JOURNAL OF SOLID STATE CHEMISTRY 79, 296–299 (1989)

Synthesis and Crystal Structure of $CsHMoO_2(P_2O_7)_2$

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Communicated by J. M. Honig, January 4, 1989

A new Mo^{6+} diphosphate, $CsHMoO_2P_2O_7$, was discovered and its crystal structure determined from single-crystal X-ray diffraction data. $CsHMoO_2P_2O_7$ crystallizes in the monoclinic space group $P2_1/a$, with $a = 9.670(5)$, $b = 14.231(10)$, $c = 6.265(5)$ Å, $\beta = 100.10(7)°$, $V = 849(2)$ Å^3, $Z = 4$, $R = 0.033$, $R_w = 0.036$ for 2778 independent reflections with $I > 9\sigma(I)$. Isolated MoO_6 octahedra share four of their oxygen atoms with three different P_2O_7 groups to build infinite ribbons spreading along the **c** direction. One of the two oxygen atoms of the molybdenyl group remains unshared while the second one takes part in the cesium coordination. P_2O_7 groups are interconnected by H bonding to form infinite monodimensional chains along the **a** direction. © 1989 Academic Press, Inc.

Introduction

Investigations of systems among molybdenum, monovalent metal oxides, and P_2O_5 have shown the great ability of PO_4 tetrahedra to build various frameworks with MoO_6 octahedra. If several different structure types have been characterized in the former systems, most of them correspond to compounds with lower oxydation states of molybdenum (Mo^{5+}, Mo^{4+}, Mo^{3+}). For compounds of this kind one can report numerous studies by K. H. Lii and co-workers (*1–5*), by R. C. Haushalter (*6, 7*), and by A. Leclaire and co-workers (*8–11*).

Nevertheless, phosphomolybdates with Mo in the 6+ oxidation state are rather rare. The first studies in this field have been undertaken by P. Kierkegaard (*12*). They concern several monophosphates, Mo $(OH)_3PO_4$, $AgMoO_2PO_4$, $NaMoO_2PO_4$; a diphosphate, $(MoO_2)_2P_2O_7$; and a polyphosphate, $MoO_2(PO_3)_2$. These pioneer works mainly performed during the sixties are unfortunately not very accurate. Recently more precise structural studies have been reported for two monophosphates Ba $(MoO_2)_2(PO_4)_2$ and $Pb(MoO_2)_2(PO_4)_2$ (*13*) and a diphosphate $(NH_4)_2MoO_2P_2O_7$ (*14*). For all these compounds the two oxygen atoms of the molybdenyl group correspond to short Mo–O bonds and do not take part in the phosphorus coordination.

Experimental

Crystals of the title compound are obtained by a flux method. MoO_3 (1.5 g), Cs_2CO_3 (5 g), and H_3PO_4 (5 cm^3) are heated in a graphite crucible at 300°C in air. After several months, colorless monoclinic prismatic crystals appear. The excess of flux is removed by hot water. A crystal (0.34 × 0.22 × 0.21 mm) suitable for X-ray intensity data collection is selected. Crystal data and experimental parameters used during the

0022-4596/89 $3.00

measurement are reported in Table I. The unit-cell parameters were determined by a least-squares refinement of 19 pieces of reflection angle data ($10.3 < \theta < 17.2°$) measured on the four-circle diffractometer before the data collection.

The intensities have been corrected for Lorentz and polarization effects, but no absorption correction has been applied. The structure was solved by a direct method (*15*). The H atom has been located by a final difference–Fourier function. After the last refinement cycles with anisotropic thermal parameters for all the atoms except the H atom, the final R value is 0.033 for 2778 reflections such that $I_{obs} > 9\sigma_I$ (R_w = 0.036). The same factor R is 0.035 for the total set of 2881 independent measured reflections.

