Heterobinuclear manganese-molybdenum and mercury-molybdenum complexes of dithiocarbamates

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Heterobinuclear complexes $[\text{MnMoO}_2(L)_4(H_2O)]$ and $[\text{HgMoO}_2(L)_2(H_2O)]$ (L = diethyldithiocarbamate, 4-morpholinyldithiocarbamate, 1-piperidinyldithiocarbamate) have been prepared and characterized. The magnetic moment, EPR and PES spectral data suggest the presence of manganese(III) or mercury(II) with molybdenum(V) in the complexes. The $^1$H and $^{13}$C NMR chemical shifts of the complexes indicate the presence of two types of dithiocarbamates coordinated to molybdenum and a heterometal atom. The redox behaviour of the complexes are discussed from CVM data. The proposed structure consists of an octahedral manganese(III) or mercury(II) and distorted octahedral molybdenum(V) bridged by an oxo group.

Molybdenum plays an active role in xanthine oxidase, aldehyde oxidase and sulphite oxidase which brings out the oxidation reactions. The nitrogenase enzyme which is responsible for the fixation of atmospheric nitrogen has molybdenum atom surrounded by sulphur ligands. Iron-molybdenum complexes have been studied extensively as they are considered as model compounds of nitrogenase.

The mixed metal molybdenum complexes assume greater importance due to the involvement of the elements in the biological and catalytic systems. Recently binuclear oxobridged complexes of Fe-Mo, Ni-Mo, Ag-Mo, V-Mo and Cd-Mo have been reported. We hereby present the preparation and characterization of heterobinuclear Mn-Mo and Hg-Mo complexes of dithiocarbamates. The ligands used are diethyldithiocarbamate (Et$_2$dtc), 4-Morpholinyldithiocarbamate (4-Morphdtc) or 1-piperidinyldithiocarbamate (1-Pipdtc).

Preparation of MnMoO$_2$(Et$_2$dtc)$_4$(H$_2$O)$_1$ (1)

Manganese(II) molybdate was prepared by mixing manganese(II) chloride tetrahydrate (1.97 g) in water (20 cm$^3$) with ammonium molybdate (1.76 g) in water (20 cm$^3$). The buff coloured manganese(II) molybdate was filtered and dried. MnMoO$_4$ (0.25 g) was dissolved in DMF (20 cm$^3$) and conc. HCl (1 cm$^3$) and heated over a water bath for half an hour. The solution was filtered to which an aqueous solution of sodium diethyldithiocarbamate (1.50 g) in water (60 cm$^3$) was added with constant stirring under ice cold condition. The red-brown complex obtained was filtered, washed with methanol and dried. Yield: 60%. The complexes 2 and 3 were prepared by following the similar procedure whereas 4, 5 and 6 were prepared starting from mercury(II) molybdate, which was obtained by mixing mercury(II) nitrate and ammonium molybdate in aqueous solution.

The carbon, hydrogen and nitrogen analyses were carried out on a Heraeus CHN-O-rapid analyser. Manganese and molybdenum were determined by wet chemical analyses. Mercury was estimated by flameless atomic absorption spectrophotometric method. The TLC studies were conducted over alumina plates using a CH$_2$Cl$_2$-CH$_3$OH mixture as eluant. The conductivity measurements of the complexes in DMF were carried out on a Philips conductivity bridge. A redox titrimetric procedure was adopted to assign the oxidation state of molybdenum. The magnetic sus-

Materials and Methods

Ammonium molybdate, manganese(II) chloride, mercury(II) nitrate, sodium diethyldithiocarbamate and solvents used were of laboratory grade. Morpholinium 4-morpholinyldithiocarbamate and sodium piperidinyldithiocarbamate were prepared by the reported procedures. Doubly distilled water was used in the preparation of solutions.

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ceptibility of the powder complexes were determined at room temperature using VSM technique. The EPR, visible and IR spectra were recorded on varian E-4 X-band, Perkin-Elmer 781 and polytech IR spectrometers respectively. The $^1$H NMR spectrum of the complexes were studied using a Hitachi R-600 high resolution spectrometer. The $^{13}$C NMR spectrum was obtained at 25.2 MHz under conditions of complete proton noise decoupling in the Fourier transform modes using a Varian XL-100 NMR spectrum equipped with Varian 620 IL 100 data system. A varian Gynacode decoupler was utilized for proton decoupling. X-ray photoelectron spectra were recorded on ESCA LAB MK 11-Spectrometer using MgK$_\alpha$ radiation (1253.6 eV). Samples were deposited as thin films onto a silver plate so as to minimize charge effects. The C(1$s$) line from spectral residual pump oil contamination was used as an internal standard for spectral calibration. Cyclic voltammetric measurements were carried out with a Pt wire as working electrode, platinum foil sealed in the glass as an auxiliary electrode and Ag/AgCl as the reference electrode. Tetraethylammonium perchlorate was used as the supporting electrolyte. The CVM were recorded on an X-Y recorder of Hewlett-Packared 7004 B model.

