A novel series of cis-dioxomolybdenum(VI) carbodithioate complexes

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Complexes of cis-dioxomolybdenum(VI) having the empirical formulae (MoO₂L)⁻3H₂O (where L = piperazinyl-N,N'-bis-carbodithioate, PpzDtc) and MoO₂L₂ (where L = N'-methylpiperazinyl-N-carbodithioate, N-methyl PpzDtc, piperidinyl-N-carbodithioate, PpdDtc, morpholinyl-N-carbodithioate, MorphDtc, 1,2,3,4-tetrahydroisoquinolinyl-N-carbodithioate, ThiqDtc and 1,2,3,4-tetrahydroquinolinyl-N-carbodithioate, ThqDtc) have been synthesised and characterized. The physicochemical studies indicate that the ligand in the (MoO₂L)⁻3H₂O complex is bivalent tetradentate and the ligands in the MoO₂L₂ complexes are univalent bidentate. The oxo groups are cis to each other. The metal is hexacoordinated and the complexes have approximately octahedral geometries.

The bulk of the work reported so far on dithiocarbamato complexes of molybdenum is on dialkyl carbodithioates. A survey of earlier work on carbodithioate complexes of molybdenum shows that no systematic study on the dioxomolybdenum(VI) complexes with carbodithioate derived from heterocyclic secondary amines has been reported. The present paper describes the preparation and characterization of some cis-dioxomolybdenum(VI) complexes of the type MoO₂L⁻3H₂O and MoO₂L₂. In MoO₂L⁻3H₂O complex L is piperazinyl-N,N'-bis-carbodithioate (PpzDtc) and in MoO₂L₂ complexes L is N'-methylpiperazinyl-N-carbodithioate (N-methyl PpzDtc), piperidinyl-N-carbodithioate (PpdDtc), morpholinyl-N-carbodithioate (MorphDtc), 1,2,3,4-tetrahydroisoquinolinyl-N-carbodithioate (ThiqDtc) and 1,2,3,4-tetrahydroquinolinyl-N-carbodithioate (ThqDtc). The conductance, magnetic properties, IR spectra and thermal behaviour of the complexes have been investigated.

Experimental

All the carbodithioate ligands were prepared by a known method. The complexes MoO₂L₂ were prepared as follows. To a well cooled (5°C) solution of ammonium molybdate in 1:1 aqueous ethanol was added with stirring the ligand solution in 1:1 aqueous ethanol (Mo: N-carbodithioate was 1:2) and contents were cooled to 5°C. To the reaction mixture, 1.0N HNO₃ was added slowly dropwise with vigorous stirring till the precipitate formed coagulated (pH ~ 5.5). It was filtered, washed with water, 1:1 ethanol and finally with ethanol, and was dried over P₂O₁₀.

The complex MoO₂L⁻3H₂O was prepared from the schiff base complex, 1-isonicotinoyl-2-naphthalidenyldrazine hydro-cis-dioxomolybdenum(VI)⁶ by ligand substitution reaction with disodium piperazinyl-N,N'-bis-carbodithioate in benzene-ethanol (1:1) mixture. To the schiff base complex (0.0025 mol), dissolved in 500 cm³ of hot 1:1 ethanol-benzene mixture, the carbodithioate ligand (0.003 mol) dissolved in the minimum amount of the same solvent was added slowly with stirring. The colour of the red reaction mixture slowly changed to yellow. The solution was refluxed and the volume reduced to about 250 cm³. About 100 cm³ of benzene was added to this and again the volume reduced to about 250 cm³. This procedure was repeated till most of the ethanol from the medium had been removed and finally the volume was reduced to 150 cm³, when the orange yellow carbodithioate complex started to separate. Petroleum ether (40-60°C) was added with stirring to complete the precipitation. The complex was filtered, washed first with benzene-ethanol mixture and then with petroleum ether. The complexes were dried in vacuo over P₂O₁₀.

Molybdenum was estimated gravimetrically as oxinate. For this, the complex was decomposed with conc. H₂SO₄ and a few drops of HClO₄ to obtain a clear and colourless solution. Sulphur was estimated as BaSO₄ by bromine oxidation method.⁷

Molar conductance measurements were made in nitrobenzene and magnetic susceptibilities were measured at room temperatures as described earlier. The IR spectra of the complexes and the ligands were taken in KBr on a Perkin-Elmer 397 IR spectrophotometer in the range 4000-400 cm⁻¹. Molecular weights of the complexes were determined by Rast's method, using biphenyl as solvent. Thermogravimetric (TG) measurements were made on a Perkin-Elmer TGS-1 thermobalance using the heating rate of 300°C/hr.

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Results and discussion

Elemental analysis and TG data (Table 1) suggest the formula MoO$_2$L$_2$ for the complexes of N-methyl PpzDtc, PpdDtc, MorphDtc, ThiqDtc and ThqDtc, and MoO$_2$L·3H$_2$O for the PpzDtc complex. Molecular weight measurements showed that all the complexes, except the PpzDtc complex, were monomeric. The molecular weight of PpzDtc complex could not be determined due to lack of sufficient solubility in common organic solvents.

The complexes behaved as non electrolytes in nitrobenzene. In other solvents like methanol, acetonitrile, etc., they were only sparingly soluble. All of them were diamagnetic as expected for a $d^0$ system.

In ascertaining the electronic and structural characteristics of carbodithioate complexes, the thioureide, ν($\text{C-N}$), vibration of $S_2C-NR_2$ group expected at 1450-1550 cm$^{-1}$, the ν($\text{CSS}$) vibration at 950-1050 cm$^{-1}$ and (ν-$\text{S}$) vibration at 300-400 cm$^{-1}$ are of interest in the IR spectra. The 900 cm$^{-1}$ region is also of interest in the present system, since in this region the O = Mo = O stretch appears.

