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Synthesis and Crystal Structure of a cis-Dioxomolybdenum(VI) Complex with Two Benzenedithiolato Ligands. $(NEt_4)_2[Mo^{VI}O_2(1,2\text{-benzenedithiolato})_2]$

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$(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (bdt = 1,2-benzenedithiolato) has been synthesized as a relevant structural model complex for the active center of sulfite oxidase and characterized by X-ray crystallography, ^{1}H-NMR, UV-visible spectroscopic and cyclic voltammetric analysis. The complex has a distorted octahedral structure with two longer Mo-S bonds at the trans positions of the two Mo=O groups.

Mo-oxidases catalyze the redox reaction of several biologically important substrates. EXAFS studies have revealed that the active center of Mo-oxidases contain $Mo^{VI}O_2^{2+}$ or $Mo^{VI}OS^{2+}$ ion in sulfite oxidase or xanthine oxidase, respectively. These molybdenum centers are surrounded by two or three thiolato ligands in their oxidized state,1) and are considered to have one dithiolene ligand linked to pterin and phosphate groups.2) Numerous structural model complexes have been synthesized based on these proposed structures of the active site.3) However, no dioxomolybdenum(VI) complex surrounded by four thiolato ligands has been reported and the two thiolato ligands at the trans position toward Mo=O groups have been thought to be extremely labile.

Benzenedithiolato (bdt) ligands coordinated to oxomolybdenum(IV/V) are considered as a simple model of the complex native dithiolene ligand.4) We synthesized $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$ (**1**) by careful reaction between $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ and trimethylamine-N-oxide (1:2 ratio) in N,N-dimethylformamide (DMF) at room temperature and it was recrystallized from DMF/diethyl ether to give red purple5) microcrystals in 78% yield. A crystal for the X-ray analysis was obtained by recrystallization from DMF/diethyl ether. The complex is the first example for dioxomolybdenum(VI) ion surrounded by four thiolato ligands. Trimethylamine-N-oxide is known to be an oxidant for molybdoenzymes.6)

A perspective view of the anion part, $[Mo^{VI}O_2(bdt)_2]^{2-}$ is shown in Fig. 1.7) Substantially distorted octahedral geometry of MoO_2S_4 core was found just like as those of various crystallographically analyzed $MoO_2S_2X_2$ (X = thioketone or thioether) complexes, for example, $[Mo^{VI}O_2(S_2CNEt_2)_2]$8) and $(NEt_4)_2[Mo^{VI}O_2(dttd)_2]$ ($dttdH_2$ = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane).9) A set of Mo-O bond distances is similar to those of reported dioxomolybdenum(VI) complexes such as $[Mo^{VI}O_2(S_2CNEt_2)_2]$. The Mo-S bond distances are different between trans and cis positions to terminal-oxo ligands in the pseudo-octahedral geometry. Two Mo-S bonds have definitely longer distances by trans influence of terminal-oxo ligands. Another remarkable point is that distances of the S-C bond at the trans positions are shorter than those of the cis positions. The partial double bonding is enhanced and an approach to C=S bonding in thioketone is apparent.

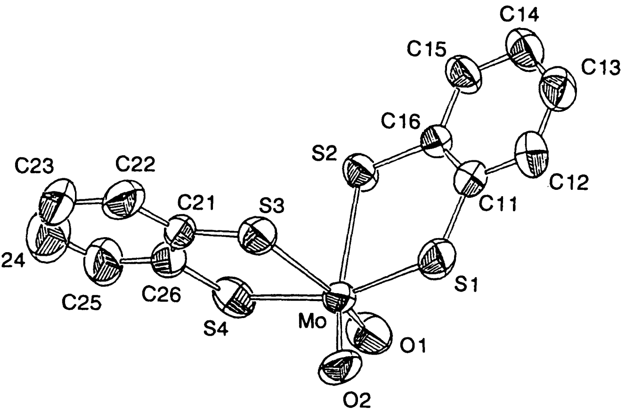

Fig. 1. Crystal structure of $(NEt_4)_2[MoO_2(bdt)_2]$.

1 exhibits clear ^{1}H-NMR signals assignable to aromatic protons at 6.5 ppm (4H ring-3,6) and 7.0 ppm (4H ring-4,5) due to an increased diamagnetic effect. Cyclic voltammogram of **1** in a DMF solution exhibits an irreversible reduction peak at -0.97 V vs. SCE and an irreversible oxidation peak at +0.04 V vs. SCE similar to the electrochemical behavior of $[Mo^{VI}O_2(S_2CNEt_2)_2]$.[10] A reversible redox couple at -0.37 V vs. SCE due to a couple of $[Mo^{V}O(bdt)_2]^-/[Mo^{IV}O(bdt)_2]^{2-}$ appeared with cathodic scanning beyond -1.0 V.

Weaker oxo-elimination reactivity of **1** with triphenylphosphine or benzoin, in comparison to that of $[Mo^{VI}O_2(S_2CNEt_2)_2]$, was found in the initial stage of the reaction. Detailed studies on the chemical reactivity of **1** will be reported at a later date.

References

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