X-ray Molecular Structure of Bis(tetrabutylammonium)-bis(4,5-dimercapto-1,3-dithiole-2-thionate)oxomolybdenum and its Oxidation

GEN-ETSU MATSUBAYASHI*, TAKASHI NOJO
and TOSHIO TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

(Received June 17, 1988)

Metal complexes with sulfur-rich dithiolene ligands are very interesting from the viewpoint of their electrically conducting behavior which is caused through intermolecular sulfur–sulfur interaction of the ligands [1–3]. dmit–metal complexes (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate; $C_3S_5^{2-}$) are reported to be the source of conductive and even superconductive materials [1, 4, 5]. Although almost of these complexes are planar, nonplanar metal–dmit complexes may also exhibit conducting behavior through sulfur–sulfur interaction of the ligand caused by partial oxidation [6]. In our study on nonplanar dmit–metal complexes as electrical conductors, we have isolated the title complex with square-pyramidal geometry, revealing a stable redox process. The present paper reports its X-ray molecular structure and the stable redox process.

An ethanol (100 cm^3) solution of [pyridinium]$_2$-[MoOCl$_5$] [7] (4.5 g, 10 mmol) was added to an ethanol (100 cm^3) solution of sodium (3 g, 0.13 mol) and 4,5-bis(benzoylthio)-1,3-dithiole-2-thione [8] (8.1 g, 20 mmol) in an ice bath. After filtration of the resulting solution, an ethanol (10 cm^3) solution of [NBu$^n_4$]Br (9.7 g, 30 mmol) was added to it and the mixture was allowed to stand overnight in a refrigerator. The precipitate obtained was recrystallized from ethanol to afford red needles of [NBu$^n_4$]$_2$-[MoO(dmit)$_2$] (17% yield); melting point 170–173 °C (decomp.). *Anal.* Calc. for $C_{38}H_{72}N_2OS_{10}Mo$: C, 46.12; H, 7.33; N, 2.83. Found: C, 45.82; H, 7.36; N, 2.82%.

Crystal data: $C_{38}H_{72}N_2OS_{10}Mo$, monoclinic, space group $P2_1/c$, with $a = 20.035(8)$, $b = 13.881(4)$, $c = 19.519(7)$ Å, $\beta = 108.33(3)°$, $V = 5153(3)$ Å^3, $Z = 4$, $D_c = 1.276(1)$ g cm^{-3}, $F(000) = 2096.0$, μ(Mo Kα) = 6.7 cm^{-1}. A structure solution and refinement based on 2064 reflections with $|F_o| > 3\sigma(F)$ converged with a conventional discrepancy factor of 0.12. The crystal structure consists of eight [NBu$^n_4$]$^+$ cations and four [MoO(dmit)$_2$]$^{2-}$ anions in the unit cell, which have no unduly short intermolecular contacts.

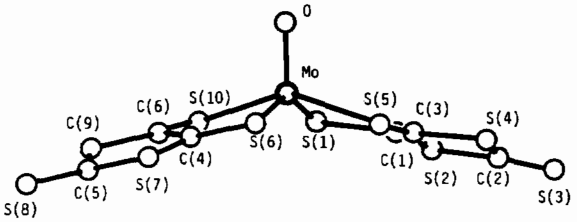

Fig. 1. The structure of the [MoO(dmit)$_2$]$^{2-}$ anion.

TABLE I. Selected Bond Lengths (Å) and Angles (°) for the Anion Moiety of [NBu$^n_4$]$_2$[MoO(dmit)$_2$] with Standard Deviations in Parentheses

Mo–O	1.65(2)	S(5)–C(3)	1.74(4)
Mo–S(1)	2.39(1)	S(6)–C(4)	1.73(3)
Mo–S(5)	2.41(1)	S(7)–C(4)	1.81(3)
Mo–S(6)	2.39(1)	S(7)–C(5)	1.74(4)
Mo–S(10)	2.399(9)	S(8)–C(5)	1.68(3)
S(1)–C(1)	1.83(3)	S(9)–C(5)	1.62(4)
S(2)–C(1)	1.65(4)	S(9)–C(6)	1.68(3)
S(2)–C(2)	1.77(4)	S(10)–C(6)	1.79(4)
S(3)–C(2)	1.63(4)	C(1)–C(3)	1.34(5)
S(4)–C(2)	1.73(5)	C(4)–C(6)	1.33(5)
S(4)–C(3)	1.73(3)		
S(1)–Mo–S(5)	84.9(4)	Mo–S(10)–C(6)	105(1)
S(1)–Mo–S(10)	84.4(4)	S(1)–C(1)–C(3)	115(5)
S(1)–Mo–O	108(1)	S(2)–C(1)–C(3)	122(3)
S(5)–Mo–S(6)	84.8(4)	S(2)–C(2)–S(4)	108(2)
S(5)–Mo–O	108.3(9)	S(4)–C(3)–C(1)	110(3)
S(6)–Mo–S(10)	85.2(4)	S(5)–C(3)–C(1)	130(2)
S(6)–Mo–O	108(1)	S(6)–C(4)–C(6)	130(3)
S(10)–Mo–O	105.2(9)	S(7)–C(4)–C(6)	112(2)
C(1)–S(1)–C(2)	98(2)	S(7)–C(5)–S(8)	119(2)
C(2)–S(4)–C(3)	101(2)	S(7)–C(5)–S(9)	117(2)
Mo–S(5)–C(3)	102(1)	S(8)–C(5)–S(9)	124(2)
Mo–S(6)–C(4)	102(1)	S(9)–C(6)–C(4)	120(3)
C(4)–S(7)–C(5)	94(2)	S(10)–C(6)–C(4)	116(2)
C(5)–S(9)–C(6)	97(2)		

