JOURNAL OF SOLID STATE CHEMISTRY 80, 144–148 (1989)

BRIEF COMMUNICATION

The Structure of $CsV(MoO_4)_2$

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Received November 30, 1988; in revised form February 8, 1989

The crystal structure of $CsV(MoO_4)_2$ was determined from single-crystal X-ray diffraction data. It crystallizes in the trigonal space group $P\bar{3}m1$ (No. 164) with $a = 5.662(3)$, $c = 7.976(2)$ Å, $Z = 1$. The structure contains layers of vanadium molybdate with the cesium cations between the layers. Each layer is built up from corner-sharing VO_6 octahedra and MoO_4 tetrahedra. The structural relationship between the title compound, $KAl(SO_4)_2$, $KV(SO_4)_2$, and a high-temperature form of $Zr(MoO_4)_2$ is discussed.

Introduction

Our recent work on the system M–Mo–P–O (M = metal cation) containing Mo in oxidation states less than +6 has led to a great number of new structures (see, e.g., (*1*)). In these compounds, MoO_6 octahedra and PO_4 tetrahedra are essential building blocks. As part of a research project devoted to discovering novel mixed frameworks built up from corner-sharing octahedra and tetrahedra, we have turned our attention to the system vanadium molybdates.

The compound $VMoO_5$ was found to be isostructural with $MoOPO_4$ and accordingly was formulated as $VOMoO_4$ (*2*). From a structural viewpoint the discovery of $VOMoO_4$ suggests the presence of new structures in the system M–V–Mo–O, which are composed of corner-sharing VO_6 octahedra and MoO_4 tetrahedra. Thus, we initiated a synthetic program to explore novel compounds in the system vanadium molybdates. We report here on a V(III) molybdate $CsV(MoO_4)_2$ which exhibits a layer structure.

Experimental

Synthesis

Black, hexagonal, plate crystals of $CsV(MoO_4)_2$ grew as a minor product by heating Cs_2MoO_4, MoO_3, and V_2O_3 (mole ratio 1 : 3 : 1) in an evacuated fused silica

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tube at 700°C for 30 hr followed by slow cooling. The compound showed a brownish streak when it was ground into powder. A powdered sample of manually selected crystals of $CsV(MoO_4)_2$ from the melt was examined by differential thermal analysis in flowing nitrogen gas at a heating rate of 5°C/min. The DTA curve revealed two endothermic peaks at 547 and 575°C, suggesting that the material did not melt congruently. Polycrystalline $CsV(MoO_4)_2$ could be obtained as a major product by heating a mixture of proper amounts of the starting materials at 520°C for 48 hr. However, powder X-ray diffraction patterns showed that the products were always contaminated with a small amount of unidentified phases. The strongest reflection of the impurities was less than 4% of that of the major product.

Single-Crystal X-Ray Structure Determination

A black plate having the dimensions 0.12 × 0.10 × 0.06 mm was selected for indexing and intensity data collection on an Enraf–Nonius CAD4 diffractometer. The orientation matrix and unit cell parameters were determined at room temperature by least-squares fit of 25 peak maxima with $13° < 2\theta < 30°$. The intensity data were corrected for absorption, Lorentz, and polarization effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. An examination of the intensity data showed $\bar{3}m$ Laue symmetry and no systematic absences, which led to $P321$, $P3m1$, or $P\bar{3}m1$ space group. Based on the statistical analysis of intensity distribution and successful solution and refinement of the structure, the space group was determined to be $P\bar{3}m1$ (No. 164). The structure was solved by direct methods using SHELXTL PLUS program and refined by full-matrix least-squares refinement based on F values. The multiplicities for the Cs, V, and Mo atoms were allowed to refine but did not deviate significantly from full occupancy. Crystal data, intensity measurement, and structure refinement parameters are collected in Table I. Table II contains the final atomic coordinates and thermal parameters. Selected bond distances and bond angles are given in Table III.

