

Synthesis and vibrational studies of molybdenum dinitrosyl complexes with hydroxamic acids as ligands

T K Banerjee, S K Brahma & S P Bag*

Department of Chemistry, Jadavpur University, Calcutta
700 032

Received 2 May 1990; revised and accepted 24 July 1990

Complexes of the type $\text{Mo}(\text{NO})_2(\text{HA})_2$, where H_2A represents benzohydroxamic acid or salicylhydroxamic acid, have been isolated by a single step process for the first time. The complexes have been prepared by reductive nitrosylation of ammonium heptamolybdate by hydroxylamine hydrochloride in presence of H_2A in aqueous aerobic conditions. When the stoichiometric ratio of molybdate: hydroxylamine is 1:4 in slightly basic (DMF) media, the formation of $\text{Mo}(\text{NO})_2(\text{HA})_2$, is achieved. The complexes have been characterised on the basis of various physicochemical data of the complexes.

Molybdenum-nitrosyl complexes have been used as homogeneous olefin disproportionation catalyst precursors^{1,2}. In acidic, neutral or alkaline medium, molybdate reacts with hydroxylamine to yield an yellow complex ion of the type of $\text{Mo}(\text{NO})^{4+}$. However, the formation of dinitrosyl species $\text{Mo}(\text{NO})_2^{3+}$ is achieved by heating oxomolybdenum salt and hydroxylamine in the stoichiometric ratio of 1:4 in slightly basic media³⁻⁵. Some hydroxamic acid derivatives of molybdenum dinitrosyl species have been isolated by a single step process for the first time. The complexes have been prepared by reductive nitrosylation of molybdate (VI) by hydroxylamine in aqueous-aerobic conditions.

Experimental

Ammonium heptamolybdate (AR grade) and hydroxylamine hydrochloride (AR grade) were used as such. Benzohydroxamic acid, $\text{C}_6\text{H}_5\text{CONHOH}$ (BH_2A), and salicylhydroxamic acid, $\text{HOC}_6\text{H}_4\text{CONHOH}$ (SH_2A), were prepared by standard methods^{6,7}. The purities of the ligands were checked by their melting points and IR spectra. DMF, used as the solvent, was purified by conventional methods. Molybdenum was estimated gravimetrically by the usual method⁸. Nitrogen and carbon were estimated by micro-analytical methods using a Perkin Elmer 240 C Elemental Analyser. The results of the elemental analysis are listed in Table 1.

Preparation of complexes

$\text{Mo}(\text{NO})_2(\text{BHA})_2$: Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were heated in 10 ml of DMF at 90°C for an hour to get a green solution. It was cooled and a solution of sodium salt of benzohydroxamic acid (150 ml, 0.1 M) in water was added with stirring at room temperature. A golden yellow product thus formed was allowed to settle for an hour, filtered off, washed with water and diethyl ether and finally dried over calcium chloride.

$\text{Mo}(\text{NO})_2(\text{SHA})_2$: It was prepared similarly as described above using salicylhydroxamic acid (SH_2A) instead of benzohydroxamic acid (BH_2A).

$\text{MoO}_2(\text{BHA})_2$ and $\text{MoO}_2(\text{SHA})_2$: An aqueous solution of ammonium heptamolybdate (20 ml, 0.1 M) was treated with hydroxamic acid (20 ml, 0.2 M) in water at room temperature. The pH of the mixture was adjusted to 3-4 by adding a few drops of dilute HCl when an orange coloured product was obtained. The product was filtered off, washed with water and ethyl alcohol and finally dried *in vacuo* over calcium chloride.

The conductances of all the complexes were measured in DMF solvent using an Elico conductivity bridge (type C M82 T). The IR spectra of the ligands and their complexes were recorded in KBr on a Perkin Elmer 1800 FTIR spectrophotometer in the region $4000-400\text{ cm}^{-1}$. Raman spectra of the powder sample were recorded on a SPEX Ramalog spectrometer using 514.5 nm radiation from a Spectra-Physics argon ion laser.

