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PREPARATION AND CHARACTERIZATION OF OXO(2,3,17,18-TETRAMETHYL-7,8,12,13-TETRAETHYLCORROLATO)MOLYBDENUM(V)†

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Oxo(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)molybdenum(V) was prepared from the corresponding corrole by the reaction with either molybdenum pentachloride or molybdenum hexacarbonyl. Spin Hamiltonian parameters were evaluated as $g = 1.967$, $A_{Mo} = 41.8 \times 10^{-4}$ cm^{-1}, and $A_N = 2.3 \times 10^{-4}$ cm^{-1}. The results from ESR and ESCA measurements indicate that the molybdenum complex has a compressed tetragonal structure of N_4O-coordination.

Several attempts to prepare one-dimensional electric conductors by stacking planar metal complexes with the formation of metal-metal bonds have been carried out,$^{1)}$ since Little pointed out the possible existence of superconductive materials with high T_c's.$^{2)}$ The model proposed by Little consists of a linear electric conductor surrounded by dielectric substance: the conducting electrons create localized excitons in the dielectric surroundings and then attractive forces among electrons are yielded by electron-exciton interaction. Some inorganic planar complexes of platinum and iridium were investigated previously$^{1)}$ in an attempt to develop materials of such nature. Transition-metal ions which belong to the latter halves of the second and third series are well known to form planar complexes. Planar complexes of those ions, however, hardly show favorable metal-metal interaction in their axial directions. Thus, those platinum and iridium complexes have shown only semiconductive behaviors. On the other hand, metal ions which belong to the initial halves of the second and third transition series have a strong tendency to form metal-metal bonding in their lower oxidation states. Rigid planar structure is a necessary requisite for ligands to form planar complexes with these latter ions. Cyclic tetrapyrrolic ligands fulfill this requisite and further can be modified by substitution of appropriate polar groups at their peripheral positions. The polar substituents may provide dielectric surroundings for a linear electric conductor to develop the superconductive behavior in accordance with Little's model.

We have prepared for the first time a molybdenum complex with 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (abbreviated hereafter as MEC), the structure of which is to be discussed here. MEC was prepared by cyclization of the corresponding biladiene.$^{3)}$ Identical products were obtained by the following two different procedures.

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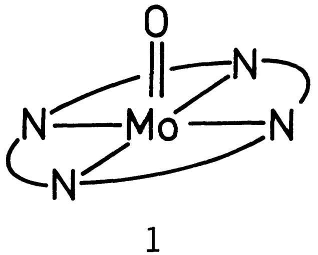
Preparation 1. ——— Oxygen was purged off by bubbling nitrogen gas through the solution which consists of MEC (150 mg) and decalin (50 ml). Molybdenum pentachloride (300 mg) and sodium acetate (2.0 g) were added to the solution, and then the reaction mixture was heated under nitrogen stream at 170-180°C. Color of the mixture varied gradually from red to dark green. The decalin solution was applied on the top of a chromatographic column of neutral aluminum oxide (Woelm, activity grade 1). A deeply colored band on the top of the column was eluted with benzene, and then with chloroform. The second deep red effluent (chloroform as eluant) was collected and evaporated to dryness *in vacuo*. The solid residue was dissolved in 10 ml of dichloromethane, and 5 ml of *n*-pentane was added to the solution to recover crystalline solid, which was subsequently recrystallized from dichloromethane – *n*-pentane to give dark purple prisms; yield 80 mg (40 %). Found: C, 64.55; H, 6.07; N, 9.74%. Calcd for $C_{31}H_{35}MoN_4O$: C, 64.68; H, 6.14; N, 9.74%.

Preparation 2. ——— Oxygen was purged off by passing nitrogen gas through the solution, which consists of MEC (150 mg) and decalin (50 ml), for 30 min. Molybdenum hexacarbonyl (105 mg) was added to the solution, which was subsequently refluxed for 5-6 h with stirring under nitrogen stream. Separation and purification procedures were similar to those described above (preparation 1). The product was confirmed to be identical with that obtained by preparation 1.

An ESCA spectrum of the molybdenum complex was recorded on a Shimadzu-Du Pont 650B spectrometer: $O(1s_{1/2})$, 529.5; $Mo(3d_{3/2})$, 233.1; $Mo(3d_{5/2})$, 230.1 eV. The visible absorption spectrum measured in benzene is shown in Fig. 1. The most intense band at 432 nm corresponds to the Soret-type band as observed for porphyrin complexes. Since only one Soret band is observed, the complex exists as a single species in benzene. Less intense bands appeared in the 500-600 nm region correspond to α and β bands as observed for porphyrin complexes. The above results indicate that the present complex has either oxomolybdenum (**1**) or di-μ-oxodimolybdenum structure (**2**). The formal oxidation state of molybdenum for both structures is +5, and the Mo(O)(MEC) unit involves one unpaired electron. The ground state for **1** is thus a spin doublet, while that for **2** may be a singlet, triplet, or double doublet. The extent of exchange interaction among two unpaired electrons involved in **2**, which results in singlet and triplet states, can not be small, and the superexchange interaction may play only a minor role.



