New Structure of High-Temperature Zirconium Molybdate

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Abstract. $Zr(MoO_4)_2$, $M_r = 411.12$, crystallizes in two phases; high-temperature form is trigonal, $P\bar{3}1c$, $a = 10.1391(6)$, $c = 11.7084(8)$ Å, $V = 1042.4(2)$ Å^3, $Z = 6$, $D_m = 3.91(4)$, $D_x = 3.927$ g cm^{-3}, $\lambda(Mo\ K\alpha_1) = 0.70926$ Å, $\mu = 53.68$ cm^{-1}, $F(000) = 1128$, $T = 293$ K, $R = 0.031$ for 855 independent reflexions with $F_{obs} > \sigma$. The zirconium atoms occupy two special positions and have octahedral coordination with normal Zr—O bond lengths. The molybdenum atoms are in a distorted tetrahedral arrangement. The outstanding feature of this revised structure is the unusual short Mo—O(4) distance of 1.690 Å with a bond strength of 1.89.

Introduction. This study is part of a systematic investigation of the correlation between the structure and the vibrational spectrum of molybdates and tungstates that contain a tetravalent cation. The $Zr(MoO_4)_2$ compound crystallizes in two different phases. The low-temperature form transforms reversibly into a high-temperature form at ~913 K (Tarte & Auray, 1982). The crystal structure of the parent compound $Hf(MoO_4)_2$ (Freundlich & Thoret, 1967), which crystallizes only in the high-temperature form, was reported by Rimsky, Thoret & Freundlich (1968). The structure was determined with only 81 reflexions for 23 variables. The reported bond distances do not match the atomic coordinates, some distances [Mo—O(1) = 1.41, O(1)—O(2) = 2.17, Hf(1)—O(2) = 2.75 Å] do not agree with the distances predicted from Shannon's (1976) ionic radii, and a twelvefold coordination for Hf^{IV} is most unlikely. Therefore we decided to carry out a conclusive detailed crystallographic redetermination of the title compound, HT $Zr(MoO_4)_2$.

Experimental. Single crystals of $Zr(MoO_4)_2$ prepared by heating some of the powder sample ($ZrO_2 : 2MoO_3$)

with an excess of MoO_3. After 3 h at 1123 K the mixture was quenched, to inhibit generation of the low-temperature form. The crystals appeared as colourless plates. Precession photographs indicated Laue symmetry $\bar{3}m$ and systematic extinctions ($hh2\bar{h}l$ for $l = 2n$) consistent with $P\bar{3}1c$. Cell dimensions obtained and refined from powder diffraction data, using Si as reference. Pycnometric density measured in toluene. Intensity data obtained on a Philips PW 1100 four-circle automatic diffractometer. Data-collection conditions: Mo $K\alpha_1$ with graphite monochromator, ω–2θ scan at 0.01° s^{-1} with (1.5 + 0.3 tanθ)° scan range. Three control reflexions (630, 0,0,12, $\bar{6}\bar{3}0$) measured every hour showed relative standard deviation of 0.008. 1020 independent reflexions measured up to $2\theta_{max} = 60°$ (h: 0 to 12, k: 0 to 7, l: −16 to 16), corrected for background, Lorentz and polarization effects, which provided 762 reflexions satisfying $F_{obs} > 3\sigma$. Absorption corrections with de Meulenaer & Tompa's (1965) analytical method, program *AGNOST* (Ahmed, 1974). Distances along a, b and c were respectively 0.316, 0.448 and 0.100 mm. Min. and max. absorption correction factors 0.673 and 0.803. Zr^{4+}, Mo^{6+} (*International Tables for X-ray Crystallography*, 1974, p. 71) and O^{2-} (Tokonami, 1965) scattering factors used and corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974, p. 148). Patterson synthesis used to determine positions of heavy atoms. Oxygens located in Fourier synthesis, using *SHELX76* (Sheldrick, 1976). Least-squares refinement on F, $w = 1/\sigma^2$, including isotropic secondary extinction performed with program *LINEX* (Becker & Coppens, 1975). Best results obtained for isotropic extinction with a prevalence of mosaic spread (type I) over particle size (type II) and Lorentzian shape for distribution function ($\eta = 3.6''$ and $r = 4\mu$m). Refinement with isotropic temperature

Table 1. *Atomic positions and equivalent isotropic thermal coefficients*

$$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{e}_i.\mathbf{e}_j.$$

	Wyckoff position	x	y	z	$B_{eq}(\text{Å}^2)$
Zr(1)	2(b)	0	0	0	1·06 (3)
Zr(2)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·98132 (8)	0·93 (2)
Mo	12(i)	0·32871 (7)	0·33891 (7)	0·14900 (3)	0·80 (2)
O(1)	12(i)	0·1731 (6)	0·1664 (6)	0·1008 (4)	1·9 (2)
O(2)	12(i)	0·3323 (9)	0·4959 (6)	0·0814 (3)	1·9 (2)
O(3)	12(i)	0·4979 (5)	0·3364 (9)	0·1178 (3)	1·7 (1)
O(4)	12(i)	0·3189 (6)	0·3522 (6)	0·2923 (3)	2·3 (2)

