

a closed f shell (Yb^{2+} , $4f^{14}$, 1S_0), no magnetic moment should be involved. Several samples of $\text{Y}_{1-x}\text{Yb}_x\text{B}_6$ ($x \leq 0.3$) were produced. Lattice parameters, which are listed in Table I, show that Vegard's law is closely obeyed. Figure 1 shows that the corresponding T_c drops almost linearly with concentration.

Since thorium is typically Th^{4+} ($5f^0$, 1S_0), it also should show no magnetic moment. Table I gives the observed lattice parameters for $\text{Y}_{1-x}\text{Th}_x\text{B}_6$ ($x \leq 0.7$). Again Vegard's law is followed but with somewhat slower lattice expansion. Figure 1 shows the dependence of T_c on concentration. At low Th doping in $\text{Y}_{1-x}\text{Th}_x\text{B}_6$, the T_c drops linearly with almost the same slope as if Yb had been added, but then the T_c levels out until about 60% replacement of Y, whereupon it again drops more rapidly.

Magnetic susceptibilities of several of the samples were measured over the range 1.5-300 K. In the case of $\text{Y}_{0.6}\text{Th}_{0.4}\text{B}_6$ the susceptibility is diamagnetic ($\chi_g = -0.12 \times 10^{-6}$) and remains at this value down to 6 K. This is almost exactly what we calculate for the diamagnetic cores plus the Pauli paramagnetism of the electron gas. Clearly the thorium has no localized moment. In the case of $\text{Y}_{0.84}\text{Yb}_{0.16}\text{B}_6$, the room-temperature susceptibility is again diamagnetic (observed $\chi_g = -0.16 \times 10^{-6}$ compared to calculated -0.23×10^{-6}) but there is a pronounced Curie tail below 100 K leading eventually to a paramagnetism of $\chi_g = +1.28 \times 10^{-6}$ at 4 K. Similar behavior is observed for $\text{Y}_{0.72}\text{Yb}_{0.28}\text{B}_6$. Chemical analysis of the samples showed that the temperature-dependent susceptibility could not be due to Fe impurities, as the amount of Fe could not account quantitatively for the observed susceptibility and in any case the samples with less impurity showed a higher paramagnetism. Hence, we concluded that the observed paramagnetic moment of $\text{Y}_{1-x}\text{Yb}_x\text{B}_6$ arises from partial occurrence of the ytterbium as Yb^{3+} ($4f^{13}$, $^2F_{7/2}$) rather than Yb^{2+} ($4f^{14}$, 1S_0). Yb^{3+} has a moment of $4.54 \mu_B$, so less than 1% of it would have been enough to account for our observations.

Comparison of the T_c vs. x data for $\text{Y}_{1-x}\text{M}_x\text{B}_6$ where $M = \text{Yb}$, Th , or La shows that in all three cases the decrease is linear with the same slope in the concentration range $0 \leq x \leq 0.2$. A sample of $\text{Y}_{0.85}\text{Ca}_{0.15}\text{B}_6$ was also made and measured; it also fits the same line.

The nonstoichiometry range of Y_{1-x}B_6 ⁹ is coincident with the above concentration range, so it might be that the observed decrease of T_c in this region is a stoichiometry effect such as is observed in carbide and nitride systems.¹⁰ However, the divergence of the curves at higher concentrations has to be blamed on the rising magnetic moment in the $\text{Y}_{1-x}\text{Yb}_x\text{B}_6$ system just as occurs in $\text{Y}_{1-x}\text{Ce}_x\text{B}_6$ ⁴ and in $\text{Y}_{1-x}\text{La}_x\text{B}_6$.⁸ Nevertheless, in the $\text{Y}_{1-x}\text{Th}_x\text{B}_6$ system no magnetic moments are involved. Therefore, the following conclusion is arrived at: Band filling in YB_6 is such that the Fermi energy coincides with a maximum in the density of states curve. Replacing trivalent Y by a divalent metal or a tetravalent metal leads to a lower density of states as the Fermi energy falls or rises, respectively. Hence, T_c generally falls. Additional magnetic effects lower the T_c even more rapidly.

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Redetermination of the Structure of $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$: Confirmation of the Usual MoO_2^{2+} Geometry

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Recent EXAFS studies^{1,2} indicate that the Mo atoms in the oxidized (Mo(VI)) forms of xanthine oxidase¹ and sulfite oxidase² are coordinated by oxygen atoms at approximately 1.7 Å. These results have led to an increased interest in the structural chemistry of oxomolybdenum(VI) species.^{3,6} A large number of structures of this type have been published.^{4,5} With the exception of the recently reported complex $\text{MoO}_2(\text{SC}(\text{CH}_3)_2\text{CH}_2\text{NHCH}_3)_2$,⁶ the dioxomolybdenum compounds have distorted octahedral geometries with the oxo groups cis to each other. Generally, the $\text{Mo}=\text{O}$ distances are between 1.68 and 1.72 Å with the $\text{O}=\text{Mo}=\text{O}$ angles ranging from 102 to 108°.

