

Experimental

A small sample of the above compound was

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kindly supplied to the Monash University group by Dr. L. H. Brixner of E. I. du Pont de Nemours and Company. The crystals are pale yellow to orange in color and one (approximately spherical but irregular) of ca. 0.04 mm in radius was selected, checked for twinning or cracking using a polarizing microscope and mounted using clear epoxy resin ("Resiweld") on a silica capillary. The crystal data were obtained using a Philips PW 1100 computer-controlled diffractometer in a manner described earlier (5).

Crystal data. $Ce_6Mo_{10}O_{39}$, $M = 2424.1$, $a = 10.148(5)$ Å, $b = 18.764(6)$ Å, $c = 9.566(5)$ Å, $\alpha = 103.12(7)^\circ$, $\beta = 78.07(7)^\circ$, $\gamma = 107.69(7)^\circ$. $U = 1671.41$ Å³, $D_c = 4.816$ g cm⁻³ for $z = 2$, Dm (Ref. (2)) = 4.518 g cm⁻³, $F(000) = 2160$. Insufficient material was available for a density measurement to be made during this study. $\mu = 117$ cm⁻¹ for MoK α radiation ($\lambda = 0.7107$ Å). Space group $P\bar{1}$ or $P1$; the most likely space group, $P\bar{1}$, according to piezoelectric and second harmonic generation tests (2), was confirmed by the successful refinement.

The unit cell reported here is not the reduced cell; however, if the matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

is applied to the above unit cell then the parameters reported by Brixner *et al.* (2) (the reduced-cell parameters) are obtained.

Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and MoK α radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to $2\theta(\text{MoK}\alpha) = 45^\circ$ using the θ - 2θ scan technique with a symmetric scan range of $\pm 0.5^\circ$ in 2θ from the calculated Bragg angle, at a scan rate of 0.06 deg sec $^{-1}$. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 3360 independent reflections measured 3113 were considered to be significantly above the background ($I \geq 4\sigma(I)$) and only these were used during refinement. Three standard reflections measured at 2-hr intervals showed no significant variation in intensity.

The data were processed in a manner described recently (5). As the crystal was approximately spherical and $\mu R = 0.47$ the effects of neglecting absorption are estimated to be very small. No extinction correction was applied. The atomic scattering factors used were Ce 0 (6) and Mo 01 and O $^{2-}$ (7). All calculations were performed on the Monash University CDC 3200 computer, the major programs used being MONLS, a modified version of the full-matrix program of Busing *et al.* (8), MONDLS, a block-diagonal least-squares program adapted from the "SF series" of Shiono (9), MULTAN (10), and the Fourier summation program, MONFR (11).

¹ Corrected for the real part of the anomalous dispersion.

Structure Solution and Refinement

An unsuccessful attempt was made to solve this multiple heavy atom structure by the so-called "P1" method used to solve the structures of Ag $_6$ Mo $_{10}$ O $_{33}$ (12), K $_2$ Mo $_4$ O $_{13}$ (13), and other complex molybdates (3). The structure was solved using direct methods (MULTAN (10)) for the 16 heavy atoms. Refinement of the positional parameters for these atoms, all treated as molybdenum initially, resulted in a conventional $R = \Sigma|F_o| - |F_c| / \Sigma|F_o| = 0.169$. The subsequent difference Fourier synthesis allowed differentiation of Ce and Mo positions and a further refinement cycle gave $R = 0.115$. All oxygen positions were located in a further difference Fourier calculation and resulted in $R = 0.094$. The large number of variables (isotropic thermal parameters + positional parameters + 1 scale = 221) and the limited capacity of the available computer dictated that further refinement be made using the block-diagonal least-squares technique. This resulted in a final $R = 0.039$ and $\omega R = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F^2]^{1/2} = 0.047$ for observed data. For all data $R = 0.043$ and $\omega R = 0.047$; $1/\sigma^2(F)$ weights were used during the refinement.

Final parameters with their estimated standard deviations are presented in Table I. See Note on Table II.

Description of the Structure

The Ce $_6$ Mo $_{10}$ O $_{39}$ structure consists of MoO $_4$ tetrahedra and CeO $_8$ irregular polyhedra. One pair of MoO $_4$ tetrahedra (Mo(6) and Mo(7)) share a corner, O(19), forming an Mo $_2$ O $_7$ unit. With the exception of O(19), all oxygen atoms are bound to one molybdenum atom and at least one cerium atom.