factors gave $R = 0·097$; correction for isotropic extinction (type I) resulted in $R = 0·063$. Refinement with anisotropic temperature factors gave $R = 0·027$. Since Hamilton's (1965) ratio $\mathcal{R}_{27,708,0.005} = 1·0536$ is much less than $R_{iso+ext}/R_{aniso}$ (2·33), the anisotropic model was justified at a confidence level of more than 95%. The atomic and thermal parameters are given in Table 1. A last refinement was done with 855 reflexions ($F_{obs} > \sigma$), which resulted in $R = 0·031$, $wR = 0·028$, $S = 2·638$, $(\Delta/\sigma)_{max} = 0·007$, $g = 1·30 \ (3) \times 10^{-4}$, improving the standard deviations on the interatomic distances. The highest peak in a difference Fourier synthesis was $0·73 \ e \ \text{Å}^{-3}$ near Zr(1).*

Discussion. *Zirconium environment.* The Zr^{4+} cations occupy two sets of special equivalent positions of multiplicity two and four. They are at the centre of a trigonal antiprism which will be subsequently likened to a ZrO_6 octahedron. Zr(1) with point symmetry $\bar{3}$ has six O(1)-atom neighbours. Zr(2) with point symmetry 3 has two sets of three O-atom neighbours. The average distance Zr—O is 2·086 Å which is in good agreement with the distance of 2·07 Å predicted from Shannon's (1976) ionic radii. Bond lengths, bond angles and bond strengths are listed in Table 2.

Molybdenum environment. The Mo^{6+} cation is in a distorted tetrahedral arrangement. One oxygen O(4) is bonded only to molybdenum while the three other oxygens are shared by one zirconium and one molybdenum. As a consequence, there are two types of Mo—O distances: one unusual short Mo—O(4) distance of 1·690 (3) Å and three longer distances with an average value of 1·764 Å for a predicted distance of 1·76 Å (Shannon, 1976). Bond lengths, bond angles and bond strengths are listed in Table 2.

Crystal network. The structure is a two-dimensional network with layers parallel to (001) at $c/2$ intervals. The MoO_4 tetrahedra are connected to the ZrO_6

octahedra *via* three monodentate common corners: O(1), O(2), O(3). The bonding along [001] between two close layers is of van der Waals type; it takes place through 12 O(4)—O(n) distances which lie between 3·01 and 4·04 Å (Table 2). The O(4) coordination

Table 2. *Bond lengths (Å), bond angles (°) and bond strengths (s)*

MoO_4 tetrahedra

		s	Bond distribution		
Mo—O(1)	1·763 (7)	1·50	$1\sigma + 0·5\pi$	O(1)—O(2)	2·903 (17)
—O(2)	1·762 (5)	1·50	$1\sigma + 0·5\pi$	—O(3)	2·860 (16)
—O(3)	1·767 (5)	1·48	$1\sigma + 0·5\pi$	—O(4)	2·825 (12)
—O(4)	1·690 (3)	1·89	$1\sigma + 1\pi$	O(2)—O(3)	2·887 (12)
				—O(4)	2·836 (8)
				O(3)—O(4)	2·790 (9)

O(1)—Mo—O(2)	110·89 (4)		O(2)—Mo—O(3)	109·79 (3)
O(1)—Mo—O(3)	108·26 (3)		O(2)—Mo—O(4)	110·45 (3)
O(1)—Mo—O(4)	109·74 (4)		O(3)—Mo—O(4)	107·62 (2)

ZrO_6 polyhedra

				s
Zr(1)—O($1^{i \ to \ vi}$)	(6×)	2·088 (8)		0·68
Zr(2)—O($2^{i,ix,x}$)	(3×)	2·087 (8)		0·68
O($3^{vi,vii,viii}$)	(3×)	2·081 (7)		0·69

O(1^i)—Zr(1)—O(1^{ii})	(6×)	91·19 (3)	O(3^{vii})—Zr(2)—O(3^{vi}) (3×)	91·91 (3)
O(1^i)—Zr(1)—O(1^v)	(6×)	88·81 (3)	O(2^i)—Zr(2)—O(3^{vii}) (3×)	87·92 (3)
O(2^i)—Zr(2)—O(2^{ix})	(3×)	91·54 (3)	O(2^i)—Zr(2)—O(3^{vi}) (3×)	88·62 (3)

O(4) coordination polyhedron

O(4)—O(1^{xi})	3·99 (1)		O(4)—O(1^{xii})	3·29 (2)*
—O(2^{xi})	3·88 (1)		—O(1^{xiii})	3·13 (2)*
—O(3^{xi})	4·06 (1)		—O(2^{xiii})	3·01 (1)*
—O(4^{xii})	4·03 (2)		—O(2^{xiv})	3·15 (2)*
—O(4^{xiii})	3·06 (1)		—O(3^{xii})	3·41 (1)*
—O(4^{xiv})	3·48 (2)		—O(3^{xiv})	3·21 (2)*

