Isolation of $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4S)]_2$, a Binuclear Mo(VI) Complex Containing a Disulfide Bond

SUE A. ROBERTS, GARY P. DARSEY, W. E. CLELAND, JR.* and JOHN H. ENEMARK**

Department of Chemistry, University of Arizona, Tucson, Ariz. 85721, U.S.A.

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Abstract

Aerial recrystallization of the mononuclear molybdenum(V) complex $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$ produced the novel binuclear Mo(VI) complex $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$ which contains a disulfide bond. The dimer crystallizes as the dioxane solvate in the space group $C2/c$ with cell parameters $a = 23.46(2)$, $b = 11.100(4)$, $c = 21.571(8)$ Å, $\beta = 104.23(4)°$, $Z = 4$. Final $R_w = 0.062$ (2236 reflections with $F_o > 3\sigma(F_o)$, 301 variable parameters). The dimer contains two crystallographically identical distorted octahedral MoO_2^{2+} centers. One face of each octahedron is occupied by two oxo ligands and a phenolate oxygen atom; the opposite face is occupied by three nitrogens of the $HB(Me_2pz)_3^-$ ligand. The two Mo(VI) centers of the dimers are linked by a disulfide bond formed upon oxidation of the 2-mercaptophenolate ligand of the original molybdenum(V) compound.

Introduction

Complexes with molybdenum–sulfur bonds undergo a wide variety of oxidation–reduction reactions that can include changes in oxidation state of the metal alone, the sulfur alone, or both sites simultaneously [1]. An attempt to grow single crystals of the previously reported mononuclear oxomolybdenum(V) complex $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$ [2], ($HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethylpyrazolyl)borate; $OC_6H_4\text{-}o\text{-}S$ = 2-mercaptophenolate), resulted in oxidation of both the molybdenum(V) center and the sulfur of the 2-mercaptophenolate ligand to form a binuclear molybdenum(VI) compound containing a disulfide bond. The structure of this dimer, $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$, is described below.

Experimental

Preparation

The dark brown complex $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$ was prepared as described previously [2]. Crystals of what proved to be $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$ were obtained by slow evaporation in air of a 1,4-dioxane/hexane solution of $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$. The resulting binuclear Mo(VI) complex is somewhat lighter in color than the brown starting material.

Structure Determination

$[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2\cdot C_4H_8O_2$ crystallizes in the space group $C2/c$ with lattice parameters $a = 23.46(2)$, $b = 11.100(4)$, $c = 21.571(8)$ Å, $\beta = 104.23(4)°$, $Z = 4$, $V = 5445$ Å^3. Data were collected to $2\theta = 45°$ on a Syntex $P2_1$ diffractometer equipped with a graphite crystal, incident beam monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were not made ($\mu = 5.8$ cm^{-1}). Intensities of equivalent reflections were averaged ($R_{int} = 0.032$). The molybdenum atom position was determined from the Patterson map; remaining atoms were found in succeeding difference Fourier syntheses. Solvent atoms, excluding hydrogen atoms, were included in the calculations, but only their thermal parameters were refined. Hydrogen atoms of the ligands were added to the structure factor calculations at idealized positions and not refined. Hydrogen atoms on the solvent molecule were not included in the calculations. After final refinement, $R_w = 0.062$ (2236 reflections, 301 variable parameters). The highest peak in the final difference Fourier was located near the solvent molecule and had a height of 0.8 e$^-$/Å^3. All calculations were performed on a PDP-11/34a computer using SDP-Plus [3]. Scattering factors were taken from the usual sources [4, 5]. Final positional parameters for all refined atoms are given in Table I.

Results and Discussion

The molecular structure of $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$ contains two crystallographically

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*Present address: Department of Chemistry, University of Mississippi, Miss. 38677, U.S.A.