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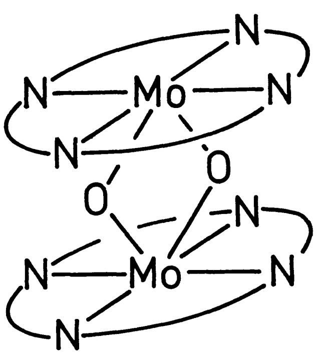

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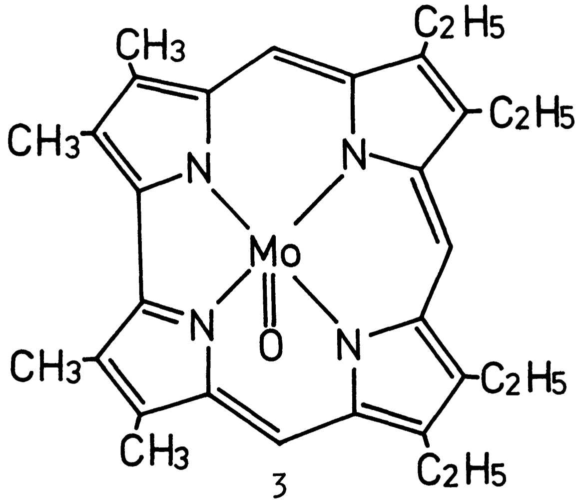

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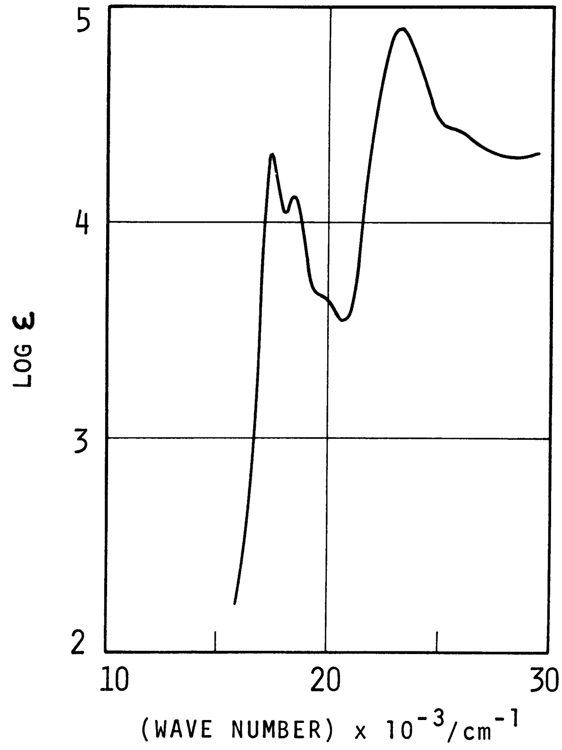

Fig. 1. Electronic absorption spectrum of Mo(O)(MEC) in benzene at room temperature.

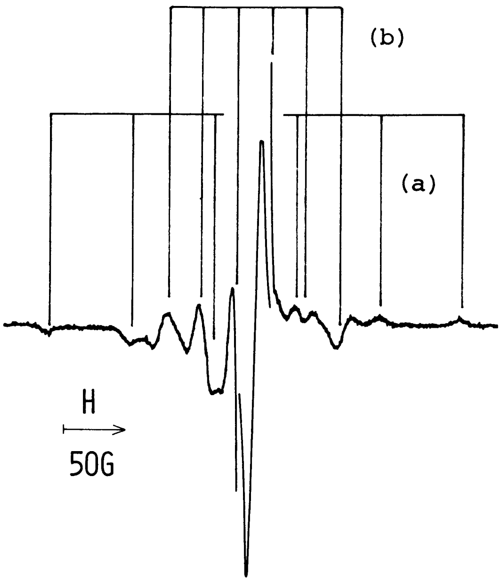

Fig. 3. ESR spectrum of Mo(O)(MEC) in benzene-xylene (2:1) at 77 K; vertical lines indicate the parallel (a) and perpendicular (b) components of hyperfine structure.

