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cis-Dioxomolybdenum(VI) Complex with a Tripod-Like Tetradentate Ligand, *N′*,*N′*-Bis(2-hydroxy-3,5-dimethylbenzyl)-*N*,*N*-dimethylethylenediamine

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A *cis*-dioxomolybdenum(VI) complex with *N′*,*N′*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N*,*N*-dimethylethylenediamine (H_2L), *cis*-[MoO_2(L)], was synthesized and characterized by measurements of NMR, infrared, and electronic spectra. The X-ray crystal structure shows that the compound has a distorted octahedral geometry with an N_2O_4 coordination environment.

The chemistry of high-valent oxomolybdenum complexes has attracted considerable attention during the last few decades,[1] since such a center has been identified in several molybdenum enzymes, oxotransferase and hydroxylase enzymes, which contain a universal cofactor in which a mononuclear oxomolybdenum is bound to one or two pterin dithiolene ligands.[2] Although a number of mononuclear oxomolybdenum complexes have been synthesized and studied as models for the oxomolybdenum enzymes, molybdenum complexes having tripodal ligands are not well developed, except for the most thoroughly studied examples of symmetric tris(pyrazolyl)borate ligands.[3] We are particularly interested in metal complexes with unsymmetrical tripodal ligands, while pursuing new aspects of coordination chemistry.[4] In this study, we synthesized a unsymmetrical tripod-like ligand, *N′*,*N′*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N*,*N*-dimethylethylenediamine (H_2L), which was expected to give a unsymmetrical trigonal NO_2 plane for MoO_2^{2+}, and obtained a dioxomolybdenum(VI) complex, *cis*-[MoO_2(L)] (**1**), by a reaction of H_2L with the dioxomolybdenum ion. Herein, we report on the synthesis and structural characterization of **1**.

A treatment of H_2L with *cis*-[$MoO_2(acac)_2$] in methanol afforded a yellow precipitate. Recrystallization from dichloromethane–hexane gave crystals of **1**. An X-ray crystallographic study revealed that the dioxomolybdenum is coordinated by the L^{2-} ligand with the two phenoxo-oxygen atoms and the two nitrogen atoms, giving a distorted octahedral coordination environment (Fig. 1). The two terminal oxo groups are *cis* to each other and to the phenolate groups of the tetradentate ligand. The two tertiary amine nitrogen atoms are *cis* to each other and approximately *trans* to the terminal oxo groups. The Mo=O distances [1.706(2) (O3) and 1.710(2) (O4) Å] and the O=Mo=O angle [108.16(9)°] are typical for *cis*-dioxomolybdenum(VI) complexes.[1] The O=Mo=O angle of ~110° was explained by the maximum utilization of vacant d orbitals in π-bonding with oxygen lone pairs in the *cis* case.[5] The presence of the *cis*-MoO_2^{2+} center can be confirmed by the IR spectrum of **1** [ν_{as}(Mo=O) 924 cm^{-1}, ν_s(Mo=O) 902 cm^{-1}].[1] The Mo–N distances are significantly longer (> 2.4 Å) than those of the Mo–O (phenoxo) bonds, which shows the strong *trans* influence of the oxo ligands. In the cases of dioxomolybdenum(VI) complexes with tris(pyrazolyl)borate, the distance of the Mo–N bond *cis* to the oxo ligands is up to 0.16 Å longer than those of the Mo–N bond *trans* to the oxo groups, which are in the range 2.167(4)–2.209(2) Å.[3] During the course of the present work, an analogous titanium(IV) complex with a similar tetradentate ligand, [Ti(L′)(OCH(CH_3)$_2$)$_2$] (**2**, $H_2L′$ = *N′*,*N′*-bis(2-hydroxy-4,5-dimethylbenzyl)-*N*,*N*-dimethylethylenediamine), which has an octahedral geometry around the metal center, was reported.[6] A structural

