

Crystal Structure of Dinuclear Molybdenum(VI) Complex Involving *trans*-Dioxo Mo^{VI}O₂ Core

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The fact that molybdenum-oxygen bonds are present in molybdo enzymes has extensively stimulated research in molybdenum complexes with oxygen environments.¹ This class of compounds is interesting also in the study of problems associated with the *trans* influence of the oxygen donor atoms.² So far lots of molybdenum(V), (VI) complexes with *cis*-directed terminal oxygens in the Mo₂O₃- or Mo₂O₄-core structures have been reported.³ However, those of *trans*-directed oxygens are little known, especially molybdenum(VI) complexes of Mo₂O₄-core structure with *trans*-directed terminal oxygens are very uncommon.⁴ As part of our studies on molybdenum(VI) complexes with oxygen, sulfur, and/or nitrogen donor ligands we describe here the synthesis and structure of molybdenum(VI) complex [Mo₂O₄(sabp)₂], where sabp is *N*-salicylidene-2-amino-4-*t*-butylphenolate with *trans*-directed terminal oxygens.

Experimental Section

Materials. Molybdenylacetylacetonate, [MoO₂(acac)₂] was obtained from Tokyo Kasei Chem. Ind. Co. Ltd. Salicylaldehyde and 2-amino-4-*t*-butylphenol were obtained from Aldrich Chem. Co. Ltd. The Schiff base was prepared under Ar gas by the literature method,⁵ but it was not isolated from methanol solution. All other chemicals used for this work were reagent grade and were employed without further purification. Reagent grade solvents were dried and distilled before use.

Physical measurements. C, H, N, for the complexes were analyzed by using a Carlo-Erba EA-1106R. The m.p. measurements were performed by using a Haake melting point apparatus. The molar conductances of the complexes were measured by YSI-31 conductivity bridge. The IR spectra of solid samples in KBr were recorded on a Mattson Polaris FT-IR. ¹H NMR spectra in DMSO-*d*₆ were recorded on a Bruker AM 200 spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Spectronic Gemini 2 spectrophotometer. Cyclic Voltammograms were recorded on a Electrochemical Research System 270/6/0 (EG&G) consisting of PAR 263 Potentiostat/Galvanostat and Electrochemical analysis software 270. The electrochemical studies were conducted in a oxygen-free DMSO solution containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. We employed a three-

electrode cell configuration consisting of a platinum working, platinum counter, and silver/silver ion reference electrode.

Preparation of the complexes. [MoO₂(sabp)(MeOH)] (1). This compound was prepared by the procedure of literature reported⁸ previously. Yield: 0.214 g (50%), mp 171-173 °C. Anal. Calcd. for C₁₈H₂₁NO₅Mo: C, 50.59; H, 4.95; N, 3.27. Found: C, 50.29; H, 4.88; N, 3.19. *A*_M (Mho cm² mol⁻¹): 1.1. UV/Vis. (nm, log ϵ): 428 (3.63), 406 (3.61), 311 (4.24). Significant infrared bands (cm⁻¹): 909 ($\nu_{Mo-O, asym}$), 933 ($\nu_{Mo-O, sym}$), 1612 (ν_{C-N}). ¹H NMR (200 MHz, DMSO-*d*₆): δ 1.33 (s, 9H, -C(CH₃)₃), 3.17 (d, 3H, CH₂OH), 4.09 (q, 1H, CH₂OH), 6.73-7.82 (m, 7H, ArH), 9.32 (s, 1H, N=CH).

[Mo₂O₄(sabp)₂] (2). The excess amount of complex 1 was dissolved in dichloromethane (10 ml) to give a saturated solution. The deep red solution was filtered and left undisturbed at room temperature. After 2-3 days transparent red blocks suitable for crystallographic study had crystallized. The crystal was filtered off, washed with ether, and dried under vacuum. Yield: 0.14 g (35%), mp 261 °C. Anal. Calcd. for C₃₄H₃₄N₂O₈Mo₂: C, 51.66; H, 4.33; N, 3.53. Found: C, 51.27; H, 4.35; N, 3.52. *A*_M (Mho cm² mol⁻¹): 1.3. UV/Vis. (nm, log ϵ): 428 (3.99), 356 (4.30), 314 (4.64). Significant infrared bands (cm⁻¹): 949 (ν_{Mo-O}), 760 (ν_{Mo-OH}), 1604 (ν_{C-N}). ¹H NMR (200 MHz, DMSO-*d*₆): δ 1.33 (s, 9H, -C(CH₃)₃), 6.75-7.83 (m, 7H, ArH), 9.33 (s, 1H, N=CH).