For the calculations, the Enraf–Nonius Structure Determination Package was employed (*16*). Atomic scattering factors and anomalous dispersion were taken from the "International Tables for X-Ray Crystallography," Table 2.2B (*17*). Refinements were run using full-matrix, with a unitary weighting scheme. The extinction factor g defined according to Stout and Jensen (*18*) has been refined to the value 1.37×10^{-6}. The final atomic coordinates are reported in Table II.[1]

TABLE I

CRYSTAL DATA AND EXPERIMENTAL PARAMETERS FOR INTENSITY DATA COLLECTION

Cell parameters	$a = 9.670(5)$, $b = 14.231(10)$, $c = 6.265(5)$ Å $\beta = 100.10(7)°$
Z, V, M_w	4, 849 Å^3, 435.79
Space group	$P2_1/a$
Density (cal.)	3.410 g/cm^3
μ (Mo$K\bar{\alpha}$)	6.21 mm^{-1}
Apparatus	Enraf–Nonius CAD 4
Wavelength	Mo$K\bar{\alpha}$ (0.7107 Å)
Monochromator	Graphite plate
Scan mode	ω
Theta range	3–35°
Scan width	1.20°
Scan speed	from 0.02 to 0.04° sec^{-1}
Number of independent collected reflections	2881
Total background measuring time	14 to 28 sec
Intensity reference reflections	$2\bar{8}2$, $\bar{2}8\bar{2}$
Orientation reference reflections	$26\bar{4}$, $2\bar{6}\bar{4}$

TABLE II

ATOMIC COORDINATES AND B_{eq} (BISO FOR H ATOM) FOR $CsHMoO_2P_2O_7$

Atom	x	y	z	B_{eq}
Mo	0.71584(3)	0.46363(2)	0.29654(4)	1.123(3)
Cs	0.82724(3)	0.17081(2)	0.18713(5)	3.057(5)
P(1)	0.51790(9)	0.12887(6)	0.6031(1)	1.18(1)
P(2)	0.28471(9)	0.08906(6)	0.8137(1)	1.16(1)
O(E11)	0.9264(3)	0.4052(2)	0.4003(4)	1.70(4)
O(E12)	0.1662(3)	0.4061(2)	0.6486(4)	1.53(4)
O(E13)	0.5151(3)	0.2374(2)	0.5994(5)	2.11(5)
O(L)	0.9492(3)	0.4022(2)	0.8065(4)	1.61(4)
O(E21)	0.7209(3)	0.4704(2)	0.6163(4)	1.55(4)
O(E22)	0.7252(3)	0.3155(2)	0.8232(5)	2.03(5)
O(E23)	0.2804(3)	0.0273(2)	0.0113(4)	1.48(4)
O(1)	0.1528(3)	0.1479(2)	0.2610(5)	2.17(5)
O(2)	0.4311(3)	0.4708(2)	0.7670(5)	2.23(5)
H	0.07(1)	0.235(8)	0.69(2)	6(3)

Note. Estimated standard deviations are given in parentheses. $B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Structure Description

Figure 1, representing the projection of the structure along the **b** axis, shows clearly the ribbons made by MoO_6 octahedra and P_2O_7 groups running along the **c** direction. Each MoO_6 octahedra shares four of its oxygen atoms with four PO_4 tetrahedra belonging to only three different P_2O_7 groups. The two oxygens O(1) and O(2) of the molybdenyl group do not take part in the phosphorus coordination. The Mo–O mean distances (Table III) corresponding to the latter oxygen atoms are significantly shorter

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[1] Lists of structure factors and anisotropic thermal parameters are available on request.

(Mo–O, 1.694 Å) than the other distance (Mo–O, 2.089 Å).

In the P_2O_7 groups interatomic distances and bond angles (Table III) are similar to those usually observed in previously reported diphosphates:

—Two long P–O distances corresponding to the P–O–P bonds.

—Six shorter P–O distances corresponding to the remaining oxygen atoms of the group shared between only one phosphorus and associated cations.

Each of these P_2O_7 groups is linked to three MoO_6 octahedra.

The cesium and H atoms line the channels (Fig. 2) delimited by the anionic ribbons. At about 3.5 Å the cesium atoms are surrounded by six oxygen atoms. The hydrogen bonding scheme is clearly shown in Fig. 2. The H atoms link P_2O_7 groups to form a chain running along the **a** axis. This same scheme has already been encountered in the $MnHP_2O_7$ structure (*19*). The figures have been drawn using the STRUPLO program (*20*).

