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X-Ray Molecular Structure of $[NBu^n_4]_2[Mo(C_3S_5)_3]$ and Electrical Conductivities of the Oxidized Species

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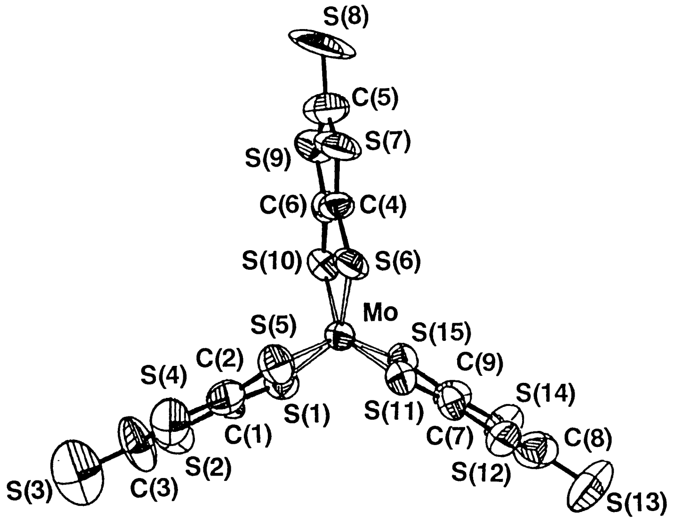
A reaction of $MoCl_5$ with $Na_2C_3S_5$ in acetonitrile afforded the title complex. The X-ray crystal structure analysis revealed the geometry of the anion with a distorted trigonal prismatic coordination. The partially oxidized complex $[NBu^n_4]_{0.3}[Mo(C_3S_5)_3]$ has the electrical conductivity of 0.15 S cm^{-1} at room temperature (compacted pellet).

Planar metal complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate (2-) ($C_3S_5^{2-}$) ligand attract much attention, because their partially oxidized species behave as good electrical conductors$^{1,2)}$ and some of them have been reported to become superconductors.$^{3)}$ Two- or three-dimensional molecular interactions through sulfur-sulfur contacts form electron-conduction pathways in the crystal phase. Nonplanar bulky metal complexes with this ligand are also expected to become new conductors having effective conduction pathways due to multi-dimensional molecular inter-actions through the ligand sulfur atoms. However, few nonplanar C_3S_5-metal complexes as conductors have been studied.$^{4-6)}$ We have isolated a bulky tris(C_3S_5)-molybdenum(IV) anion complex and clarified its molecular structure. The complex is partially oxidized to exhibit high electrical conductivities.

The reaction of an acetonitrile solution of $MoCl_5$ with a methanol solution containing three molar amounts of $Na_2C_3S_5$$^{7)}$ in the presence of $[NBu^n_4]Br$ gave black microcrystals of $[NBu^n_4]_2[Mo(C_3S_5)_3]$ (**1**) together with a large amount of dark red crystals of $[NBu^n_4]_2[MoO(C_3S_5)_2]$.$^{8)}$ The solid mixture was washed with methanol several times to exclude the red crystals and filtered off and the remaining black solids were recrystallized from a methanol-dichloromethane mixture to afford black plates of complex **1** (7% yield). A reaction of complex **1** with an equimolar amount of $[Fe(C_5Me_5)_2]$-$[BF_4]$$^{4)}$ in acetonitrile yielded black solids of $[Fe(C_5Me_5)_2][Mo(C_3S_5)_3]$ (**2**) (47% yield). Similarly, complex **1** reacted with excess amounts of iodine and $[TTF]_3[BF_4]_2$(TTF = tetrathiafulvalene)$^{9)}$ in acetonitrile to afford $[NBu^n_4]_{0.3}[Mo(C_3S_5)_3]$ (**3**) (76% yield) and $[NBu^n_4]_{0.05}[Mo(C_3S_5)_3]$ (**4**) (63%



Bond lengths (Å): Mo-S(1) 2.402(10), Mo-S(5) 2.412(8), Mo-S(6) 2.405(8), Mo-S(10) 2.406(9), Mo-S(11) 2.386(9), Mo-S(15) 2.413(8), S(1)-C(1) 1.74(3), S(3)-C(2) 1.66(2), S(5)-C(3) 1.73(2), S(6)-C(4) 1.72(2), S(8)-C(5) 1.65(4), S(10)-C(6)1.73(3), S(11)-C(7) 1.74(3), S(13)-C(8)1.66(3), S(15)-C(9)1.73(3), C(1)-C(3) 1.35(4), C(4)-C(6) 1.35(3), C(7)-C(9) 1.35(4).