Crystal structure determination of 2. X-ray-quality crystals of 2, approximately 0.12 × 0.16 × 0.16 mm, were obtained by slow evaporation of a saturated dichloromethane solution of the brown powder and mounted in glass capillary. Measurement was made on a Enraf-Nonius CAD4 TURBO diffractometer using Mo-K α radiation ($\lambda = 0.71069$ Å) monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample and anode generator. Preliminary experiments for the cell parameters and orientation matrix for crystal was carried out by least-squares refinement, using the setting angles of 25 carefully centered reflections in the range 20° < 2 θ < 35°. Diffraction intensity was collected at a constant temperature of 20(1) °C using the ω -2 θ scan technique with variable scan speeds. Omega scans of several intense reflections were made prior to the data collection to optimize the proper scan width for crystal.

The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability for crystals. Of the reflections collected, those with

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Table 1. Crystallographic Data and Intensity Collection for Complex 2

Empirical formula	C ₃₄ H ₃₄ N ₂ O ₈ Mo ₂
F_w	790.53
Cryst. system	monoclinic
Space group	C2/c(#15)
Z	4
Cell parameters	
a (Å)	11.659(2)
b (Å)	10.666(2)
c (Å)	26.664(4)
β (°)	101.37(1)
V (Å ³)	3251(1)
D_{calc} (g/cm ³)	1.615
μ (cm ⁻¹ with Mo-K α)	8.0
Transmission factor ^a (%)	97.8370-99.8458
Scan type	ω -2 θ
Scan width (ω) (deg)	0.89 + 0.60 tan (θ)
2 θ_{max} (deg)	52.64
No. of reflections measured	3665
No. of reflections observed ($I > 3\sigma(I)$)	2570
$F(000)$	1600
No. of variable	259
Discrepancy indices	
R^b	0.031
R_w^b	0.041
Goodness of fit indicator ^c	1.352
Maximum shift in final cycles	less than 0.01

^aA semi-empirical absorption correction was applied. ^b $R = \sum |F_o - F_c| / \sum F_o$. ^c $R_w = [(\sum w(F_o - F_c)^2) / \sum w(F_o^2)]^{1/2}$, where $w = [\sigma(F_o)]^{-2}$. ^dEstimated standard deviation of an observation of unit weight: $[(\sum w(F_o - F_c)^2) / (N_o - N_v)]^{1/2}$, where N_o = Number of observations and N_v = Number of variables.

$I > 3\sigma(I)$ were used for structure determination. The structure was solved by direct method (MULTAN)⁶ and subsequent Fourier difference technique, and refined on F^2 (program MoLEN)⁷ by full-matrix least-squares cycles. An absorption correction (Ψ -scan) was applied to all data. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms were refined isotropically in the final refinement cycles. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indices R and R_w .

Results and Discussion

The reaction of MoO₂(acac)₂ with the Schiff base ligand derived from salicylaldehyde and 2-amino-4-*t*-butylphenol in methanol solution gave a monomeric molybdenum(VI) complex 1, and then if a saturated dichloromethane solution of the complex 1 was allowed to evaporate slowly in air dimeric molybdenum(VI) complex 2 suitable for crystallographic study yielded. The details for the preparation and identifications of complex 1 were described previously.⁸ The molar conductivity of complex 2 in dimethylsulfoxide showed 1.3 Mho cm² mol⁻¹ similar to mononuclear complex 1. The IR spectra of complex 2 showed a intense absorption peaks at 949 and 760 cm⁻¹ belong to the Mo-O

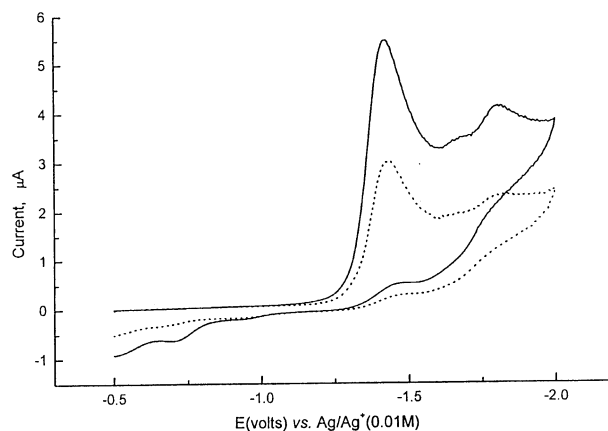


Figure 1. Cyclic voltammograms ($\sim 1 \times 10^{-3}$ M in DMSO, 0.01 M TEAP) of complex 1 (···) and 2 (—) at scan rate of 50 mVs⁻¹.