The molybdenum-oxygen and cerium-oxygen distances are listed in Table II. The Mo-O distances within the single tetrahedra range from 1.72 to 1.85 (average 1.77) Å, and within the corner-shared pair of tetrahedra from 1.71 to 1.89 (average 1.77) Å. The two longest distances are those from Mo(6) and Mo(7) to O(19), the common oxygen. The O-

TABLE I

FINAL POSITIONAL PARAMETERS (METALS $\times 10^4$, OXYGEN $\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS (METALS $\times 10^2$, OXYGEN $\times 10$)^a

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
Ce(1)	3362(2)	2888(1)	772(2)	72(4)	O(12)	215(3)	368(2)	258(3)	17(5)
Ce(2)	6826(2)	2026(1)	9487(2)	65(4)	O(13)	481(3)	369(1)	261(3)	10(5)
Ce(3)	5911(2)	1255(1)	3010(2)	71(4)	O(14)	264(3)	222(2)	312(3)	19(5)
Ce(4)	9493(2)	5074(1)	3045(2)	87(4)	O(15)	751(3)	396(2)	322(3)	16(5)
Ce(5)	3756(2)	3851(1)	7301(2)	70(4)	O(16)	560(3)	-10(1)	636(3)	14(5)
Ce(6)	13(2)	192(1)	6976(2)	78(4)	O(17)	719(3)	256(2)	420(3)	14(5)
Mo(1)	3465(3)	684(2)	195(4)	75(6)	O(18)	124(3)	490(2)	431(3)	16(5)
Mo(2)	6733(3)	4238(2)	-181(4)	79(6)	O(19)	-17(3)	233(2)	461(3)	17(5)
Mo(3)	9570(3)	1362(2)	1049(4)	78(6)	O(20)	99(3)	115(2)	500(3)	18(5)
Mo(4)	5865(3)	3302(2)	3316(4)	78(6)	O(21)	846(3)	16(1)	525(3)	11(5)
Mo(5)	2707(3)	4488(2)	3826(4)	75(6)	O(22)	711(3)	120(1)	488(3)	11(5)
Mo(6)	1465(3)	2064(2)	4681(4)	81(6)	O(23)	441(3)	168(1)	523(3)	20(5)
Mo(7)	8404(3)	2782(2)	5418(4)	83(6)	O(24)	511(3)	333(2)	514(3)	17(5)
Mo(8)	7127(3)	629(2)	6116(3)	69(6)	O(25)	281(3)	430(2)	551(3)	19(5)
Mo(9)	4004(3)	1662(2)	7085(3)	71(6)	O(26)	922(3)	373(2)	550(3)	16(5)
Mo(10)	443(3)	3525(2)	9477(4)	81(6)	O(27)	214(3)	266(2)	618(3)	19(5)
O(1)	343(3)	159(2)	-10(3)	16(5)	O(28)	417(3)	514(2)	315(3)	20(5)
O(2)	662(3)	332(2)	13(3)	24(6)	O(29)	232(3)	104(1)	729(3)	13(5)
O(3)	522(3)	86(1)	51(3)	12(5)	O(30)	-236(3)	263(2)	715(3)	19(5)
O(4)	1094(3)	219(2)	109(3)	18(5)	O(31)	61(3)	384(2)	784(3)	21(6)
O(5)	-13(3)	417(2)	1095(3)	28(6)	O(32)	529(3)	133(1)	757(3)	12(5)
O(6)	307(3)	-3(2)	-127(3)	14(5)	O(33)	788(3)	111(2)	773(3)	14(5)
O(7)	795(3)	162(1)	125(3)	11(5)	O(34)	406(3)	261(2)	803(3)	18(5)
O(8)	716(3)	498(2)	134(3)	17(5)	O(35)	803(3)	448(2)	-167(3)	22(6)
O(9)	234(3)	45(2)	176(3)	15(5)	O(36)	216(3)	346(2)	951(3)	16(5)
O(10)	572(3)	237(1)	212(3)	12(5)	O(37)	501(3)	412(2)	-55(3)	15(5)
O(11)	960(3)	92(2)	246(3)	17(5)	O(38)	-76(3)	263(2)	937(3)	19(5)
					O(39)	987(3)	76(2)	-58(3)	20(5)

^a Estimated standard deviations are given in parentheses.

