

## Preparation and Characterization of Dinitrosylmolybdenum Chelate Complexes

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**Synopsis.** Nitrosyl complexes of molybdenum with the composition  $\text{Mo}(\text{NO})_2\text{L}_2$  (HL=8-quinolinol, 2-mercaptobenzothiazole, 2-pyridinethiol, or ethylmercaptoacetate) have been prepared. The infrared spectral absorptions at 1740 and  $1625\text{ cm}^{-1}$  indicate that the nitrogen monoxide groups are coordinated as  $\text{NO}^+$  and are cis to each other. The  $^1\text{H-NMR}$  spectral studies are also presented. The analytical, magnetic and spectral data suggest that molybdenum is in formal zero oxidation state with octahedral coordination completed by univalent bidentate ligands.

Nitrogen monoxide is a potent inhibitor for *nitrogenase*<sup>1)</sup>, a molybdoenzyme, and further nitrosyl complexes of molybdenum have been found by Zeuch<sup>2,3)</sup> to be active disproportionation catalysts. With this view, the preparation and characterization of nitrosyl complexes of molybdenum with 8-quinolinol (Hoxine), 2-mercaptobenzothiazole (Hmbt), 2-pyridinethiol (Hmp), and ethylmercaptoacetate (Hetg) have been reported in the present note.

### Experimental

The chemicals employed such as ammonium heptamolybdate, hydroxylammonium chloride, and ligands are pure and of Laboratory grade.

**Preparation of Dinitrosylbis(8-quinolinato)molybdenum,  $\text{Mo}(\text{NO})_2(\text{oxine})_2$ .** The interaction of ammonium heptamolybdate (0.5 g) with hydroxylammonium chloride (2.0 g) in *N,N*-dimethylformamide (20 ml) yielded green solution. 8-quinolinol (2.0 g) in ethanol (60 ml) was added to the above solution and refluxed for 1 h. The fine precipitate separated out was filtered, washed with ethanol and dried. Yield: 60%

The other complexes were also prepared by following the similar procedure as described above. The complexes are red in colour and the analytical data are listed in Table 1. The infrared, far infrared, UV-visible and  $^1\text{H-NMR}$  spectra were recorded on Perkin-Elmer 257, Polytech IR 12, Carl Zeiss DMR 21 and Varian XL-100 spectrometers, respectively.

### Results and Discussion

The complexes are found to be diamagnetic from the magnetic susceptibility measurements. The electronic transitions at 470 nm (Table 2) is attributed to charge transfer transition involving  $t_{2g} \rightarrow \pi^*$  ( $\text{NO}$ ) or may be represented as  $e(\pi^b)[d_{xz}, d_{yz}] \rightarrow e(\pi^*)$  charge transfer, which has been identified<sup>4)</sup> in a number of metal nitrosyl complexes. The other higher energy and intense absorptions are assigned<sup>5)</sup> to internal ligand transitions. The strong absorptions observed at 1730 and  $1625\text{ cm}^{-1}$  in the IR spectra (Fig.1) of the complexes are assigned to sym and asym stretching of  $\text{NO}$  groups. The bands suggest<sup>6)</sup> that the  $\text{NO}$  groups are coordinated as  $\text{NO}^+$  and further two  $\text{NO}$  groups are cis to each other. For trans configuration there will be only one mode of vibration. The strong absorption

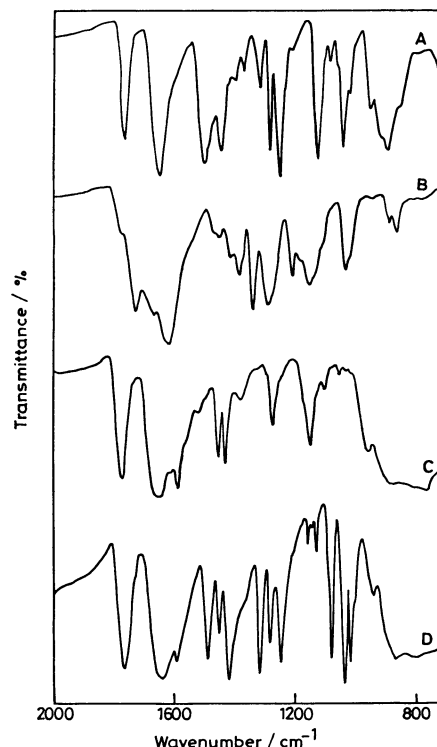


Fig. 1. Infrared spectra of (A)  $\text{Mo}(\text{NO})_2(\text{oxine})_2$ , (B)  $\text{Mo}(\text{NO})_2(\text{etg})_2$ , (C)  $\text{Mo}(\text{NO})_2(\text{mp})_2$ , and (D)  $\text{Mo}(\text{NO})_2(\text{mbt})_2$ .

in the IR spectrum of  $\text{Mo}(\text{NO})_2(\text{oxine})_2$  at  $1120\text{ cm}^{-1}$  (C-O) is the characteristic of the coordinated 8-quinolinol.<sup>7)</sup> The bands at 540 and  $315\text{ cm}^{-1}$  are due to Mo-O and Mo-N. The IR spectra of  $\text{Mo}(\text{NO})_2(\text{mbt})_2$  and  $\text{Mo}(\text{NO})_2(\text{mp})_2$  showed absorption at  $1595\text{ cm}^{-1}$  (C=N) of heterocyclic ring. The absorptions in the far IR spectra at 390 and  $235\text{ cm}^{-1}$  are due to Mo-S and Mo-N.  $\text{Mo}(\text{NO})_2(\text{etg})_2$  has a shoulder peak at  $1650\text{ cm}^{-1}$  (C=O). The lower value when compared with aliphatic ester ( $1730\text{ cm}^{-1}$ ) indicates that the carbonyl oxygen is involved in coordination. Mo-O and Mo-S absorptions are found at 500 and  $375\text{ cm}^{-1}$ . The absence of peak due to S-H in the last three complexes indicate deprotonation of the mercapto group. The IR spectral studies suggest that  $\text{NO}$  is coordinated as  $\text{NO}^+$  and the complexes are of cis configuration. The univalent and bidentate nature of the ligands are also suggested by IR spectral studies.