Description of the Structure and Discussion

As shown in Fig. 1, the most prominent structural feature of $CsV(MoO)_2$ is the layers of vanadium molybdate with the cesium atoms between the layers. Each layer is built up from corner-sharing VO_6 octahedra

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENT, AND REFINEMENT PARAMETERS FOR $CsV(MoO_4)_2$

Crystal data	
Space group	$P\bar{3}m1$ (No. 164)
Cell constants	$a = 5.662(3)$, $c = 7.976(2)$ Å
	$V = 221.4(3)$ Å^3
Z	1
Density (calcd)	3.777 g/cm^3
Abs. coeff. (Mo$K\alpha$)	77.6 cm^{-1}
Intensity measurement	
λ (Mo$K\alpha$)	0.70930 Å
Scan mode	$\theta/2\theta$
Scan rate	5.5°/min
Scan width	$0.65° + 0.35° \tan\theta$
Maximum 2θ	60°
Standard reflections	three measured every 1 hr (no decay)
Unique reflections measured	279
Structure solution and refinement	
Reflections included	254 with $I > 2.5\ \sigma(I)$
Parameters refined	18
Agreement factors	$R = 0.032$, $R_w = 0.034$
GOF	2.02
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	2.90, −2.33 e/Å^3 (peak max. is at a distance of 0.78 Å from Cs)

TABLE II

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR $CsV(MoO_4)_2$

Atom	Site	Site symmetry	x	y	z
Cs	1a	$\bar{3}m$	0	0	0
V	1b	$\bar{3}m$	0	0	$\frac{1}{2}$
Mo	2d	3m	$\frac{2}{3}$	$\frac{2}{3}$	0.28729(7)
O(1)	6i	m	0.1627(4)	−0.1627	0.6445(4)
O(2)	2d	3m	$\frac{2}{3}$	$\frac{1}{3}$	0.0735(8)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}[a]
Cs	20.3(4)	20.3	16.2(4)	0	0	10.2(2)	19.0(3)
V	4.2(5)	4.2	13.0(7)	0	0	2.1(2)	7.1(4)
Mo	6.6(3)	6.6	12.1(4)	0	0	3.3(2)	8.4(3)
O(1)	30(1)	30	27(2)	4.4(6)	−4.4	23(2)	26(1)
O(2)	24(2)	24	17(2)	0	0	12(1)	21(2)

[a] U_{eq} is defined as one-third of the orthogonalized U_{ij} tensor.

and MoO_4 tetrahedra. A view of a layer approximately parallel to the c-axis clearly shows how the polyhedra are connected (Fig. 2). Each VO_6 octahedron shares its six corners with six MoO_4 tetrahedra. Each MoO_4 tetrahedron shares three corners with three VO_6 octahedra in the ab-plane with the fourth corner being coordinated to a Cs atom. Alternatively, the structure can be described as hexagonal close-packed MoO_4 groups with the octahedral sites filled with V and Cs atoms. In other words, MoO_4 groups replace As atoms, and V and Cs atoms take the place of Ni atoms in the NiAs structure.

TABLE III

BOND DISTANCES (Å) AND ANGLES (°) FOR $CsV(MoO_4)_2$

Distances		Angles	
Cs–O(1)	3.254(4) (6×)	O(1)–Mo–O(1)	110.9(1)
Cs–O(2)	3.321(2) (6×)	O(1)–Mo–O(2)	108.0(1)
V–O(1)	1.969(3) (6×)	O(1)–V–O(1)	89.2(1)
Mo–O(1)	1.759(2) (3×)		90.8(1)
Mo–O(2)	1.705(6) (1×)	Mo–O(1)–V	162.2(2)