(terminal) and to the Mo-O (bridging) stretching frequencies, respectively. The peak at 1604 cm⁻¹ is assigned to the azomethine C-N stretching vibration. Lower frequency shift of the vibration compared to 1619 cm⁻¹ of the free ligand indicates that the azomethine nitrogen coordinates to the molybdenum moiety. The ¹H NMR spectra of the complex 2 showed the proton resonances for each of the phenolic aromatic, 4-*t*-butyl, and azomethine group at 6.75-7.82, 1.33, and 9.33 ppm. However, the proton resonances of methyl, OH group of methanol in the complex 1 are disappeared in the complex 2. The UV/Vis spectrum of the complex 2 was recorded in the range of 200-700 nm and showed the same spectral pattern as complex 1. The absorption band at 428 nm (log ϵ 4.63) due to the charge transfer transition from oxygen orbital to a metal d-orbital was observed.⁹

Electrochemical studies were carried out by cyclic voltammetry using a Pt working electrode and NEt₄ClO₄ as supporting electrolyte in DMSO solvent. The complexes exhibited two successive reductive responses in the potential range -1.4 to -1.8 V as shown in other dioxomolybdenum(VI) complexes reported previously (Figure 1).¹⁰ The reductions are irreversible. Though no precise assignments for the each of reduction waves are accomplished, it is important to note here that the cyclic voltammogram of the complex 2 in DMSO is identical with that of the complex 1. This observation indicates that both complexes have essentially similar electrochemical behavior. On the basis of results for electronic and electrochemical studies, it was assumed that complex 2 has dissociated into mononuclear complex 1 in the solution.

Crystal structure of [Mo₂O₄(sabb)₂]. Atomic coordinates are listed in Table 2 and selected bond distances and angles in Table 3. The molecular structure is shown in Figure 2.

Although a number of di-oxo-bridged molybdenum complexes are reported to date, *cis*-species of two terminal oxygen atoms are domain. However, in the present complex 2 the oxygen atoms O(1) and O(1)' are characteristically oriented toward *trans*-position. For complexes having planar *trans*-di- μ -oxo bridges, isomers having C_1 or C_2 symmetry should in general be theoretical possibilities. The present

Table 2. Fractional Positional Parameters and Displacement Parameters of Non-Hydrogen Atoms for Complex 2

Atom	x	y	z	Beq/Å ² ^a
Mo(1)	0.22580(2)	0.14225(3)	0.54148(1)	2.591(5)
O(1)	0.1478(2)	0.0830(3)	0.5826(1)	4.12(6)
O(2)	0.1559(2)	0.2797(2)	0.5171(1)	3.05(5)
O(3)	0.1763(2)	0.0307(3)	0.4852(1)	3.47(6)
O(4)	0.3467(2)	0.2254(2)	0.5913(1)	2.91(5)
N(1)	0.3765(3)	0.0080(3)	0.5558(1)	2.31(5)
C(1)	0.3999(3)	-0.0821(3)	0.5265(1)	2.42(6)
C(2)	0.3256(3)	-0.1189(3)	0.4795(1)	2.48(7)
C(3)	0.3621(3)	-0.2197(4)	0.4521(1)	3.02(7)
C(4)	0.2920(3)	-0.2626(4)	0.4081(2)	3.50(8)
C(5)	0.1838(3)	-0.2085(4)	0.3909(2)	3.76(9)
C(6)	0.1455(3)	-0.1112(4)	0.4166(2)	3.45(8)
C(7)	0.2165(3)	-0.0647(3)	0.4608(1)	2.66(7)
C(8)	0.4308(3)	0.1543(3)	0.6211(1)	2.53(7)
C(9)	0.4957(3)	0.1960(4)	0.6668(2)	3.08(7)
C(10)	0.5775(3)	0.1174(4)	0.6943(2)	3.21(8)
C(11)	0.6001(3)	-0.0031(4)	0.6782(1)	2.68(7)
C(12)	0.5364(3)	-0.0416(3)	0.6312(1)	2.49(7)
C(13)	0.4517(3)	0.0361(3)	0.6032(1)	2.29(6)
C(14)	0.6919(3)	-0.0864(4)	0.7109(1)	3.29(8)
C(15)	0.6771(4)	-0.0881(5)	0.7662(2)	5.5(1)
C(16)	0.8124(4)	-0.0349(5)	0.7097(2)	5.6(1)
C(17)	0.6876(5)	-0.2197(5)	0.6904(2)	5.8(1)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1)+b^2(2,2)+c^2B(3,3)+ab(\cos \gamma)B(1,2)-ac(\cos \beta)B(1,3)-bc(\cos \alpha)B(2,3)]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 2