$^1\text{H-NMR}$  spectra of  $\text{Mo}(\text{NO})_2(\text{mbt})_2$ ,  $\text{Mo}(\text{NO})_2(\text{mp})_2$  and  $\text{Mo}(\text{NO})_2(\text{etg})_2$  were recorded (Table 3) in  $\text{CDCl}_3$  using TMS as reference. The spectrum of  $\text{Mo}(\text{NO})_2(\text{oxine})_2$  is not recorded due to poor solubility. The NMR spectrum of  $\text{Mo}(\text{NO})_2(\text{mbt})_2$  has a doublet of multiplet in the range  $\delta\ 7.4\text{--}7.8$  which is attributed to aromatic protons. The signals of the aromatic

TABLE 1. ANALYTICAL DATA OF THE COMPOUNDS

Compound	Found (Calcd) (%)				
	H	C	N	S	Mo
Mo(NO) <sub>2</sub> (oxine) <sub>2</sub>	2.69(2.72)	48.68(48.66)	12.59(12.61)	—	21.5(21.6)
Mo(NO) <sub>2</sub> (mbt) <sub>2</sub>	1.67(1.65)	34.39(34.42)	11.45(11.46)	26.21(26.25)	19.6(19.6)
Mo(NO) <sub>2</sub> (mp) <sub>2</sub>	1.99(2.01)	36.06(36.01)	13.97(13.99)	16.00(16.02)	23.9(24.0)
Mo(NO) <sub>2</sub> (etg) <sub>2</sub>	4.32(4.30)	28.37(28.43)	6.64 (6.63)	15.16(15.18)	22.4(22.7)

TABLE 2. UV-VISIBLE<sup>a)</sup> AND IR<sup>b)</sup> SPECTRAL DATA

Compound	$\lambda_{\text{max}}^{\text{a)}}$ /min ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )		$\nu_{(\text{N-O})}/\text{cm}^{-1}$
	$t_{2g} \rightarrow \pi^*(\text{NO})$	Internal ligand transitions	
Mo(NO) <sub>2</sub> (oxine) <sub>2</sub>	460(200)	310(19980), 250(23450)	1700 s, 1640 s
Mo(NO) <sub>2</sub> (mbt) <sub>2</sub>	450(98)	340(15000), 285(19900)	1740 s, 1620 s
Mo(NO) <sub>2</sub> (mp) <sub>2</sub>	465(120)	275(14800), 240(20100)	1755 s, 1620 s
Mo(NO) <sub>2</sub> (etg) <sub>2</sub>	425(106)	305(12100), 250(17750)	1715 s, 1620 s

a) In methanol, b) KBr pellet.

TABLE 3. <sup>1</sup>H NMR SPECTRAL DATA

Compound	$\delta$	Assignment
Mo(NO) <sub>2</sub> (mbt) <sub>2</sub>	7.40, 7.50, 7.54, 7.68, 7.80, 7.82, 7.84, 7.86	Aryl protons
Mo(NO) <sub>2</sub> (mp) <sub>2</sub>	7.78, 7.80, 7.82, 7.84, 7.88	Aryl protons
Mo(NO) <sub>2</sub> (etg) <sub>2</sub>	4.10, 4.14, 4.20, 4.22, 4.26 1.14, 1.24, 1.28, 1.30, 1.32	-SCH <sub>2</sub> - and -OCH <sub>2</sub> -COCH <sub>2</sub> and -CH <sub>3</sub>

protons in the spectrum of Mo(NO)<sub>2</sub>(mp)<sub>2</sub> are observed at  $\delta$  7.82 as complex multiplet. Mo(NO)<sub>2</sub>(etg)<sub>2</sub> has two sets of multiplet resonances in the range  $\delta$  4.2—4.8 (4H) and  $\delta$  1.40—1.80 (5H). The integrated ratio and the  $\delta$  values suggest that the first set of peaks are

due to -SCH<sub>2</sub>- and -OCH<sub>2</sub>- and second are due to -COCH<sub>2</sub>- and -CH<sub>3</sub> protons. In fact even the simple compound Mo(NO)<sub>2</sub>(Me<sub>2</sub>dtc)<sub>2</sub>, which was prepared similarly, exhibited complex multiplet resonances in its <sup>1</sup>H and <sup>13</sup>C-NMR spectra, indicating cis configuration of the complex.<sup>8)</sup>

The nitrosyls formulated as NO<sup>+</sup>, the complexes contain 4d<sup>6</sup> configuration with molybdenum in formal zero oxidation state. The presumed octahedral structure is consistent with low-spin molybdenum complex thus explaining diamagnetic behaviour.

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