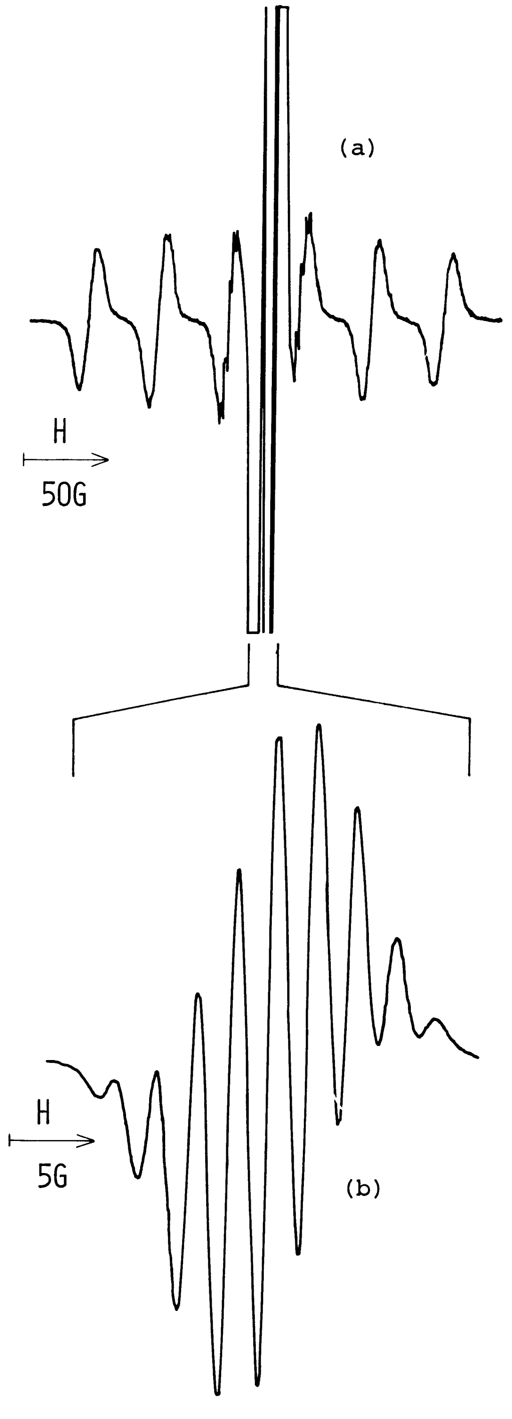

Fig. 2. ESR spectrum of Mo(O)(MEC) in benzene-xylene (2:1) at room temperature: (a), hyperfine structure due to ^{95}Mo and ^{97}Mo; (b), superhyperfine structure due to four nitrogen nuclei (the central lines of (a) are expanded).

Table. Spin Hamiltonian parameters for Mo(O)(MEC)

Temp./K	g	$A_{Mo} \times 10^4/cm^{-1}$	$A_N \times 10^4/cm^{-1}$
293	1.967	41.8	2.3
77	1.967,[a) 1.970][b)]	67.9,[a) 26.7][b)]	

a) A parallel component. b) A perpendicular component.

ESR spectra for the complex measured in benzene-xylene (2:1) are shown in Figs. 2 and 3. The spectrum at room temperature (Fig. 2) shows nine intense lines at the center and six weaker bands in a wider range. The central intense lines are assigned to the superhyperfine structure due to the interaction with four nitrogen nuclei (I = 1) around ^{96}Mo nucleus (I = 0). The six weaker bands are assigned to the hyperfine structure caused by the interaction with ^{95}Mo and ^{97}Mo nuclei (I = 5/2). A small difference in the hyperfine splitting constant between ^{95}Mo and ^{97}Mo gives rise to the slight broadening effect on the highest and lowest field bands. A strong absorption attributable to the ^{96}Mo species is observed at the center for the frozen solution (Fig. 3). The weaker hyperfine bands are classified into two sets as indicated in Fig. 3. These sets of bands are consistent with the spin Hamiltonian of axial symmetry for doublet ground state with nuclear spin of 5/2, and are assigned to perpendicular and parallel components. No signals other than those described above were observed in the range from 77 K to room temperature. This observation excludes the possibility of a triplet spin state. The evaluated spin Hamiltonian parameters are listed in Table. According to the ESR measurements, the present molybdenum complex is thus consistent with **1** [monomeric oxomolybdenum(V)], and its ground spin state is doublet. The strong π-bonding interaction between molybdenum and axial oxygen atom destabilizes the d_{xz} and d_{yz} orbitals of the metal, so that the unpaired electron occupies the d_{xy} orbital with high population. This explanation is consistent with the fact that the very intense ESR signal for the ^{96}Mo complex was observed in the range from 77 K to room temperature. The very small superhyperfine interaction with nitrogen nuclei is attributed to the significant contribution of the in-plane π-interaction between molybdenum nucleus and donor atoms. The g-value of nearly 2.0 suggests that the coordinate bonds possess highly covalent nature. In conclusion, the molybdenum complex has N_4O-pentacoordinated structure and the local symmetry is very close to a tetragonal pyramid (**3**).

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