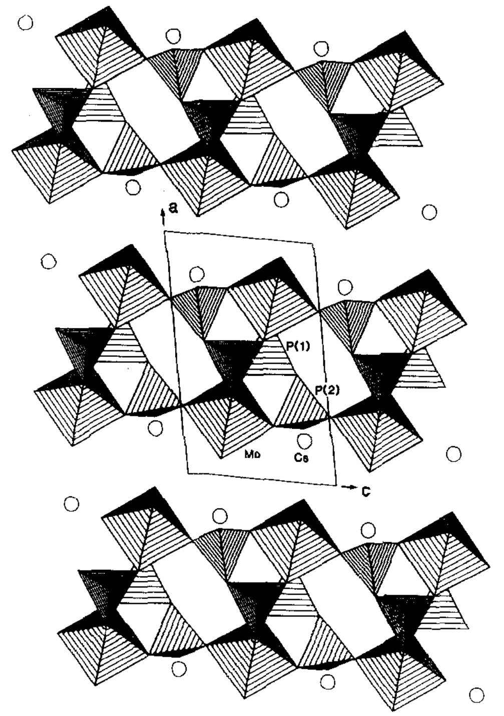

FIG. 1. Projection along the **b** axis of the atomic arrangement of $CsHMoO_2P_2O_7$ $(0.70 < y < 1.30)$.

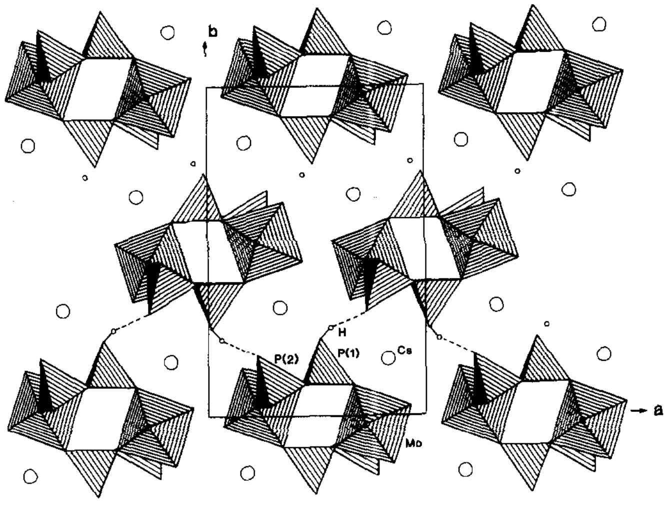

FIG. 2. Projection along the **c** axis of the atomic arrangement of $CsHMoO_2P_2O_7$.

TABLE III

Main Interatomic Distance (Å) and Bond Angles (°) for $CsHMoO_2P_2O_7$

		MoO_6 octahedron		
Mo-O(E11)	2.190(3)	Mo-O(E23)		1.998(2)
Mo-O(E12)	2.173(2)	Mo-O(1)		1.701(3)
Mo-O(E21)	1.997(2)	Mo-O(2)		1.688(3)
Mo-P(1)	3.4623(9)	Mo-P(2)		3.2960(9)
Mo-P(1)	3.4621(8)	Mo-P(2)		3.2781(8)
		P_2O_7 group		
P(1)	O(E11)	O(E12)	O(E13)	O(L)
O(E11)	1.496(2)	2.556(3)	2.456(4)	2.516(3)
O(E12)	117.3(1)	1.497(3)	2.498(4)	2.473(4)
O(E13)	107.7(2)	110.4(1)	1.545(3)	2.515(4)
O(L)	108.7(1)	105.9(1)	106.2(2)	1.599(3)
P(2)	O(E21)	O(E22)	O(E23)	O(L)
O(E21)	1.536(2)	2.554(4)	2.441(3)	2.512(3)
O(E22)	115.7(1)	1.481(3)	2.542(4)	2.511(4)
O(E23)	105.8(1)	115.5(2)	1.525(2)	2.460(4)
O(L)	106.3(1)	108.9(2)	103.6(1)	1.604(3)
P(1)-P(2)	2.862(1)	P(1)-O(L)-P(2)		126.6(1)
		CsO_6 coordination polyhedron		
Cs-O(E13)	3.167(3)	Cs-O(E23)		3.182(2)
Cs-O(E21)	3.173(3)	Cs-O(1)		3.118(3)
Cs-O(E22)	3.102(3)	Cs-O(1)		3.160(3)
		Hydrogen bonding		
O(E13)-H	0.78(1)	O(E13)-H...O(E22)		159(12)
O(E22)...H	1.77(10)	O(E13)-O(E22)		2.516(4)

Note. Estimated standard deviations are given in parentheses.

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