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SYNTHESIS AND REDOX BEHAVIOR OF [Mo(2,4,6-TRIALKYLBENZENETHIOLATO)$_4$]. UNIQUE REDOX PROPERTIES OF TETRA-COORDINATED Mo(IV) COMPLEXES WITH BULKY THIOLATES

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Two new molybdenum(IV) complexes having bulky thiolato ligands, [Mo(2,4,6-trimethylbenzenethiolato)$_4$] and [Mo(2,4,6-triisopropylbenzenethiolato)$_4$], were synthesized. These complexes show paramagnetic properties due to a nearly tetrahedral coordination and exhibit the quasi-reversible redox couples of Mo(V)/Mo(IV) at -0.07 V and +0.47 V vs. SCE, respectively in 1,2-dimethoxyethane. The two bulky isopropyl groups at o-position prevent π-interaction between Mo(IV) and sulfur, providing an ionic character at the Mo-S bond and stabilizing Mo(IV) state against oxidation.

The molybdenum(IV) species coordinated with sulfur-donor ligands are important for its relevance to the Mo center of nitrogenase.$^{1)}$ However, apart from 8-coordinated dithiocarbamates, [Mo(dtc)$_4$], such complexes with 4 – 6 coordinated structure have been scarce.$^{2)}$ Recently, on the basis of EXAFS study Mo ion in FeMo-cofactor is proposed to be surrounded by three oxo (or N) and three sulfur ligands and exists in hydrophobic environments.$^{3)}$ Otsuka et al. reported the synthesis of highly air sensitive [Mo(S-t-Bu)$_4$] and found to have a D_{2h} structure.$^{4)}$ The study of [Mo(S-t-Bu)$_2$(Z-Ala-cys-OMe)$_2$] (Z = benzyloxycarbonyl) and [Mo(Z-cys-Ala-Ala-cys-OMe)$_2$] indicated their remarkably modified reactivity compared with that of [Mo(S-t-Bu)$_4$] due to the bulk of the peptide.$^{5)}$ Recently, some metal complexes having such bulky ligands were found to exhibit unusual stability in the oxidized state, e.g. [Fe(2,3,5,6-tetramethylbenzenethiolato)$_4$]$^-$,$^{6)}$ [Fe$_4$S$_4$(2,4,6-triisopropylbenzenethiolato)$_4$]$^{2-}$.$^{7)}$

[Mo(tmbt)$_4$] (tmbt = 2,4,6-trimethylbenzenethiolato) (**1**) was synthesized from [MoCl$_4$(thf)$_2$] and Na(tmbt) in 1,2-dimethoxyethane (DME) under argon atmosphere as black needles, mp 150 °C (decomp). Found: C, 61.5; H, 7.5%. Calcd for $C_{36}H_{44}S_4Mo$: C, 61.7; H, 6.3%. The complex is extremely succeptible to air and moisture and, paramagnetic (μ_{eff} = 2.6 BM in solution)$^{8)}$ and exhibits an absorption maximum at 340, 400(sh), 530 (ε 1900 $M^{-1}cm^{-1}$), and 820 nm (ε 60) in DME. **1** can be regarded as being monomeric and having not the same D_{2h} structure as that of dimagnetic [Mo(S-t-Bu)$_4$], but a nearly tetrahedral structure. The steric hindrance of methyl groups at o-position in the phenyl group prevents a π-interaction between Mo(IV) and sulfur, resulting in formation of the nearly tetrahedral structure. In the cyclic voltammogram, **1** exhibited a quasi-reversible redox couple ($E_{1/2}$= -0.07 V vs. SCE) in DME as shown in Fig. 1, which is due to the redox couple of Mo(V)/Mo(IV). Such a stable redox couple caused by the sterically demanding ligands seems to be quite unusual in view of irreversible redox couples of Mo(IV) complexes with conventional ligands.

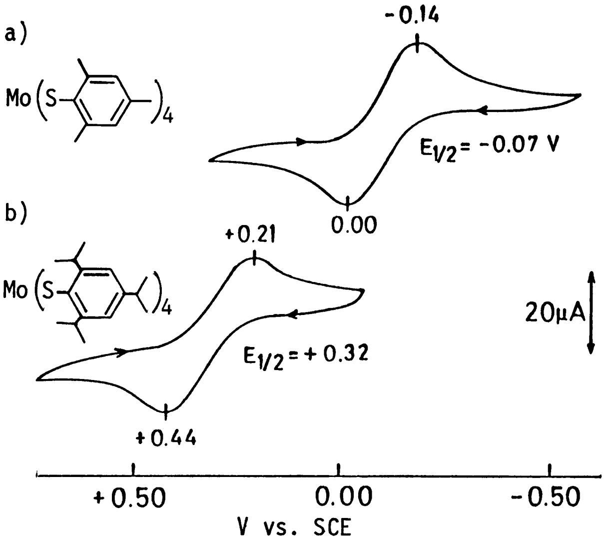

Fig. 1. Cyclic voltammograms of Mo(V)/Mo(IV) couple of a) [Mo(tmbt)$_4$] and b) [Mo(tipbt)$_4$] in DME solution (0.1 M (n-Bu)$_4$NClO$_4$) at a carbon electrode and scan rate 100 mV s^{-1}.

[Mo(tipbt)$_4$] (tipbt = 2,4,6-triisopropylbenzenethiolato) (**2**), which has more bulky thiolato ligands, was synthesized from [MoCl$_4$(thf)$_2$] and Na(tipbt) by the same method described above. **2** is paramagnetic (μ_{eff} = 2.6 BM in solution) and less susceptible against air and moisture, mp 149 °C (decomp). Found: C, 69.46; H, 8.95%. Calcd for $C_{60}H_{92}S_4Mo$: C, 69.46; H, 8.94%. It has an absorption maximum at 558 nm (ε 1600) and a quasi-reversible redox couple at +0.32 V vs. SCE in DME (Fig. 1). The remarkable difference of redox potentials between **1** and **2** presumably arises from the ionic character of Mo-S in **2** having no appreciable π-interaction between Mo(IV) and sulfur. Such an ionic character was also observed in [Fe_4S_4(2,4,6-trimethylbenzenethiolato)$_4$]$^{2-}$ where similar steric interaction has been verified by X-ray analysis.

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8) The reproducibility of the magnetic susceptibility measured in CD_3CN solution was invariably poor because of the instability of **1** in air.

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