The molecular structure of the anion moiety is illustrated in Fig. 1 and selected bond lengths and angles are summarized in Table I. The oxomolybdenum(IV) group is coordinated by two dmit ligands. The geometry around molybdenum is square-pyramidal, where S(1), S(5), S(6) and S(10) atoms form an approximately square basal plane (±0.026 Å) and the molybdenum atom is located 0.718 Å above the plane. The geometry of the complex as well as its Mo–O and Mo–S bond lengths are essentially close to those of the recently reported bis(dithiolene)-oxomolybdenum(IV) complex [NEt$_4$]$_2$[MoO(bdt)$_2$] [bdt = benzene-1,2-dithiolate; Mo–O, 1.699(6) and Mo–S, 2.388(2) Å] [9]. However, the Mo–O bond of the present complex is appreciably short compared with that of the bdt complex, which is consistent with the fact that the IR band of ν(Mo=O) of the

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

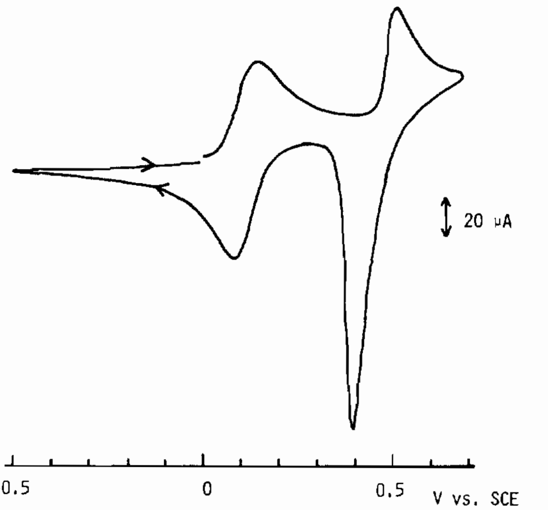

Fig. 2. A cyclic voltammogram of $[\mathrm{NBu^n_4}]_2[\mathrm{MoO(dmit)_2}]$ (1×10^{-3} mol dm^{-3}) in acetonitrile; 0.1 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{ClO_4}]$, scan rate 100 mV s^{-1}.

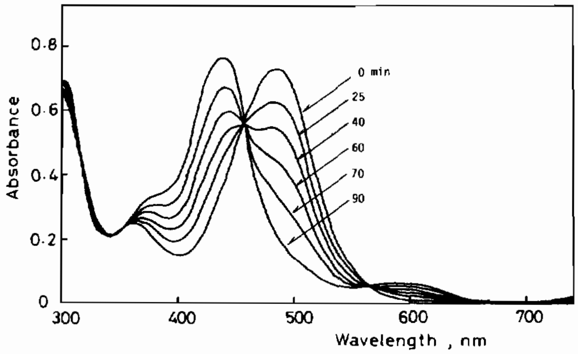

Fig. 3. Electronic absorption spectra of $[\mathrm{NBu^n_4}]_2[\mathrm{MoO(dmit)_2}]$ (1.5×10^{-3} mol dm^{-3}) on the electrochemical oxidation at 0.3 V *vs.* SCE in dichloromethane; 0.1 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{ClO_4}]$.