The lower C–N stretch (1448-1460 cm$^{-1}$) for the present N-carbodithioate ligands than that reported$^{13}$ for the dialkyl carbodithioates is due to the lower electron donating ability of heterocyclic system to the C=$\text{N}$ bond. The C=$\text{N}$ stretch assigned at 1585 cm$^{-1}$ for the piperazinyl N,N'-bis-carbodithioate is higher than that for the other dithio ligands studied presently. This increase in double bond character of C=$\text{N}$ bond of the double-ended ligand may be due to the low masses attached to the nitrogen of the thioureide group.$^{13}$ Here, it is assumed that half the skeleton of piperazine (two-CH$_2$-group is attached to the nitrogen of each thioureide group. The shift of C=$\text{N}$ stretch to a higher frequency observed for the Mo(VI) complexes is consistent with the reported trend.$^{14,15}$

The appearance of two IR bands in the 890-1040 cm$^{-1}$ region in the complexes indicates univalent bidentate nature of the ligands.$^{16-18}$ The double-ended PpzDtc ligand is univalent bidentate at each end and in toto the ligand is bivalent tetradeinate. Both C = S and C–S stretch of vibrations of the ligands are shifted to higher frequencies on complexation.

The two new strong bands in the IR spectra of the complexes of PpdDtc, MorphDtc, ThiqDtc and ThqDtc at 900-908 and 874-880 cm$^{-1}$ are assignable to the symmetric and asymmetric stretching modes of cis-MoO$_2^{2+}$ moiety.$^{16-19}$ For the PpzDtc complex, only one new band at 960 cm$^{-1}$ is observed and is assigned to the $\nu_s$ mode of O = Mo = O. The $\nu_{as}$O = Mo = O is coupled$^{10,20}$ with the C–S stretch of the free ligand at 885 cm$^{-1}$ and appears at 890 cm$^{-1}$. For N-methyl PpzDtc complex, no new band is observed in the expected region. The symmetric and asymmetric stretching modes of cis-MoO$_2^{3+}$ of the complex occur at 970 and 915 cm$^{-1}$. This may be coupled with the free ligand's C=S (962 cm$^{-1}$) and C–S (904 cm$^{-1}$) stretches respectively. A new band in the IR spectrum of the complex at 420-485 cm$^{-1}$ is assigned to Mo–Sstretchagreement with previous work.$^{10,21,22}$

A band occurring at 3250-3400 cm$^{-1}$ in the ligands is assigned to $\nu$(O–H) of water of crystallization.$^{23}$ The corresponding δ(O–H) band (except for PpzDtc) was also observed at 1610-1625 cm$^{-1}$. For PpzDtc the δ(O–H) was coupled with $\nu_{as}$C=$\text{N}$ stretch at 1585 cm$^{-1}$. Of all the complexes, only MoO$_2$(PpzDtc)·3H$_2$O exhibited bands due to
ν(O–H). For anhydrous PpzDtc and the MoO₂₃(PpzDtc) complex, both obtained by heating the samples to ~200°C, the ν(O–H) was absent.

The yellow MorphDtc complex on heating to ~100°C changed to violet colour without any mass loss. The transformation was irreversible. IR spectrum of the violet form showed marked changes in some of the important bands; the ν(C–N) was lowered by 5 cm⁻¹, the symmetric and asymmetric stretches of cis-MoO₂⁺ were shifted to higher energy by 17 and 30 cm⁻¹ respectively, and the ν(Mo–S) increased by 5 cm⁻¹. A new band at 765 cm⁻¹ assignable to Mo–O–Mo stretch was an additional feature of the spectrum.

Interesting correlations of IR bands of the complexes were noticed. The ν(Mo–S) showed antiparallel correlation with ν(C=S), which increased in the order: N-methyl PpzDtc < PpzDtc < PpDtc < ThiqDtc < MorphDtc < ThqDtc. This satisfies the general consideration that complexes with lower ν(C=S) are more stable, since they are most strongly bonded to the metal.

All the MoO₂L₂ complexes except the PpdDtc complex were stable up to ~150°C and decomposed in a single stage. [MoO₂₂(PpdDtc)] decomposed in two stages. The first stage [162-205°C] corresponds to the elimination of one ligand, gaining half an atom of oxygen. The complex [MoO₂(PpzDtc)]·3H₂O decomposed in five stages; 110-130, 148-169, 181-219, 253-315 and 335-525°C. The first three stages represent successive elimination of H₂O, the fourth stage shows the elimination of half ligand molecule-gaining half an atom of oxygen, and in the final stage the decomposition is complete. Final product at ~525°C approximated to MoO₃ in all the cases.

In agreement with earlier authors, we propose octahedral structure with cis-MoO₃ group for MoO₂L₂ complexes and a polymeric structure with octahedral units and cis-MoO₂ group for the MoO₅L·3H₂O complex. Presence of two carbodiithioato groups in para centres of the rigid heterocyclic system in PpzDtc rules out the possibility of coordination of both the carbodiithioato groups to one and the same metal atom and necessitates two MoO₂⁺ centres attached to opposite sides of ligand leading to polymerization. The 1:1 metal:ligand in the complex suggests a cyclic structure with even number of metals and ligands in the molecule. Elimination of half ligand molecule from the complex at a lower temperature during pyrolysis indicates its weaker coordination to the metal.

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