**Author to whom correspondence should be addressed.

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TABLE I. Refined Positional Parameters for $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4S)]_2$

Atom	x	y	z	B_{eq}
Mo	0.69157(3)	0.16350(8)	0.14519(3)	3.79(1)
S	0.5343(1)	0.1088(3)	0.2295(1)	5.28(6)
O1	0.7523(3)	0.1230(6)	0.2019(3)	5.1(2)
O2	0.7035(3)	0.3115(5)	0.1337(3)	4.9(2)
O3	0.6351(2)	0.1756(6)	0.1959(2)	4.8(1)
N11	0.6108(3)	0.1714(7)	0.0594(3)	3.9(2)
N12	0.5993(3)	0.0840(7)	0.0129(3)	3.9(2)
N21	0.6615(3)	−0.0337(7)	0.1355(3)	4.0(2)
N22	0.6472(3)	−0.0918(6)	0.0772(3)	4.0(2)
N31	0.7312(3)	0.1056(6)	0.0675(3)	3.4(1)
N32	0.7038(3)	0.0329(6)	0.0185(3)	3.7(2)
C1	0.6340(3)	0.2366(8)	0.2502(4)	4.0(2)
C2	0.5848(3)	0.2148(8)	0.2743(4)	3.8(2)
C3	0.5796(4)	0.272(1)	0.3286(4)	5.6(2)
C4	0.6236(4)	0.351(1)	0.3586(4)	6.1(3)
C5	0.6713(5)	0.370(1)	0.3353(5)	6.8(3)
C6	0.6762(4)	0.3129(9)	0.2811(5)	5.7(2)
C11	0.5689(4)	0.2532(9)	0.0436(4)	4.6(2)
C12	0.5306(4)	0.220(1)	−0.0133(5)	5.7(3)
C13	0.5514(4)	0.1120(9)	−0.0317(4)	4.9(2)
C14	0.5660(4)	0.358(1)	0.0836(5)	6.6(3)
C15	0.5255(5)	0.035(1)	−0.0879(5)	7.6(3)
C21	0.6626(4)	−0.1172(9)	0.1795(4)	4.7(2)
C22	0.6505(4)	−0.2292(9)	0.1513(5)	5.0(2)
C23	0.6404(4)	−0.2098(9)	0.0867(4)	4.7(2)
C24	0.6768(4)	−0.087(1)	0.2496(4)	5.6(3)
C25	0.6276(5)	−0.2991(9)	0.0338(5)	6.5(3)
C31	0.7837(3)	0.1361(8)	0.0584(4)	3.8(2)
C32	0.7901(4)	0.0804(9)	0.0037(4)	4.6(2)
C33	0.7396(3)	0.0172(8)	−0.0211(4)	3.9(2)
C34	0.8261(4)	0.213(1)	0.1025(4)	5.3(2)
C35	0.7233(4)	−0.055(1)	−0.0796(4)	5.8(3)
B	0.6422(4)	−0.019(1)	0.0152(4)	4.1(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

identical six-coordinate molybdenum atoms, each ligated by a facially-coordinated $HB(Me_2pz)_3^-$ ligand, two oxo ligands, and a phenolate oxygen atom. The two halves of the dimer are linked by a disulfide bond derived from oxidation of the 2-mercaptophenolate ligand of the original molybdenum(V) complex. Figure 1 illustrates the structure of the dimer viewed along the crystallographic two-fold axis at $1/2, y, 1/4$ that passes through the midpoint of the disulfide bond. The symmetry equivalent sulfur atoms are not coordinated to the molybdenum atoms (Mo–S = 4.56 Å). The distance between the two molybdenum atoms is 11.0 Å, nearly the same distance as the shortest molybdenum–molybdenum contact between different molecules (11.3 Å). Thus, the compound may be described as two mononuclear Mo(VI) complexes coupled by a disulfide linkage. The oxo ligands are both 1.694(5) Å from the molybdenum atom, whereas Mo–O3 = 1.920(4) Å. These bond distances are normal for Mo(VI) [6]. The molybdenum–nitrogen bonds of $HB(Me_2pz)_3^-$ show a *trans* influence of the expected magnitude; the Mo–N distances *trans* to the oxo ligands are 2.302(5) and 2.293(6) Å, while Mo–N31 = 2.202(5) Å. There are no unusual distances or angles in the ligands [7]. Selected bond distances and angles are given in Table II.