(a) Distances			
Mo(1)-O(1)	1.680(3)	Mo(1)-N(1)	2.241(3)
Mo(1)-O(2)	1.740(2)	O(3)-C(7)	1.341(5)
Mo(1)-O(2)'	2.426(5)	O(4)-C(8)	1.363(4)
Mo(1)-O(3)	1.913(3)	C(1)-N(1)	1.301(5)
Mo(1)-O(4)	1.950(3)	Mo(1)···Mo(1)'	3.314(4)
(b) Angles			
O(1)-Mo(1)-O(2)	106.7(1)	O(2)-Mo(1)-O(4)	95.4(1)
O(1)-Mo(1)-O(2)'	177.6(2)	O(2)-Mo(1)-N(1)	153.7(1)
O(1)-Mo(1)-O(3)	99.2(1)	O(3)-Mo(1)-O(4)	152.0(1)
O(1)-Mo(1)-O(4)	97.9(1)	O(3)-Mo(1)-N(1)	80.8(1)
O(1)-Mo(1)-N(1)	99.0(1)	O(3)-Mo(1)-O(2)'	80.2(2)
O(2)-Mo(1)-O(2)'	75.9(2)	O(4)-Mo(1)-O(2)'	81.6(2)
O(2)-Mo(1)-O(3)	100.6(1)	O(4)-Mo(1)-N(1)	74.8(1)

and other structure determinations¹¹ show a predominance of the former type C_i symmetry. The structure of complex 2 consists of a dinuclear, doubly-bridged $[\text{Mo}_2\text{O}_4(\text{Sabp})_2]$. As will be seen from Figure 2, each molybdenum atom is in a distorted-octahedral coordination environment being bonded to three functional groups, ONO of a Sabp ligand and to two bridging and one terminal oxygen atoms. Each ligand develops a five- and six-membered ring on one molybdenum center. The rings are excellent individual planes but there is 14.1(4)° fold at their intersection. Due to ligand rigidity, the MoO_5N_1 coordination spheres are subject to considerable

distorted octahedral, with the bridging oxygens O(2) and O(2)' occupying the edge positions. Thus, the geometry around Mo(VI) center deviates from the ideal octahedral values of 90° and 180° (Table 3). The plane Mo(1)O(2)O(2)' and Mo(1)O(1)N(1) fragment constitute a very mediocre planes, respectively and their dihedral angle is 5.9(1.0)°, indicating that the fragment O(1)O(2)O(2)'N(1) around Mo(VI) center is approximately planarity. The Mo(1)···Mo(1)' distance is 3.314(4) Å, which is similar to that of typical dioxo-bridged Mo(VI) complexes.¹² Owing to the trans influence of the terminal oxo, the Mo(1)-O(2)' and Mo(1)-O(2) distances (2.426(5) Å) are very longer than those remaining both bonds (1.740(2) Å) trans to the nitrogen atom of ligand. This value is also longer than phenolic oxygen Mo(1)-O(3) and Mo(1)-O(4) distances (1.913(3) Å and 1.950(3) Å, respectively). The azomethine Mo(1)-N(1) distance (2.241(3) Å) is typical of relating complexes.¹²

Supplementary material available. Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles (52 pages) and calculated and observed structure factors (28 pages) for complex 2. The supporting materials will be given upon your request to the corresponding author.

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