Mo—O angles around all molybdenum atoms range generally from 101.1 to 114.7° with the exception of the following: O(21)—Mo(8)—O(33) = 97.7°, O(22)—Mo(8)—O(33) = 116.0°, O(15)—Mo(4)—O(10) = 117.2°, and O(24)—Mo(4)—O(10) = 118.4°. These correspond with the relatively long Mo—O distances Mo(8)—O(33) of 1.80 Å and Mo(4)—O(10) of 1.85 Å. The molybdenum polyhedra are shown in Fig. 1 and the cerium polyhedra in Fig. 2. The coordination about Ce(5) approaches that of an Archimedean square antiprism, the remaining cerium ions are irregularly coordinated.

Discussion

The formula of the compound $Ce_6Mo_{10}O_{39}$ was established by the structure determination. Attempts were made to prepare $Ce(MoO_4)_2$ by heating CeO_2 and MoO_3 in the mole ratio of 1:2, in platinum ware under an oxygen atmosphere; the finely ground mixture fused to a dark red mass, with loss of MoO_3 , and heating was continued at 800°C for 14 hr followed by 900°C for 3 hr. The mass was then cooled to 400°C and removed from the furnace.

Examination with a microscope showed that there were yellow crystals (shown to be

TABLE II
 BOND LENGTHS^{a, b}

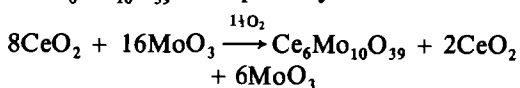
Cerium–Oxygen < 3.50 Å				Molybdenum–Oxygen < 2.57 Å			
Ce(1)–O(4) ^a	2.40(2)	Ce(2)–O(38) ^c	2.36(3)	Mo(1)–O(6)	1.72(2)	Mo(2)–O(35)	1.77(2)
O(1)	2.40(3)	O(2) ^d	2.42(3)	O(9)	1.74(2)	O(2)	1.78(3)
O(12)	2.41(3)	O(33)	2.44(3)	O(3)	1.79(3)	O(8)	1.79(2)
O(13)	2.45(2)	O(32)	2.52(3)	O(1)	1.80(3)	O(37)	1.80(3)
O(36) ^b	2.47(3)	O(3) ^d	2.56(3)	Mo(3)–O(4)	1.74(3)	Mo(4)–O(15)	1.75(2)
O(34) ^b	2.55(3)	O(10) ^d	2.56(3)	O(39)	1.74(3)	O(24)	1.75(2)
O(14)	2.68(3)	O(7) ^d	2.58(3)	O(11)	1.75(3)	O(13)	1.77(3)
O(37)	2.80(3)	O(30)	2.60(3)	O(7)	1.81(3)	O(10)	1.85(2)
Ce(1)–O(2)	3.12(3)	Ce(2)–O(1) ^d	3.25(3)	Mo(5)–O(28)	1.72(3)	Mo(6)–O(20)	1.72(3)
O(10)	3.40(3)			O(12)	1.72(2)	O(14)	1.73(3)
Ce(3)–O(16) ^{ie}	2.37(2)	Ce(4)–O(5) ^g	2.37(2)	O(25)	1.76(3)	O(27)	1.73(3)
O(22)	2.40(3)	O(31) ⁱ	2.42(3)	O(18)	1.81(3)	O(19)	1.89(3)
O(7)	2.41(2)	O(15)	2.43(3)	Mo(7)–O(26)	1.71(3)	Mo(8)–O(16)	1.74(3)
O(23)	2.47(3)	O(18) ^c	2.47(3)	O(30) ^e	1.73(3)	O(22)	1.77(3)
O(10)	2.50(3)	O(18) ⁱ	2.48(3)	O(17)	1.76(3)	O(21)	1.79(3)
O(3)	2.52(2)	O(26) ^{ie}	2.50(3)	O(19) ^e	1.85(3)	O(33)	1.80(2)
O(17)	2.53(2)	O(35) ^{ie}	2.57(3)	Mo(9)–O(23)	1.74(3)	Mo(10)–O(38)	1.74(3)
O(6) ^{ie}	2.85(3)	O(25) ⁱ	2.90(3)	O(29)	1.76(2)	O(31)	1.74(3)
		Ce(4)–O(8)	3.08(3)	O(32)	1.79(3)	O(5)	1.76(3)
Ce(5)–O(28) ⁱ	2.41(2)	Ce(6)–O(39) ^h	2.33(2)	O(34)	1.79(3)	O(36)	1.79(3)
O(24)	2.42(3)	O(11) ^{ie}	2.43(3)				
O(36)	2.49(3)	O(29)	2.43(2)				
O(27)	2.50(2)	O(21) ^{ie}	2.45(3)				
O(37) ^d	2.51(3)	O(21) ^a	2.49(3)				
O(25)	2.53(3)	O(9) ⁱⁱ	2.52(3)				
O(8) ⁱ	2.61(3)	O(20)	2.73(3)				
O(34)	2.70(3)	O(20) ⁱⁱ	2.83(3)				
Ce(5)–O(31)	3.12(3)	Ce(6)–O(33) ^a	3.04(4)				