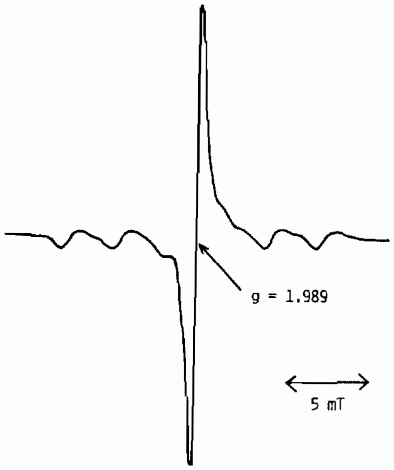

Fig. 4. The ESR spectrum of an equimolar mixture of $[\mathrm{NBu^n_4}]_2[\mathrm{MoO(dmit)_2}]$ and iodine in acetonitrile at room temperature.

former is observed at a higher frequency (930 cm^{-1}) than that of the latter (905 cm^{-1}) [9]. These findings indicate some preferable charge transfer from molybdenum to the dmit ligands.

A cyclic voltammogram of the complex in acetonitrile gives a reversible redox wave at $E_{1/2}{}^0 = 0.12$ V (*versus* SCE) ($\Delta E = E_{\mathrm{cp}} - E_{\mathrm{ap}} = 60$ mV) and a quasi-reversible wave at 0.52 V (*versus* SCE) ($\Delta E = 130$ mV) (Fig. 2). The electronic absorption spectral change of the complex in dichloromethane under potential-controlled electrolysis is illustrated in Fig. 3. By the electrical oxidation at the controlled potential of 0.30 V (*versus* SCE) the intense band at 485 nm is lessened in its intensity, and a new band appears concomitantly at 436 nm which is due to the $[\mathrm{MoO(dmit)_2}]^-$ anion. The subsequent electrical reduction at -0.20 V reproduces reversibly almost the original absorption band of the $[\mathrm{MoO(dmit)_2}]^{2-}$ anion. The spectrum of the $[\mathrm{MoO(dmit)_2}]^-$ anion exhibits another new band at 590 nm, which can be reasonably assigned to a sulfur-to-molybdenum charge-transfer transition, as reported for $[\mathrm{NEt_4}][\mathrm{MoO(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4}]$ (582 nm in acetonitrile) [10]. Under potential-controlled electrolysis at 0.70 V, no electronic absorption spectrum has been successfully observed, probably because of an intense adsorption of the oxidized species $[\mathrm{MoO(dmit)_2}]^0$ on the platinum mesh electrode.

Reaction of the complex with iodine in acetonitrile afforded almost the same absorption spectrum as the above one obtained under the electrolysis of the salt at 0.30 V (Fig. 3), indicating the oxidation of $[\mathrm{MoO(dmit)_2}]^{2-}$ to $[\mathrm{MoO(dmit)_2}]^-$ by iodine. In accordance with this, an acetonitrile solution containing equimolar amounts of the complex and iodine shows an isotropic ESR signal at room temperature, which has six satellites which are due to the hyperfine spin-coupling with the $^{95/97}$Mo nuclei ($I = 5/2$) [$a(^{95/97}\mathrm{Mo}) = 28.2 \times 10^{-4}$ cm^{-1}] (Fig. 4). The magnitude is close to that of $[\mathrm{PPh_4}][\mathrm{MoO(SCH_2CH_2S)_2}]$ [$a(^{95/97}\mathrm{Mo}) = 30.3 \times 10^{-4}$ cm^{-1}] [11] and essentially smaller than those of many inorganic Mo(V) salts [12].

Based on the stable oxidation properties of this complex, studies on partially oxidized $[\mathrm{MoO(dmit)_2}]$ complexes are in progress.

References

1 J. S. Miller (ed.), 'Extended Linear Chain Compounds', Vols. 1, 2, Plenum Press, New York, 1982; Vol. 3, 1983.
2 J. M. Williams and K. Carneiro, *Adv. Inorg. Chem. Radiochem.*, *29*, 249 (1985).
3 L. Valade, P. P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, 783 (1985).
4 M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M.

Garbauskas and L. V. Interrante, *J. Am. Chem. Soc., 108,* 1908 (1986).

5 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishino, K. Kajita and W. Sasaki, *Chem. Lett.,* 1819 (1987).

6 G. Matsubayashi, K. Akiba and T. Tanaka, to be published.

7 G. R. Hanson, A. A. Brunette, A. C. McDonell, K. S. Murray and A. G. Wedd, *J. Am. Chem. Soc., 103,* 1953 (1981).

8 G. Steimecke, H.-J. Sieler, R. Krimse and E. Hoyer, *Phosphorus Sulfur, 7,* 49 (1979).

9 S. Boyde, S. R. Ellis, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.,* 1541 (1986).

10 S.-L. Soong, V. Chebolu, S. A. Koch, T. O'Sullivan and M. Miller, *Inorg. Chem., 25,* 4067 (1986).

11 S. R. Ellis, D. Collison, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.,* 1483 (1986).

12 E. I. Stiefel, *Prog. Inorg. Chem., 22,* 1 (1977).