The structure of $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$, originally reported in 1972, appears to be substantially inconsistent with similar structures with regard to the reported $\text{Mo}=\text{O}$ distances (1.634 (25) Å) and $\text{O}=\text{Mo}=\text{O}$ angle (114.0 (20)°).⁷ Despite the fact that the uncertainty about the accuracy of this structure had been noted,^{5,8} it has continued to be cited in the literature for comparison with other dioxomolybdenum(VI) complexes.⁹ We report here a redetermination of this structure which reveals that the structure of $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ is, in fact, completely consistent with similar structures and has $\text{Mo}=\text{O}$ distances of 1.703 (2) Å and an $\text{O}=\text{Mo}=\text{O}$ angle of 105.61 (12)°.

Experimental Section

The compound was prepared by the method of Moore and Larson.¹⁰ Large, well-formed orange crystals were grown from hot toluene. A relatively small hexagonal rod (0.15 × 0.15 × 0.20 mm) was mounted on a glass fiber for X-ray diffraction studies. The diffraction experiments were performed on a Syntex P2₁ diffractometer using $\text{Mo K}\alpha$ radiation. Fifteen reflections chosen from a rotation photograph were used to determine preliminary cell parameters which were found to be essentially identical with those originally reported.⁷ Least-squares refinement of the setting angles for 15 reflections with $15^\circ < 2\theta < 20^\circ$ yielded the monoclinic cell dimensions $a = 17.350$ (6) Å, $b = 8.662$ (2) Å, $c = 13.575$ (3) Å, and $\beta = 124.61$ (2)°. There are four molecules in the unit cell. All reflections of the form $+h, +k, \pm l$ with $3^\circ < 2\theta < 60^\circ$ were collected by using the θ - 2θ scan method. Three standard reflections were monitored every 60 reflections, and no significant variations in intensity were observed. The data were processed as described previously.¹¹ An analytical absorption cor-

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Table I

atom	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.0 (0)	0.05424 (3)	0.25 (0)	2.640 (6)	1.992 (8)	2.349 (6)	0 (0)	1.169 (4)	0 (0)
S1	0.04847 (4)	0.13099 (7)	0.45127 (4)	4.28 (1)	3.24 (2)	2.85 (1)	-1.40 (2)	2.263 (9)	-0.28 (1)
S2	0.11876 (3)	0.28756 (7)	0.33052 (4)	3.56 (1)	3.14 (2)	2.78 (1)	-0.83 (1)	2.138 (8)	-0.31 (1)
O1	0.0810 (1)	-0.0644 (2)	0.2564 (1)	3.85 (5)	3.10 (6)	3.75 (5)	1.13 (5)	1.83 (3)	0.32 (5)
N1	0.1440 (1)	0.3968 (2)	0.5309 (1)	2.91 (4)	2.74 (6)	2.74 (4)	-0.50 (5)	1.77 (3)	-0.29 (5)
C1	0.1099 (1)	0.2879 (2)	0.4490 (1)	2.45 (5)	2.67 (7)	2.37 (5)	-0.22 (5)	1.34 (3)	0.11 (5)
C2	0.1911 (1)	0.5321 (3)	0.5225 (2)	2.70 (5)	2.65 (8)	3.29 (6)	-0.52 (6)	1.61 (4)	-0.24 (6)
C3	0.1343 (1)	0.3951 (3)	0.6323 (2)	4.08 (6)	4.2 (1)	3.31 (5)	-0.83 (7)	2.69 (3)	-0.89 (6)
C4	0.1237 (2)	0.6629 (3)	0.4554 (2)	3.99 (8)	3.2 (1)	5.12 (9)	0.28 (8)	2.07 (6)	0.77 (8)
C5	0.2241 (2)	0.3554 (4)	0.7489 (2)	6.20 (9)	5.4 (1)	3.33 (6)	0.6 (1)	3.07 (5)	0.71 (8)

^a The form of the anisotropic temperature factor is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