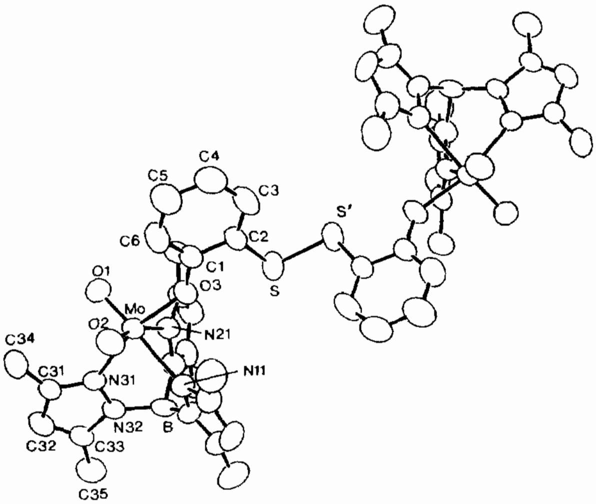

Fig. 1. The structure of $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4S)]_2$ viewed down the two-fold axis through the midpoint of the S-S bond. Hydrogen atoms have been omitted for clarity. Pyrazole rings are labelled such that the first digit following the atomic symbol refers to the ring containing that atom and the second digit is a sequence number assigned in the same manner for all rings.

The formation of $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$ presumably results from the reaction of the original molybdenum(V) complex, $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$, with oxygen present in the solution during crystal growth. The overall stoichiometry of the reaction is two moles of Mo(V)–SR complex plus one mole of dioxygen yields one mole of the dimer. Thus, each starting Mo(V)–SR unit undergoes a two electron oxidation. The detailed pathway for this oxidation is unknown, but at least three things must occur: oxidation of Mo(V) to Mo(VI); cleavage of the Mo–SR bond; oxidation of the thiolates to a disulfide.

The present conversion of a coordinated thiolate to a non-coordinated disulfide may be related to the catalytic oxidation of thiols to disulfides by oxomolybdenum(V) porphyrin complexes [8]. The catalytic cycle involves rapid reduction of the Mo(V) porphyrin complex to Mo(IV) by thiolate, coupling of the resulting RS• radicals to form a disulfide, and reoxidation of Mo(IV) to Mo(V) by dioxygen.

A similar sequence of reactions can be invoked to explain the oxidation of the coordinated thiolate group of $\{HB(Me_2pz)_3\}MoO(OC_6H_4\text{-}o\text{-}S)$. An internal redox reaction of the Mo(V)–SR unit would result in

TABLE II. Selected Bond Distances (Å) and Angles (°) of $[\{HB(Me_2pz)_3\}MoO_2(OC_6H_4\text{-}o\text{-}S)]_2$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo	O1	1.694(5)	Mo	N21	2.293(6)
Mo	O2	1.694(5)	Mo	N31	2.202(5)
Mo	O3	1.920(4)	S	S'	2.016(4)
Mo	N11	2.302(5)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Mo	O2	102.9(3)	O1	Mo	O3	100.6(2)
O1	Mo	N11	166.0(3)	O1	Mo	N21	89.8(2)
O1	Mo	N31	92.0(2)	O2	Mo	O3	100.2(2)
O2	Mo	N11	88.8(2)	O2	Mo	N21	165.9(2)
O2	Mo	N31	93.2(2)	O3	Mo	N11	84.7(2)
O3	Mo	N21	83.0(2)	O3	Mo	N31	159.0(2)
N11	Mo	N21	77.9(2)	N11	Mo	N31	79.5(2)
N21	Mo	N31	80.2(2)	Mo	O3	C1	133.5(4)
S'	S	C2	105.1(2)				

one-electron reduction of the Mo(V) to Mo(IV) and concomitant one-electron oxidation of the coordinated RS^- to $RS\cdot$. Homolytic cleavage of the Mo(V)–SR bond would give an Mo(IV)–RS· species, in which only the oxygen atom of the 2-mercaptophenolate ligand remains coordinated to the molybdenum atom. Such homolytic scission of the Mo–SR bond would be facilitated by the severe non-bonded steric interactions between the $HB(Me_2pz)_3^-$ ligand and the chelating aromatic ligand, and by the donor ability of the dioxane in the solvent. Reaction of the Mo(IV) center with dioxygen and coupling of the pendant RS· groups of two molecules could give the observed dimeric product. This is similar to the mechanism proposed for the dimerization of $CpFe(CO)_2SR$ upon oxidation by $NO\cdot PF_6$ [9].

The reactivity of oxo-Mo(IV) complexes towards dioxygen depends strongly on the other ligands in the coordination sphere. Compounds with an accessible coordination site are very oxygen sensitive, e.g. $MoO(S_2CNR_2)_2$, whereas related coordinatively saturated oxo- and sulfidomolybdenum(IV) complexes of the $HB(Me_2pz)_3^-$ ligand, e.g. $\{HB(Me_2pz)_3\}MoO(S_2CNEt_2)$, are stable toward oxygen, even in solution [10].

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