Symmetry code: (i) x, y, z; (ii) $-y, x-y, z$; (iii) $y-x, -x, z$; (iv) $-x, -y, -z$; (v) $y, y-x, -z$; (vi) $x-y, x, -z$; (vii) $1-x, 1-y, -z$; (viii) $y, 1+y-x, -z$; (ix) $1-y, 1+x-y, z$; (x) $y-x, 1-x, z$; (xi) $y, x, \frac{1}{2}+z$; (xii) $x, x-y, \frac{1}{2}-z$; (xiii) $y-x, y, \frac{1}{2}-z$; (xiv) $1-y, 1-x, \frac{1}{2}-z$.
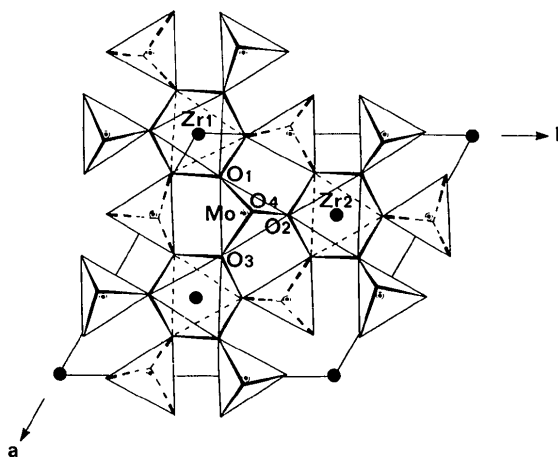
Fig. 1. Projection of the HT $Zr(MoO_4)_2$ structure along the c axis.

polyhedron can be visualized as a strongly distorted Archimedean cuboctahedron, which is the coordination polyhedron of an anion with respect to its nearest-neighbour anions in ideal cubic close packing. The pseudo-hexagon with six oxygen atoms, asterisked in Table 2, is nearly parallel to (001). A projection of the HT $Zr(MoO_4)_2$ structure along the c axis is given in Fig. 1.

The outstanding feature of this structure is the oxygen O(4) bonded only to molybdenum. As a result, the Mo—O(4) bond strength (Zachariasen, 1978) has a much higher value than that of the other three (Table 2) and the O(4) average quadratic vibration is 1·5 times lower along the z axis than in the (001) plane. According to Schröder (1975) this structural deformation goes along with a modification of the π-bond distribution around the Mo atom, which gives to the Mo—O(4) bond a pronounced covalent character (Table 2). This structure, common to $Hf(MoO_4)_2$ and HT $Zr(MoO_4)_2$, is unique since, to our knowledge, there is no other isostructural $A(XO_4)_2$ compound. However, the structural unit made up of ZrO_6 octahedra surrounded by six monodentate MoO_4 tetrahedra, alternately pointing up and down, is very similar in configuration to several structures that have tetrahedral anions, such as the glaserite $K_3Na(SO_4)_2$ structure (Moore, 1973).

The differences between the structure reported by Rimsky, Thoret & Freundlich (1968) and ours lie in the Wyckoff position of the $M^{IV}(1)$ cation [2(a) instead of 2(b)] and in the orientation of the MoO_4 tetrahedra, which led them to a three-dimensional network and a twelvefold-coordinated $M^{IV}(1)$ cation.

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Structure du Sulfure d'Europium et de Bismuth Eu₁,₁Bi₂S₄

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Abstract. $M_r = 698·18$, hexagonal, $P6_3/m$, $a = 24·820(8)$, $c = 4·080(1)$ Å, $V = 2176·7(1·9)$ Å³, $Z = 12$, $D_m = 6·2(1)$, $D_x = 6·39(1)$ Mg m⁻³, $\lambda(Mo K\bar{\alpha}) = 0·71069$ Å, $\mu = 55·5$ mm⁻¹, $F(000) = 3516$, $T = 293$ K, $R = 0·053$ for 1216 independent observed reflections. The Eu atoms have eightfold prismatic coordination [trigonal prism (Eu–S: 3·02 to 3·17 Å) with Eu contacts to two other S atoms in the equatorial plane of the prism (Eu–S: 3·10 to 3·26 Å)] and the Bi atoms have sixfold octahedral coordination (Bi–S: 2·52 to 3·63 Å). There are large channels around the sixfold axes, which are not completely empty and contain two six-coordinated sites partially occupied by europium.

Introduction. L'étude du système Eu₃S₄–Bi₂S₃ nous a permis de décrire le composé Eu₂BiS₄ où l'europium présente deux états de valence (Lemoine, Carré & Guittard, 1982). L'étude du système EuS–Bi₂S₃ nous conduit au composé Eu₁,₁Bi₂S₄ dans lequel l'europium possède la valence 2 et qui présente un caractère semi-métallique. Des monocristaux de cette nouvelle phase ont été isolés dans une préparation obtenue par mélange de Bi₂S₃ + EuS, en ampoule de silice scellée sous vide, chauffée à 1073 K et refroidie lentement. On peut également l'obtenir à partir du mélange EuS + 2 Bi (en poudre) + 3 S, en ampoule de silice scellée sous vide et chauffée lentement à 1073 K ou encore par sulfuration dans un courant de sulfure d'hydrogène du