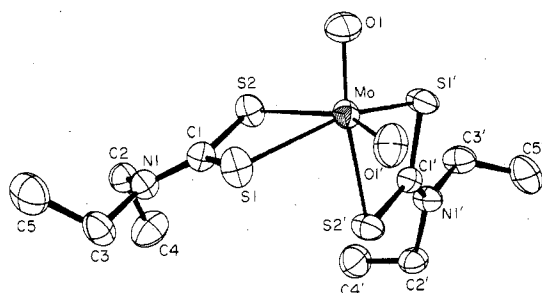


Figure 1. View of $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$. The atom labels used in the text are shown.

rection was applied to the complete data set. The systematic absences (hkl , $h + k \neq 2n$; $h0l$, $l \neq 2n$) are consistent with the space groups $C2/c$ and Cc . The structure had been originally solved⁷ in the centric space group $C2/c$, and our refinement confirms this choice. The starting coordinates were taken from Kopwille,⁷ transformed so that all of the atoms belong to the same molecule. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms, calculated on the basis of tetrahedral geometries and C-H distances of 0.98 Å, were included as fixed contributions in the final refinement cycles. The orientations of the methyl groups were determined from a difference Fourier map, and the temperature factors for all hydrogen atoms were set equal to 5.0 Å². The structure was refined to $R = 0.030$ and $R_w = 0.038$ with the error in an observation of unit weight equal to 1.12 electrons. Final atomic positional and thermal parameters are compiled in Table I. A listing of observed and calculated structure factors (Table III) is included as supplementary material.

Results and Discussion

The $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ complex has crystallographically imposed twofold symmetry. The overall structure and the atom numbering scheme are shown in Figure 1. The structure is a distorted octahedron with the oxo groups cis to each other and trans to sulfur atoms. The remaining two sulfur atoms are approximately trans to each other. Relevant bond distances and angles are given in Table II.

As expected, these data are substantially different from those found in the original determination⁷ and quite similar to those for $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_3\text{H}_7)_2)_2$.⁸ In particular, the average Mo=O distance and the O=Mo=O angle are 1.703 (2) Å and 105.81 (12)°, respectively, compared to 1.696 (5) Å and 105.7 (1)° for the propyl analogue. The sulfur atoms trans to the oxo groups must compete with the strongly bound oxo groups for the same orbitals.⁵ This trans effect is reflected in the Mo-S2 distance of 2.639 (1) Å compared to 2.450 (1) Å for the sulfur atoms trans to each other. The ligand has the expected geometry. The atoms S1, S2, C1, N1, C2, and C3 are essentially coplanar with the greatest deviation from the weighted least-squares plane being 0.04 Å. The Mo atom lies 0.43 Å out of this plane.

Therefore, the structure of $\text{MoO}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ is completely consistent with other dioxomolybdenum structures with similar donor atoms. This constancy of structure for octahedral dioxomolybdenum complexes should be useful in elu-

Table II. Selected Bond Angles (Deg) and Distances (Å)

Bond Distances			
Mo-S1	2.450 (1)	C1-N1	1.315 (3)
Mo-S2	2.639 (1)	N1-C2	1.470 (3)
Mo-O1	1.703 (2)	N1-C3	1.478 (3)
S1-C1	1.738 (2)	C2-C4	1.507 (3)
S2-C1	1.700 (2)	C3-C5	1.499 (4)
Bond Angles			
S1-Mo-S1'	148.51 (3)	S2-Mo-S2'	80.06 (3)
S1-Mo-S2	68.76 (2)	S2-Mo-O1	90.75 (6)
S1-Mo-S2'	86.95 (2)	S2-Mo-O1'	155.58 (6)
S1-Mo-O1	110.88 (6)	O1-Mo-O1'	105.81 (12)
S1-Mo-O1'	88.33 (6)		

cidating the structure and the mechanism of action of the metal sites in molybdenum-containing enzymes.

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Supplementary Material Available: Table III, a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Oxidation of Cerium(III) Phosphate by Steam in the Presence of Lithium Halides and Its Use in Thermochemical Water-Splitting Cycles

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Thermochemical cycles for water splitting¹ employ thermal energy to drive a cyclic series of chemical reactions, the sum of which is just $\text{H}_2\text{O} + \text{H}_2 + 1/2\text{O}_2$. Our previous work^{2,3} showed that cerium(IV) oxide, CeO_2 , reacts with alkali metal hydrogen phosphates— MH_2PO_4 or M_2HPO_4 , where $\text{M} = \text{Li}, \text{Na}, \text{K}$ —at $>600^\circ\text{C}$ to produce $\text{O}_2(\text{g})$, cerium(III) phosphate, CePO_4 , and alkali metal orthophosphates, M_3PO_4 . When $\text{M} = \text{Na}$ or K , the double phosphate $\text{M}_3\text{Ce}(\text{PO}_4)_2$ forms from the CePO_4 and the

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