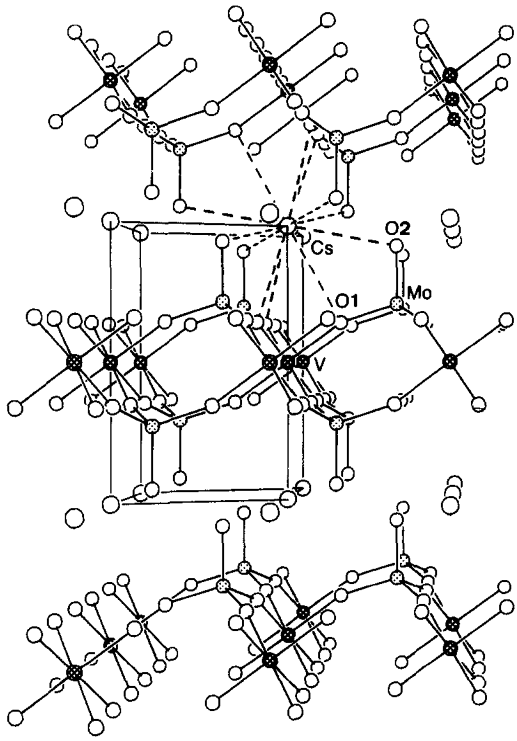

FIG. 1. A view of the structure of $CsV(MoO_4)_2$ in a direction approximately parallel to the a-axis.

The V^{3+} cation with point symmetry $\bar{3}m$ has six O(1) atom neighbors at a distance of 1.969(3) Å, which is a little shorter than the distance of 2.00 Å predicted from Shannon's effective ionic radii (3). The VO_6 octahedron is nearly regular as shown by the O–O distances (2.803(6) (6×) and 2.764(2) Å (6×)). The Mo^{6+} cation with point symmetry $3m$ is in a slightly distorted tetrahedral arrangement (d(O–O) = 2.898(2) (3×), 2.804(6) Å (3×)). One oxygen O(2) is bonded to molybdenum while the other three oxygen atoms (O(1)) are each shared by one vanadium atom and one molybdenum atom. As a consequence, there are two types of Mo–O distances: one short Mo–O(2) distance of 1.705(6) Å and three longer distances of 1.759(1) Å. The longer distance is in agreement with the distance of 1.77 Å predicted from Shannon's radii. The Cs^+

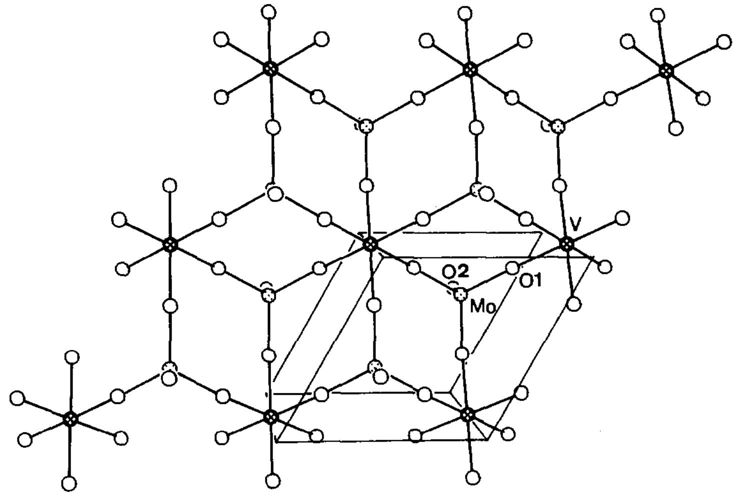

FIG. 2. A view of a layer in $CsV(MoO_4)_2$.

cation, which is situated at (0, 0, 0), is in a 6 + 6 oxygen coordination, formed by an elongated trigonal antiprism of O(1) atoms with equatorial corrugated hexagon of O(2) atoms. Each Cs^+ cation is surrounded by six O(1) atoms at a distance of 3.254(4) Å and six more (O(2)) at 3.321(2) Å with an average value of 3.288 Å for a predicted distance of 3.26 Å. An assessment of the valence of the V and Mo atoms using the bond-length bond-strength formula for V^{3+}–O and Mo^{6+}–O bonds (*4*) yields +3.26 for V and +6.20 for Mo.