Results and discussion

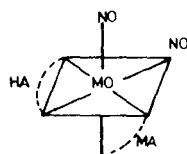
Analytical data of the complexes (Table 1) show that the stoichiometric ratio of $\text{Mo}(\text{NO})_2^{3+}$: hydroxamic acid is 1:2. All the complexes are thermally stable and are diamagnetic. They are sparingly soluble in water and chloroform but are soluble in ethanol and acetone. The conductivities of these molybdenum complexes were measured in DMF. The molar conductance values for the complexes ($17-23\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) indicate that the complexes are nonelectrolytes.

For BH_2A ligand the most characteristic bands in the IR (Raman) spectra are: 1602 (1601) [$\nu_{\text{C=O}}$]; 1575 (1580) [$\nu_{\text{C=C}}$]; 905 (900) [ν_{NO}]. For SH_2A the corresponding bands are 1618 (1608), 1576 (1577) and 906 (900) cm^{-1} respectively. The very strong absorption peaks at 945 cm^{-1} for $\text{MoO}_2(\text{BHA})_2$

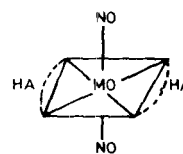
Table 1—Analytical and physical data of complexes

Complex (colour)	Found (Calc.), %			
	C	N	H	Mo
MoO ₂ (BHA) ₂ (Orange)	42.55 (42.00)	6.35 (7.00)	3.02 (3.00)	25.21 (24.00)
MoO ₂ (SHA) ₂ (Light green)	39.45 (38.88)	5.85 (6.48)	3.25 (3.70)	23.15 (22.22)
Mo(NO) ₂ (BHA) ₂ (Golden yellow)	41.17 (39.25)	12.71 (13.08)	3.12 (2.80)	21.18 (22.42)
Mo(NO) ₂ (SHA) ₂ (Light brown)	36.98 (36.52)	10.89 (12.17)	2.998 (2.60)	20.15 (20.86)

and 930 cm^{-1} for MoO₂(SHA)₂, are assigned to the symmetric stretching mode of the terminal Mo=O bond⁹. However, the corresponding Raman band is observed as a weak absorption at 930 cm^{-1} . It has also been observed that in the IR spectra of MoO₂(BHA)₂ and MoO₂(SHA)₂, the sharp NO (hydroxamic acid) band which appears in the simple hydroxamic acids is split up due to the appearance of $\nu_{\text{Mo}=\text{O}}$ and ν_{NO} mode of vibrations in the same region. For the nitrosyl complexes Mo(NO)₂(BHA)₂ and Mo(NO)₂(SHA)₂, the $\nu_{\text{N}=\text{O}}$ bands appear at 1675 and 1780 cm^{-1} ; and 1670 and 1780 cm^{-1} respectively. Though the Raman spectra of the nitrosyl complexes were not very good due to the strong absorption of the complexes by laser (because of their dark colour), the characteristic peak



1(a)



1(b)

positions could be clearly identified. The frequencies of the bands ($1600\text{--}1800\text{ cm}^{-1}$) in the nitrosyl complexes suggest that the NO⁺ formalism is appropriate here¹⁰. If valence shell electron population of 18 is to be achieved, these compound might occur in either *cis* or *trans* form (1a, 1b). Since the vibrational spectra of these complexes contain two strong well separated bands near 1700 cm^{-1} in addition to the characteristic bands of other ligands, the two nitrosyl groups are *cis* to one another.

References

- 1 Zuech E A, Hughes W B, Kubieck D M & Kittleman, *J Am chem Soc*, 92 (1970) 528.
- 2 Hughes W B, *Inorg Chem*, 13 (1974) 1531.
- 3 Cotton F A & Johnson B F G, *Inorg Chem*, 3 (1964) 1609.
- 4 Enemark J H & Feltham R D, *Coord Chem Rev*, 13 (1974) 339.
- 5 Connelly N G, *Inorg chim Acta Rev*, 6 (1972) 48.
- 6 Werner A, *Ber.* 41 (1908) 1062.
- 7 Mussante C, *Gazz chim ital*, 78 (1948) 536.
- 8 Vogel A I, *Vogel's text book of quantitative inorganic analysis* (Longmans, London), 1978, 472.
- 9 Mitchell P C, *J inorg nucl Chem*, 23 (1963) 963.
- 10 Lewis J, Irving R J & Wilkinsons, *J inorg nucl Chem*, 7 (1958) 32.