Results and Discussion
The elemental analyses (Table 1) suggested the proposed composition of the complexes. A lower molar conductivity values (12 ohm$^{-1}$ cm$^{-2}$ mol$^{-1}$) suggested the non-ionic nature of the complexes. A single spot obtained in TLC for the complexes suggested the discrete nature. The thermal decomposition data of the complexes indicated the loss of one coordinated water molecule in the temperature range 90-150°C. In the second stage decomposition of complexes 1-3, MnS and MoO$_2$L were formed. MnMoO$_4$ was the end residue in the last stage of decomposition as suggested by the weight loss data. The complexes 5 and 6 gave non-stoichiometric mercury(II) molybdates. The complex 4 gave MoO$_3$ as the final product of decomposition.

The complexes 1-3 liberated iodine on treatment with KI solution indicating the presence of Mn(III). Redox titration with acidified KMnO$_4$ revealed the involvement of one electron transfer, which may be due to the oxidation of Mo(V) to Mo(VI). The magnetic moment values (Table 1) in the range 6.02-6.24 B M for manganese-molybdenum complexes corresponds to four unpaired electrons from Mn(III) $(t_2g)^6$ and one electron from Mo(V). The mercury-molybdenum complexes have the $\mu_{eff}$ values $\approx$ 1.40 B M and the EPR spectra show a six line pattern ($I = 5/2$ for $^{95}$Mo and $^{97}$Mo) characteristic of Mo(V). A low symmetry octahedral geometry was inferred from the EPR spectral data. The electronic spectral absorptions for the manganese-molybdenum dithiocarbamates observed at 560 and 500 nm are attributed to $^5B_{2g} \rightarrow ^5E_g$ transitions of Mn(III). The bands observed at 680 and 430 nm are due to $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ of Mo(V). The absorption at 300 nm is due to $^1] \rightarrow ^1]$ transition of the dithiocarbamate ligand. The electronic spectra of mercury-molybdenum complexes exhibit low

| Table 1—Characterization data of manganese-molybdenum and mercury-molybdenum complexes of dithiocarbamates |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Sl no. | Complex (Colour) | Found (Calcd), % | $A_{\text{Mn}}$ (ohm$^{-1}$ cm$^{-2}$ mol$^{-1}$) | $A_{\text{Mo}}$ (ohm$^{-1}$ cm$^{-2}$ mol$^{-1}$) | $g_{av}$ | EPR |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | MnMoO$_4$(Et$_2$dtc)$_4$H$_2$O (Red brown) | 30.5 (30.2) 5.2 (5.3) 7.1 (7.0) 32.0 (32.6) 6.6 (6.9) 12.2 (12.0) | 12 | 6.24 (6.03) | 2.006 (4.0) | 40 |
| 2   | MnMoO$_4$(4-Morphdtc)$_4$H$_2$O (Pale brown) | 34.4 (34.2) 4.2 (4.0) 6.2 (6.4) 29.6 (30.4) 6.2 (6.5) 11.2 (11.4) | 10 | 6.02 (6.62) | 1.987 (62) |
| 3   | MnMoO$_4$(1-pipdtc)$_4$H$_2$O (Pale brown) | 28.6 (28.2) 4.7 (4.9) 6.2 (6.5) 29.5 (30.1) 6.6 (6.4) 11.6 (11.2) | 14 | 6.17 (6.63) | 1.980 (62) |
| 4   | HgMoO$_2$(Et$_2$dtc)$_3$H$_2$O (Grey) | 22.9 (22.8) 4.1 (4.0) 5.0 (5.3) 24.4 (24.3) 25.6 (25.4) 12.3 (12.1) | 12 | 1.40 (1.73) | 1.991 (40) |
| 5   | HgMoO$_2$(4-Morphdtc)$_3$H$_2$O (Pale pink) | 21.8 (21.6) 3.2 (3.1) 5.1 (5.0) 23.2 (23.0) 24.2 (24.0) 11.6 (11.5) | 18 | 1.26 (1.73) | 1.872 (50) |
| 6   | HgMoO$_2$(1-Pipdtc)$_3$H$_2$O (Pale pink) | 26.3 (26.1) 3.9 (3.8) 5.2 (5.0) 23.6 (23.2) 24.5 (24.2) 11.8 (11.6) | 22 | 1.32 (1.73) | 1.860 (50) |
energy weak intensity bands ≈690 and 450 nm which are assigned to d-d transitions \(^{2}B_{2g} \rightarrow ^{2}E_{g}\) and \(^{2}B_{2g} \rightarrow ^{2}B_{1g}\) of Mo(V) respectively. The absorption ≈260 nm is due to \(\pi \rightarrow \pi^*\) transition of the dithiocarbamate ligand. The electron core binding (eV) values measured (Fig. 1) from X-ray photoelectron spectrum of 4 are given. The binding energy values observed at 232.2 and 234.9 eV are due to Mo (3d\(_{5/2}\)) and Mo (3d\(_{3/2}\)) in the pentavalent state\(^{14}\). A shoulder in the spectrum near this range is attributed to the presence of Mo–S linkage. The binding energy values \(\operatorname{Hg}(4f_{7/2})\) and \(\operatorname{Hg}(4f_{5/2})\) were observed\(^{15}\) at 100.2 and 104.42 eV, which suggested the presence of \(\operatorname{Hg}(II)\). The S(2p), N(1s) and O(1s) peaks were observed\(^{16}\) at 162.4, 399.2 and 529.4 eV respectively.