Fig. 1. Perspective view of the anion of $[NBu^n_4]_2[Mo(C_3S_5)_3]$ (**1**) with the atom numbering.

yield), respectively.[10]

Complex **1** crystallizes in an orthorhombic system, space group $Pca2_1$ (No. 29). Crystal data: a = 32.881(13), b = 10.788(5), c = 16.382(9) Å, Z = 4, D_c = 1.338 g cm^{-3}, D_m(flotation) = 1.33 g cm^{-3}. Intensity data ($2\theta < 55°$) were collected on a Rigaku AFC-5R diffractometer with graphite-monochromatized Mo-Kα radiation. Based on 3303 unique reflections [$|F_o|>3\sigma(F)$] the structure was solved by the heavy-atom method and the subsequent Fourier procedure and refined by the full-matrix least-squares method with anisotropic thermal vibrations for the anion atoms and with isotropic parameters for the nonhydrogen atoms of the cations to R = 0.087. The X-ray structure analysis revealed that the anion moiety has a distorted trigonal prismatic coordination around the molybdenum atom, as illustrated in Fig. 1. The S-Mo-S bite angles are 81.8-82.4° and the S-Mo-S angles between the C_3S_5 ligands are 122.5-124.4°, which are close to those of $[NBu^n_4]_2$-$[Mo(mnt)_3]$ [mnt = maleonitriledithiolate (2-)].[11] In the crystal phase the bulky $[Mo(C_3S_5)_3]^{2-}$ anions are separated from each other by the $[NBu^n_4]^+$ cations.

Figure 2 shows the cyclic voltammogram of complex **1** in dimethylformamide. Two reversible redox waves due to $[Mo(C_3S_5)_3]^{2-}$-$[Mo(C_3S_5)_3]^-$ and $[Mo(C_3S_5)_3]^-$-$[Mo(C_3S_5)_3]^0$ couples are observed

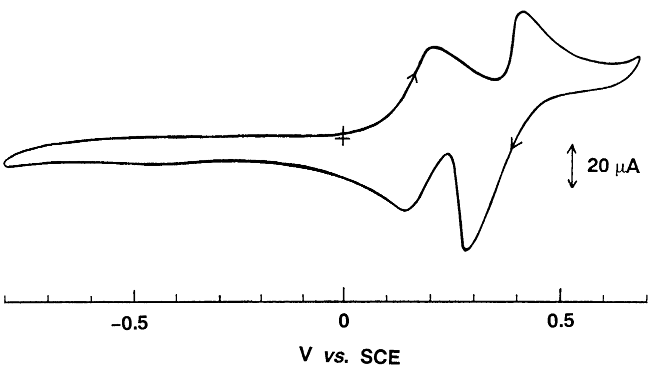


Fig. 2. Cyclic voltammogram of complex **1** (1.0×10^{-3} mol dm^{-3}) in dimethylformamide: 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$, sweep rate 100 mV s^{-1}.