^a Estimated standard deviations are given in parentheses.

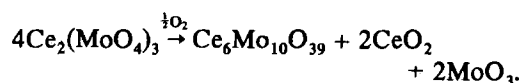
^b The numbering of the atoms is in accordance with that shown in Table I, with the Roman numeral I indicating the symmetry operation $1 - x$, $1 - y$, $1 - z$, and letters indicating that the atom is in an adjacent cell, the relationship of which to the primary cell is given by a: $-, O, O$; b: $O, O, -$; c: $+, O, O$; d: $O, O, +$; e: $O, -, O$; f: $O, -, -$; g: $+, O, -$; h: $-, O, +$; i: $-, -, O$.

Note. A table of observed and calculated structure factors has been deposited as Document No. NAPS 03207 with the ASIS National Auxiliary Publications Service c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number and by remitting \$7.50 for photocopies or \$3.00 for microfiche. Advance payment is required. Make cheque or money order payable to "Microfiche Publications."

$Ce_6Mo_{10}O_{39}$ using the diffractometer) and clear crystals of CeO_2 (diffractometer). On the basis of the formula established by the complete structure analysis, and the above observations, it is suggested that the formation of $Ce_6Mo_{10}O_{39}$ takes place by the reaction



or in terms of the decomposition of $Ce_2(MoO_4)_4$; as prepared earlier (2)



In a study of the formation of cerium molybdates under different atmospheric and thermal conditions, Castellan *et al.* (14)

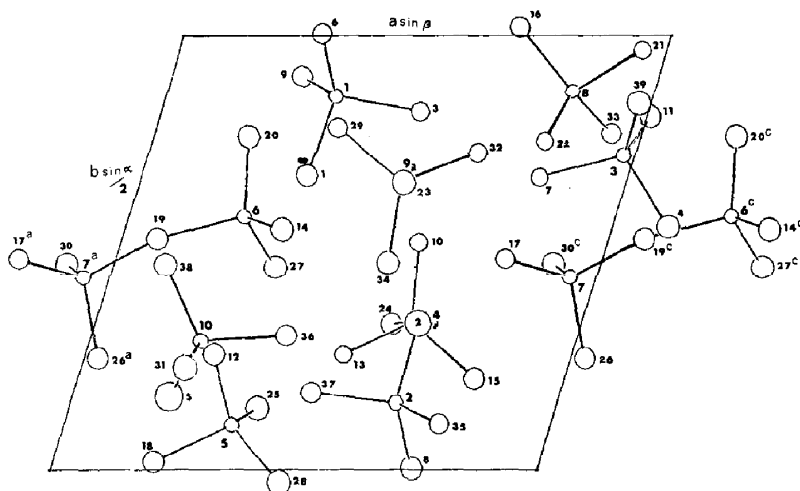


FIG. 1. The MoO_4 tetrahedra in $Ce_6(MoO_4)_8(Mo_2O_7)$ viewed along $[00\bar{1}]$. The molybdenum and oxygen atoms are numbered as in the tables.