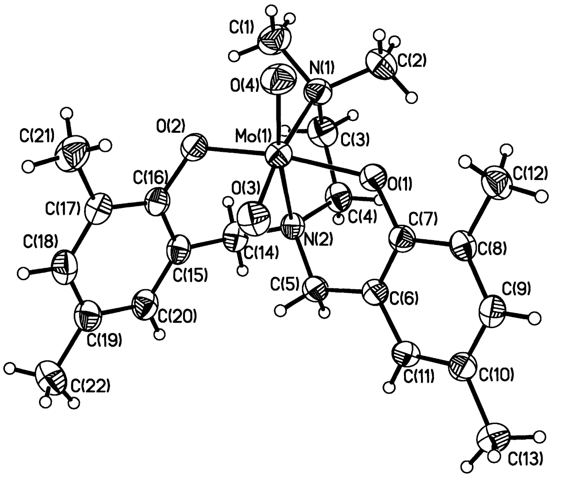

Fig. 1. Perspective view of the structure of **1** showing the atom labeling scheme. Selected bond distances (Å) and angles (°): Mo(1)–O(3) 1.706(2), Mo(1)–O(4) 1.710(2), Mo(1)–O(1) 1.946(2), Mo(1)–O(2) 1.969(2), Mo(1)–N(2) 2.417(2), Mo(1)–N(1) 2.434(2); O(3)–Mo(1)–O(4) 108.16(9), O(3)–Mo(1)–O(1) 94.55(7), O(4)–Mo(1)–O(1) 100.20(7), O(3)–Mo(1)–O(2) 94.57(7), O(4)–Mo(1)–O(2) 99.30(7), O(1)–Mo(1)–O(2) 154.68(7), O(3)–Mo(1)–N(2) 93.02(8), O(4)–Mo(1)–N(2) 158.81(7), O(1)–Mo(1)–N(2) 76.65(6), O(2)–Mo(1)–N(2) 79.33(6), O(3)–Mo(1)–N(1) 166.44(6), O(4)–Mo(1)–O(1) 85.17(8), O(1)–Mo(1)–N(1) 80.23(6), O(2)–Mo(1)–N(1) 85.48(7), N(2)–Mo(1)–N(1) 73.64(7), C(7)–O(1)–Mo(1) 128.4(1), C(16)–O(2)–Mo(1) 117.0(1), C(3)–N(1)–Mo(1) 111.0(1), C(1)–N(1)–Mo(1) 110.0(1), C(2)–N(1)–Mo(1) 109.3(1), C(5)–N(2)–Mo(1) 108.6(1), C(4)–N(2)–Mo(1) 107.8(1), C(14)–N(2)–Mo(1) 114.5(1).

comparison with this complex has disclosed a severe distortion from the regular octahedral geometry of **1**. The *trans* angles, O(1)–Mo(1)–O(2) [154.68(7)°], N(1)–Mo(1)–O(3) [166.44(6)°], and O(4)–Mo(1)–N(2) [158.81(7)°], are considerably reduced from the ideal value of 180°. The chelate angles, O(1)–Mo(1)–N(2) [76.65(6)°], O(2)–Mo(1)–N(2) [79.33(6)°], and N(1)–Mo(1)–N(2) [73.64(7)°], are significantly smaller than the corresponding chelate angles of **2** [83.27(6)°, 83.49(6)°, and 75.58(6)°].[6] The severe distortion in the octahedral environment around the Mo atom may come from the repulsion from the oxo groups with the obtuse O=Mo=O angle and the small bite angles taken by the tripod-like tetradentate ligand to accommodate this repulsion.

The ^{1}H NMR spectrum of **1** can be assigned to only one set of the tetradenate ligand resonances. This is in harmony with the belief that the mononuclear structure of **1** is maintained in solution.

The electronic spectrum of **1** displays absorptions at 265 (sh) and 358 nm. The former absorption may be attributed to an internal ligand transition band and the latter may be assigned to a O(pπ)→Mo(dπ) charge-transfer transition band, which is in the range usually observed for *cis*-MoO_2 complexes.[7]

Experimental

The ligand, H_2L, was synthesized by a similar reaction to that reported for H_2L' from 2,4-dimethylphenol (3.67 g, 0.03 mol), *N*,*N*-dimethylethylenediamine (1.32 g, 0.015 mol), and formaldehyde (37%, 0.9 g, 0.03 mol) in ethanol.[6]

Synthesis of 1. *cis*-[MoO_2(acac)$_2$] (33 mg, 0.10 mmol), which was prepared as described in the literature,[8] was dissolved in methanol (10 cm^3), and then H_2L (36 mg, 0.10 mmol) was added. The reaction mixture was stirred at room temperature for 24 h and then filtered, washed with methanol and then dried in vacuo: Yield 46 mg (95%). Crystals for X-ray analysis were obtained by recrystallization from dichloromethane–hexane. Found: C, 54.78; H, 6.36; N, 5.67%. Calcd for $C_{22}H_{30}MoN_2O_4$: C, 54.77; H, 6.27; N, 5.81%. ^{1}H NMR (CD_2Cl_2): δ 6.97 (s, 2H, aryl), 6.78 (s, 2H, aryl), 4.41 (d, J = 13.9 Hz, 2H, aryl CH_2), 3.75 (d, J = 13.9 Hz, 2H, aryl CH_2), 2.68 (s, 8H, N-C*H*$_2$-CH$_2$-N(CH$_3$)$_2$ and N-CH$_2$-CH$_2$-N(C*H*$_3$)$_2$), 2.51 (m, 2H, N-CH$_2$-C*H*$_2$-N(CH$_3$)$_2$), 2.24 (d, J = 21.5 Hz, 12H, aryl CH_3). Electronic spectrum in CH_2Cl_2: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 265sh (10400), 358 (6720).

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. ^{1}H NMR spectra were recorded on a Varian 300-NMR Spectrometer at ambient temperature, and the chemical shifts were reference to the internal TMS. Infrared spectra were recorded as KBr discs with a Mattson FT-IR spectrophotometer model Galaxy 7020A in the 4000–400 cm^{-1} region. The electronic spectra were measured with a JASCO UV-VIS recording spectrophotometer model V-530.

X-ray Crystal Structure Analysis. A yellow crystal of **1** was mounted on a glass fiber with epoxy cement at room temperature. A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo-$K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package.

Crystallographic data for **1**; $C_{22}H_{30}MoN_2O_4$ Fw = 482.42, monoclinic, space group $P2_1/n$, a = 10.598(7), b = 15.992(11), c = 12.602(8) Å, β = 90.02(1)°, V = 2136(2) Å^3, Z = 4, D_c = 1.500 g cm^{-3}, μ(Mo $K\alpha$) = 0.644 mm^{-1}, crystal dimensions 0.25 × 0.30 × 0.40 mm, 13309 reflections collected, 5018 independent reflections, $R1$ [$I > 2\sigma(I)$] = 0.0287, w$R2$ [$I > 2\sigma(I)$] = 0.0831.

The X-ray analysis data have been deposited as Document No. 75039 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 188275.

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