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Preparation and Characterization of Dinitrosylmolybdenum Chelate Complexes

K. S. Nagaraja and M. R. Udupa*

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

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Synopsis. Nitrosyl complexes of molybdenum with the composition $Mo(NO)_2L_2$ (HL=8-quinolinol, 2-mercaptobenzothiazole, 2-pyridinethiol, or ethylmercaptoacetate) have been prepared. The infrared spectral absorptions at 1740 and 1625 cm^{-1} indicate that the nitrogen monoxide groups are coordinated as NO^+ and are cis to each other. The ^1H-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*[1], a molybdoenzyme, and further nitrosyl complexes of molybdenum have been found by Zeuch[2,3] to be active disproportionatoin 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, Mo-$(NO)_2(oxine)_2$. 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 ^1H-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 transer transition involving $t_{2g} \rightarrow \pi^*$ (NO) or may be represented as $e(\pi^b)[d_{xz},d_{yz}] \rightarrow e(\pi^*)$ charge transfer, which has been identified[4] in a number of metal nitrosyl complexes. The other higher energy and intense absorptions are assigned[5] to internal ligand transitions. The strong absorptions observed at 1730 and 1625 cm^{-1} in the IR spectra (Fig.1) of the complexes are assigned to sym and asym stretching of NO groups. The bands suggest[6] that the NO groups are coordinated as NO^+ and further two NO groups are cis to each other. For trans configuration there will be only one mode of vibration. The strong absorption in the IR spectrum of $Mo(NO)_2(oxine)_2$ at 1120 cm^{-1} (C–O) is the characteristic of the coordinated 8-quinolinol.[7] The bands at 540 and 315 cm^{-1} are due to Mo–O and Mo–N. The IR spectra of $Mo(NO)_2(mbt)_2$ and $Mo(NO)_2(mp)_2$ showed absorption at 1595 cm^{-1} (C=N) of heterocyclic ring. The absorptions in the far IR spectra at 390 and 235 cm^{-1} are due to Mo–S and Mo–N. $Mo(NO)_2(etg)_2$ has a shoulder peak at 1650 cm^{-1} (C=O). The lower value when compared with aliphatic ester (1730 cm^{-1}) indicates that the carbonyl oxygen is involved in coordination. Mo–O and Mo–S absorptions are found at 500 and 375 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 NO is coordinated as NO^+ and the complexes are of cis configuration. The univalent and bidentate nature of the ligands are also suggested by IR spectral studies.

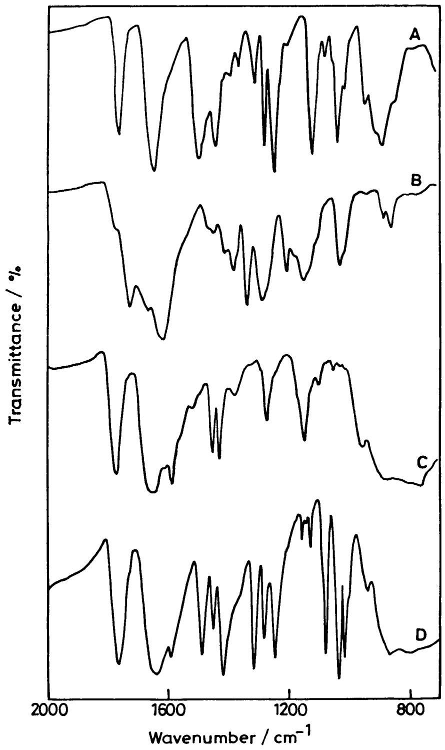

Fig. 1. Infrared spectra of (A) $Mo(NO)_2(oxine)_2$, (B) $Mo(NO)_2(etg)_2$, (C) $Mo(NO)_2(mp)_2$, and (D) $Mo(NO)_2(mbt)_2$.

^1H-NMR spectra of $Mo(NO)_2(mbt)_2$, $Mo(NO)_2(mp)_2$ and $Mo(NO)_2(etg)_2$ were recorded (Table 3) in $CDCl_3$ using TMS as reference. The spectrum of $Mo(NO)_2(oxine)_2$ is not recorded due to poor solubility. The NMR spectrum of $Mo(NO)_2(mbt)_2$ has a doublet of multiplet in the range δ 7.4—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
$Mo(NO)_2(oxine)_2$	2.69(2.72)	48.68(48.66)	12.59(12.61)	—	21.5(21.6)
$Mo(NO)_2(mbt)_2$	1.67(1.65)	34.39(34.42)	11.45(11.46)	26.21(26.25)	19.6(19.6)
$Mo(NO)_2(mp)_2$	1.99(2.01)	36.06(36.01)	13.97(13.99)	16.00(16.02)	23.9(24.0)
$Mo(NO)_2(etg)_2$	4.32(4.30)	28.37(28.43)	6.64 (6.63)	15.16(15.18)	22.4(22.7)

Table 2. UV-visible[a)] and IR[b)] spectral data

Compound	$\lambda^{c)}_{max}$/min (ε/dm^3 mol^{-1} cm^{-1})		$\nu_{(N-O)}$/cm^{-1}
	$t_{2g}\rightarrow\pi^*(NO)$	Internal ligand transitions	
$Mo(NO)_2(oxine)_2$	460(200)	310(19980), 250(23450)	1700 s, 1640 s
$Mo(NO)_2(mbt)_2$	450(98)	340(15000), 285(19900)	1740 s, 1620 s
$Mo(NO)_2(mp)_2$	465(120)	275(14800), 240(20100)	1755 s, 1620 s
$Mo(NO)_2(etg)_2$	425(106)	305(12100), 250(17750)	1715 s, 1620 s

a) In methanol, b) KBr pellet.

Table 3. ^{1}H NMR spectral data

Compound	δ	Assignment
$Mo(NO)_2(mbt)_2$	7.40, 7.50, 7.54, 7.68, 7.80, 7.82, 7.84, 7.86	Aryl protons
$Mo(NO)_2(mp)_2$	7.78, 7.80, 7.82, 7.84, 7.88	Aryl protons
$Mo(NO)_2(etg)_2$	4.10, 4.14, 4.20, 4.22, 4.26	$-SCH_2-$ and $-OCH_2$
	1.14, 1.24, 1.28, 1.30, 1.32	$-COCH_2$ and $-CH_3$

protons in the spectrum of $Mo(NO)_2(mp)_2$ are observed at δ 7.82 as complex multiplet. $Mo(NO)_2(etg)_2$ has two sets of multiplet resonances in the range δ 4.2—4.8 (4H) and δ 1.40—1.80 (5H). The integrated ratio and the δ values suggest that the first set of peaks are due to $-SCH_2-$ and $-OCH_2-$ and second are due to $-COCH_2-$ and $-CH_3$ protons. In fact even the simple compound $Mo(NO)_2(Me_2dtc)_2$, which was prepared similarly, exhibited complex multiplet resonances in its ^{1}H and ^{13}C-NMR spectra, indicating cis configuration of the complex.[8)]

The nitrosyls formulated as NO^+, the complexes contain $4d^6$ 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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