A broad band observed at 3450 cm\(^{-1}\) for the complexes are characteristic of \(\nu(\text{OH})\) due to the presence of coordinated water molecule. The peaks observed at 1500 and 1000 cm\(^{-1}\) were assigned to \(\gamma(\text{CN})\) and \(\gamma(\text{CS})\) of dithiocarbamate moiety\(^{17}\). The strong bands observed at 920 cm\(^{-1}\) in the complexes were due to \(\gamma\operatorname{Mo} = 0_{\text{terminal}}\) groups\(^{18}\) and bands at 560 cm\(^{-1}\) were due to \(\nu\operatorname{M} \rightarrow \text{O}-\text{Mo}(\text{asym})\) and \(\nu\operatorname{M} \rightarrow \text{O}-\text{Mo}(\text{sym})\) vibrations respectively. The absorption band seen\(^{19}\) ≈520 cm\(^{-1}\) was due to \(\nu(\text{M} \rightarrow \text{H}_2\text{O})\).

The \(^1\text{H}\) NMR spectrum of 1 has characteristic signals due to \(\text{CH}_2\) and \(\text{CH}_3\) at 2.81 and 0.69 ppm with an integration ratio of 1:1.3 (\(\text{CH}_2\) : \(\text{CH}_3\) ≈1:1.5). The \(^1\text{H}\) NMR spectrum of 2 has signals at 3.80 and 4.60 ppm due to \(-\text{NCH}_2\) and \(-\text{OCH}_2\) of the morpholinyl ring. A less intense and broad signal between 5.00 and 5.40 ppm in 1 and 2 was attributed to the coordinated water molecule. The \(^1\text{H}\) NMR spectrum of 4 was recorded in DMSO–\(d_6\). The signals observed at 1.08, 1.20, 1.24, 1.36, 1.44 and 3.68, 3.78, 3.80, 3.82, 3.92, 3.96, 4.06 ppm were attributed to \(-\text{CH}_3\) and \(-\text{NCH}_2\) protons respectively. The interesting observation noted is that the \(-\text{CH}_3\) signals which were expected to have a triplet appear as a double-triplet. The \(-\text{CH}_2\) signal which was expected to have a quartet also appears as double-quartet. The intensity ratio among each signal corresponds to 1:2 which suggested that one type of dithiocarbamate coordinated to one metal atom and two dithiocarbamate ligands to the other heterometal atom. The \(^{13}\text{C}\) NMR signals at 13.479, 12.067, 11.445 and 52.034, 51.457, 47.601; and 203.217 ppm were attributed\(^{20}\) to \(-\text{CH}_3\), \(\text{NCH}_2\) and tertiary carbon atoms respectively.
The differences in the signals in NCH$_2$ suggest the presence of two types of dithiocarbamate ligands coordinated to metal atoms.

The cyclic voltammogram (Fig. 2) of complex 1 showed a peak at +0.150 V which is attributed to Mn(III)$\rightarrow$Mn(IV). In the initial cycle, no peak or wave is observed at -0.425 V, but in subsequent cycles, the wave at -0.425 V becomes prominent which is attributed$^{21}$ to the reduction of manganese(IV) to manganese(III). The peak does not appear when the scanning is stopped at 0.0 V and when the scan is reversed. Thus the oxidation becomes necessary for the observation of the peak at -0.425 V and $E_p = 57$ mV confirming the one-electron transfer step. The reduction peak observed at -0.700 V is attributed to reduction of manganese(III) to manganese(II). When the potential is stopped at -1.700 V and when the cycle is reversed, a reversible wave at -1.150 V is observed. The $i_p$ values for several scans for a given peak indicate that it follows CE mechanism. The cyclic voltammogram of 4 showed two cathodic peaks at -1.026 and at -1.584 V which are attributed to the successive one-electron reduction of molybdenum(V) to molybdenum(IV) and molybdenum(III) respectively. The complex Mo$_2$O$_4$(Et$_2$dtc)$_2$ undergoes two-electron reduction irreversibly whereas Mo$_2$S$_4$(Et$_2$dtc)$_2$ showed peaks at -0.97 and -1.27 V attributed to successive one-electron reduction of molybdenum(V) centres. In the complex, similar reduction behaviour can be compared and it may be inferred that the presence of heterometal atom encourages oxo-molybdenum complexes to undergo facile reduction in two stages.

Manganese(III) or mercury(II) and molybdenum(V) are bridged(I) by an oxo group and the octahedral geometry around manganese and molybdenum are completed by oxo, aqua and bidentate dithiocarbamate ligands. A tetrahedral geometry around mercury is completed by an oxo-bridge an aqua and dithiocarbamate ligand.

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References