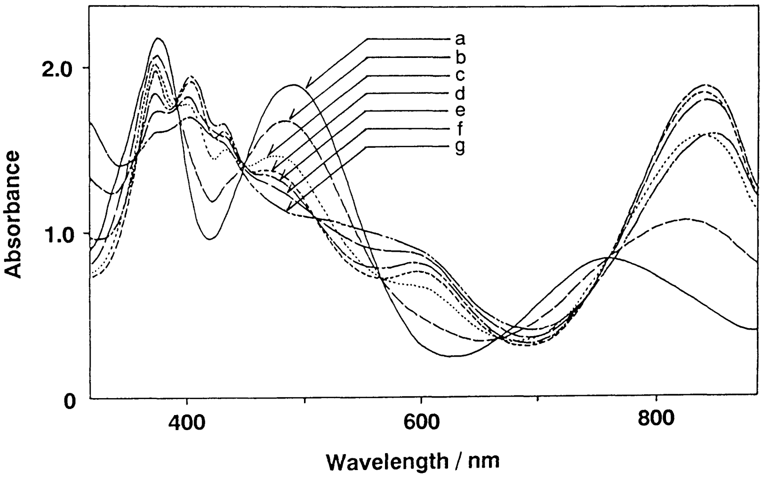


Fig. 3. Electronic absorption spectra of complex **1** (8.5×10^{-5} mol dm^{-3}) in MeCN in the presence of $[Fe(C_5H_5)_2][PF_6]$: a) 0, b) 3.4×10^{-5}, c) 6.8×10^{-5}, d) 8.5×10^{-5}, e) 1.0×10^{-4}, f) 1.3×10^{-4}, g) 1.7×10^{-4} mol dm^{-3}.

at $E_{1/2}{}^{0}$ = 0.185 and 0.38 V (*vs.* SCE), respectively. These findings are similar to those of the $[Mo(mnt)_3]^{2-}$ complex [2-/1-: 0.30 and 1-/0: 0.71 V (*vs.* Ag|AgClO$_4$ (0.1 mol dm^{-3}))][11] and the $[V(C_3S_5)_3]^{2-}$ complex [2-/1-: 0.15 and 1-/0: 0.65 V (*vs.* SCE)].[4] The reversible oxidation processes of the present complex suggest stable oxidized species of the $[Mo(C_3S_5)_3]^{2-}$ anion. In accordance with this, the stable spectral change of complex **1** in the presence of $[Fe(C_5H_5)_2][PF_6]$ as an oxidizing agent indicates two redox equilibria corresponding to the electrochemical redox processes (Fig. 3): addition of an equimolar amount of the $[Fe(C_5H_5)_2]^+$ cation forms the $[Mo(C_3S_5)_3]^-$ species, and further addition of the oxidizing agent leads to the formation of $[Mo(C_3S_5)_3]^0$ in solution.

The oxidized complexes **2-4** exhibit IR C=C stretching bands at lower frequencies (1360, 1310 and 1310 cm^{-1}, respectively) compared with the band of complex **1** (1440 cm^{-1}). Although complex **1** is essentially diamagnetic, complexes **3** and **4** give rather sharp powder ESR signals (peak-to-peak linewidths, 12 and 30 Gauss) at g = 2.008 and 2.007, respectively, at room temperature. Complex **2** exhibits a very broad ESR signal at room temperature and at 77 K. These findings suggest that the ligand-centered oxidation occurs in these complexes, as reported for the oxidized $[M(C_3S_5)_2]^{n-}$ (M = Au^{III}, n < 1; M = Ni^{II} and Pd^{II}, n < 2) complexes.[12,13]

Electrical conductivities of the complexes were measured at room temperature for the compacted pellets: **1**, 3.0×10^{-8}; **2**, 1.1×10^{-4}; **3**, 0.15; **4**, 0.042 S cm^{-1}. The oxidized species behave as electrical conductors. Especially complex **3** exhibits a high conductivity. Although the anion moiety is bulky, the partial oxidation seems to result in an effective packing of the anions suitable for the electron-conduction through sulfur-sulfur nonbonded contacts. Although the powder reflectance spectrum of complex **1** shows the bands corresponding to those observed in the absorption spectrum in solution, the oxidized complexes **2-4** exhibit broad reflectance bands at longer wavelengths than 900 nm. They suggest extended molecular interactions among the anions in the solid state.

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10) Anal. **1**, Found: C, 41.71; H, 6.21; N, 2.34%. Calcd for $C_{41}H_{72}MoN_2S_{15}$: C, 42.09; H, 6.22; N, 2.39%. **2**, Found: C, 34.23; H, 2.97%. Calcd for $C_{29}H_{30}FeMoS_{15}$: C, 34.27; H, 2.98%. **3**, Found: C, 21.63; H, 1.32; N, 0.56%. Calcd for $C_{13.8}H_{10.8}MoN_{0.3}S_{15}$: C, 21.87; H, 1.44; N, 0.55%. **4**, Found: C, 16.95; H, 0.33; N, <0.3%. Calcd for $C_{9.8}H_{1.8}MoN_{0.05}S_{15}$: C, 16.88; H, 0.26; N, 0.10%.

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