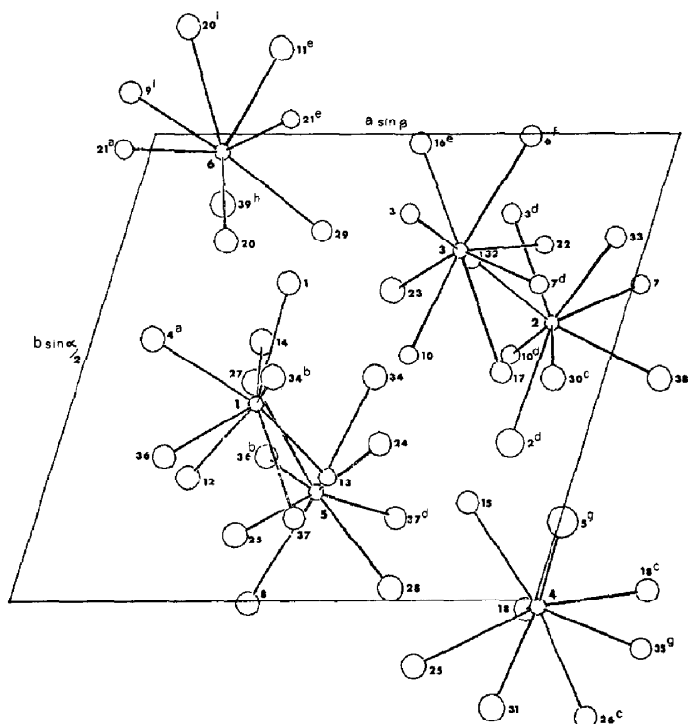


FIG. 2. The CeO_8 polyhedra in $Ce_6(MoO_4)_8(Mo_2O_7)$ viewed along $[00\bar{1}]$. The cerium and oxygen atoms are numbered as in the tables.

reported the phases $\gamma-Ce_2Mo_3O_{13}$ and $Ce_8Mo_{12}O_{49}$, commenting that on the basis of ultraviolet and visible spectroscopy these appear to contain both tetrahedral and octahedral molybdenum(VI) geometries. These

authors also list X-ray powder data for the two new phases. Attempts have been made to correlate the chemical analyses and X-ray powder data reported by Castellan *et al.* (14) with the calculated analysis and X-ray single-

crystal data for $Ce_6Mo_{10}O_{39}$, without success. A reexamination of the chemistry of cerium molybdates in terms of the result reported here would be in order, preferably with the inclusion of unit-cell dimensions obtained from single-crystal measurements.

Attention was drawn recently (15), during a study of the structures of $Ag_2Mo_2O_7$ and $Ag_2W_2O_7$, to the apparent nonexistence of the $[Mo_2O_7]^{2-}$ anion, unlike the well-known dichromate $[Cr_2O_7]^{2-}$. While it is not suggested that the dimolybdate ion, as such, exists in the compound reported here, the Mo_2O_7 unit is apparently able to exist in the solid state in the situation prevailing here. As a means of lowering the oxygen content (i.e., by further tetrahedra-sharing corners), without reduction of the metal ions present, this unit, Mo_2O_7 , could prove of interest in discussions dealing with catalyst activity.

Bismuth molybdates are of particular interest as catalysts and in a report (16) on the structure determination of $Bi_2(MoO_4)_3$ it is suggested that, since there is an additional oxygen in the vicinity of each MoO_4 tetrahedron at ca. 2.2 Å, the molybdenum should be considered as five-coordinate (irregular trigonal bipyramidal), and that pairs of these polyhedra share edges. The shortest additional contact found in $Ce_6Mo_{10}O_{39}$ is 2.57 Å between Mo(4) and O(17), and it is not considered to be part of the molybdenum coordination sphere. As distinct from the structure reported here, in which the oxygen atoms, with the exception of O(19) (mentioned above), are all bound to one Mo and at least one Ce ion, in $Bi_2(MoO_4)_3$ it appears that O(12) is not considered to be part of the coordination polyhedron of Bi(1) or Bi(2) and is part of the Mo(3) tetrahedron only. The next-nearest-neighbor of O(12) appears to be Mo(1) at 2.69 Å.

Further structural studies in the cerium

oxide-molybdenum oxide, and bismuth oxide-molybdenum oxide systems are intended.

Acknowledgement

Support given by the Australian Research Grants Committee to the project of which this work forms a part is gratefully acknowledged.

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