There is a close structural relationship between $CsV(MoO_4)_2$, $KV(SO_4)_2$ (*5*), and $KAl(SO_4)_2$ (*6*). All three structures contain layers of composition $[M(XO_4)_2^-]_n$ (M = V or Al, X = Mo or S) with the alkali metal cations between the layers. As discussed earlier $CsV(MoO_4)_2$ can be regarded as h.c.p. arrangement of molybdate anions, in which the entire layers of octahedral sites are occupied by V^{3+} and these alternate with layers of Cs^+ cations. The stacking sequence is . . . (*A*)(V)(*B*)(Cs)(*A*) . . . , where (*A*) and (*B*) label the layers of molybdate anions. In $KAl(SO_4)_2$ the sulfate anions are also hexagonal close packed, but the coordination of Al^{3+} is trigonal prismatic (Fig. 3). The structure of $KV(SO_4)_2$ can be described as a c.c.p. arrangement of sulfate anions with layers of octahedral sites alternately occupied by K^+ and V^{3+} cations, giving rise to a six-layer repeat of sulfate anions (. . . (*A*)(V)(*B*)(K)(C)(V)(*A*) (K)(*B*)(V)(C)(K)(*A*) . . .). Figure 4 is a view of a layer of $[V(SO_4)_2^-]_n$ along the *c*-axis, showing that the M^{3+}–O(1)–X^{6+} bond angle

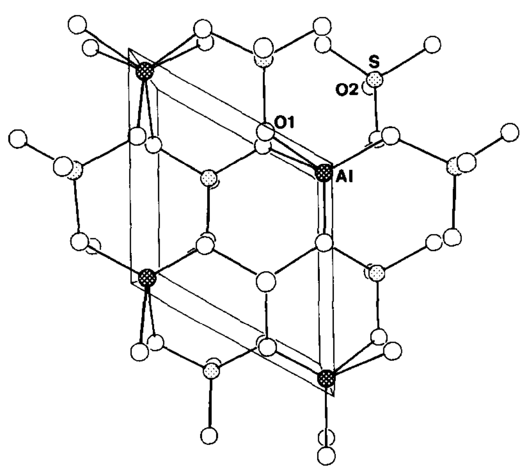

FIG. 3. A layer in $KAl(SO_4)_2$.

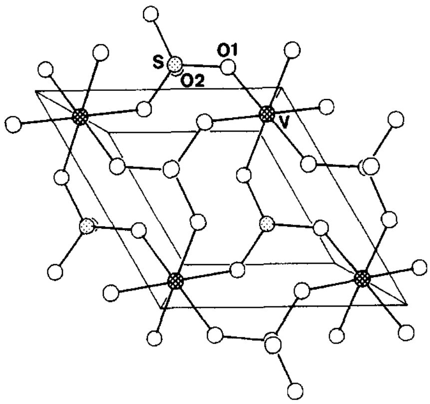

FIG. 4. A layer in $KV(SO_4)_2$.

in $KV(SO_4)_2$ (136°) is considerably smaller than the corresponding angle in CsV $(MoO_4)_2$ (162°). As pointed out by Fehrmann *et al.* (*5*) one determining factor for the different structures may be the different ratio of the metal atom ionic radii. The ratio of $r(V^{3+})$ to $r(Cs^+)$ using Shannon's effective ionic radii is 0.34 which is close to that for $KAl(SO_4)_2$ ($r(Al^{3+})/r(K^+) = 0.33$). The structural relationship between CsV $(MoO_4)_2$ and $KAl(SO_4)_2$ is close. The change from space group $P\bar{3}m1$ to $P321$ essentially retains all the atomic coordinates except O(1), thus changing the coordination of M^{3+} from octahedral V^{3+} to trigonal prismatic Al^{3+}.

$CsV(MoO_4)_2$ is also closely related to high-temperature (HT) $Zr(MoO_4)_2$ (*7*), which can be described as hexagonal close-packed MoO_4^{2-} anions with half of the octahedral sites occupied by Zr^{4+} cations. In HT $Zr(MoO_4)_2$, entire layers of octahedral sites are occupied and these alternate with layers of empty sites. The stacking sequence in the zirconium compound is . . . $(A)(Zr)(B)(A')(Zr)(B')(A)$ . . . , where (A), (B), (A'), and (B') label the layers of molybdate ions. The orientation of the MoO_4^{2-} tetrahedra in (A) (or (B)) is different from that in (A') (or (B')), which leads to a four-layer repeat of molybdate anions.

Acknowledgments

Support for this study by the National Science Council and the Institute of Chemistry Academia Sinica are gratefully acknowledged.

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