Ethylendiamine Monodithiocarbamate Complexes of Molybdenum

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Monodithiocarbamate of ethylendiamine(I) reacts with suitably generated molybdenum species in solution to give the solid complexes of the types Mo$_2$S$_4$(endtc)$_2$(II), MoO(NCS)(endtc)$_2$(III) and Mo(NO)$_2$(endtc)$_2$(IV) (endtc = NH$_2$CH$_2$NHCSS). The oxidation state of molybdenum and stereochemistry of the complexes are inferred from the magnetic and spectral data. The IR and the NMR spectral data of the complexes indicate the presence of free NH$_2$ group and univalent bidentate nature of the dithiocarbamate ligand. The compound(II) is diamagnetic and its IR spectral bands at 540, 510, 470 and 340 cm$^{-1}$ indicate the presence of MoO$_2$S$^2_4$ core. The compound(III) is a mononuclear molybdenum(V) species with oxo, isothiocyanato and dithiocarbamate groups completing six coordination around molybdenum. The bands at 1745 and 1630 cm$^{-1}$ in the IR spectrum of(IV) suggest that NO is coordinated as NO$^-$ and the two NO groups are cis to each other indicating the formal oxidation state of molybdenum to be zero.

As molybdenum passes through different oxidation states during reactions involving catalysis in biological systems and the exact coordination environment around molybdenum in the biological systems is not understood properly, there is need of carrying out extensive studies on coordination complexes of molybdenum. In the present note, we describe the preparation and characterization of sulphido, oxo, isothiocyanato and dinitrosyl molybdenum complexes with the dithiocarbamate derived from ethylendiamine.

The chemicals employed were of LR grade.

Preparation of ethylendiamine monodithiocarbamic acid (I)

To ethylendiamine (10 mmol) in methanol (30 cm$^3$) at 5$^\circ$C, carbon disulphide (10 mmol) was added with stirring. The white precipitate formed was filtered under suction, washed with methanol and dried [Found: C, 26.8; H, 5.4; N, 21.1; Calc. for C$_3$H$_8$N$_2$S$_2$: C, 26.5; H, 5.9; N, 20.6%].

| Preparation of di-$\mu$-sulphidobis(sulphido- (ethylendiaminemonodithiocarbamato)molybdenum(V)), Mo$_2$S$_4$(endtc)$_2$(II) | |
|---|---|---|---|---|---|
| Ammonium tetramethylxobylbdate (10 mmol) in water (40 cm$^3$) and 1 (20 mmol) in water (100 cm$^3$) were dissolved separately and mixed together. On stirring for 0.5 h, the precipitated dark-red complex was filtered, washed with water, finally with methanol and dried. | Mo$_2$S$_4$(endtc)$_2$ | 12.0 | 2.6 | 9.51 | 43.6 | 32.4 |
| MoO(NCS)(endtc)$_2$ | 16.1 | 3.5 | 15.7 | 36.5 | 21.8 |
| Mo(NO)$_2$(endtc)$_2$ | 16.4 | 3.1 | 22.7 | 29.7 | 22.3 |

Table 1: Analytical Data of the Molybdenum Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$S$_4$(endtc)$_2$</td>
<td>12.0</td>
<td>2.6</td>
<td>9.51</td>
<td>43.6</td>
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</tr>
</tbody>
</table>

The complexes are insoluble in common organic solvents, but are soluble in dimethylformamide and dimethyl sulphoxide. The analytical data of the complexes were determined by a Hewlett-Packard 185 CHN analyzer. The IR, far IR, electronic, $^1$H NMR and EPR spectra were recorded on Perkin-Elmer 257, Polytec IR 30 and Carl-Zeiss DMR 21 spectrophotometers and Varian XL-100 and Varian E-4 X-band spectrometers respectively. The IR and far IR spectra were recorded in KBr and polyethylene medium respectively. Magnetic measurements were carried out using a Gouy magnetic balance.

The elemental analyses of the complexes are given in Table 1. The ligand(I) has IR absorption bands at 3150 m[$\nu$(NH)], 1580 m[$\nu$(NH$_2$)], 1490 m[$\nu$(CS)], 1270 s[$\nu'$(CN)], and 1000 scm$^{-1}$[$\nu$(KS)] which suggest the presence of a protonated amine group and the dithiocarbamate groups. The sulphido complex(II) is found to be diamagnetic and its electronic spectrum recorded in nujol shows absorption bands at 465 and 325 nm, which are attributed to $\pi$(S)---$\pi$Mo charge-transfer($^a$) and $\pi$---$\pi^*$ (internal ligand $^b$ transitions) respectively. The observed characteristic IR frequencies (cm$^{-1}$) are 3390 m[$\nu$(NH)], 1660 m[$\delta$(NH$_2$)], 1520 s[$\nu$(CN)], 965 s[$\nu$(CS)], 1745 and 1630 cm$^{-1}$ in the IR spectrum of(IV) suggest that NO is coordinated as NO$^-$ and the two NO groups are cis to each other indicating the formal oxidation state of molybdenum to be zero.
presence of free NH$_2$ group in the complex$^9$. The bands occurring at 1520 s and 965 s cm$^{-1}$ show that the dithiocarbamate acts as a univalent bidentate ligand. The far IR spectral data reveal$^9$ the presence of terminal and bridged sulphido groups. A dimeric structure with Mo$_2$S$_4$ core is proposed for the complex.

The compound(III) has the magnetic moment of 1.62 B.M. which indicates the presence of one unpaired electron. The $g_\parallel$ and $A_v$ values calculated from the dichloromethane solution EPR spectrum are 1.965 and 40 G respectively. The complex is monomeric and molybdenum has $d^1$ configuration. The electronic spectrum of the complex in chloroform has absorption maxima at 750(101), 500(3650) and 260 nm (12200) (the figures in parentheses are $e$ values). The low energy low intensity band at 750 nm is attributed$^1$ to the transition $(b_2^1 \rightarrow e^1)$, characteristic of monomeric molybdenum(V) complexes$^{11}$. The band at 500 nm is assigned$^{3-6,7}$ to a $(S) \rightarrow d$(Mo) charge-transfer transition rather than $(0) \rightarrow \pi^*(MO)$ transition. The higher energy band at 260 nm is due to an internal ligand transition$^8$. The IR spectrum of compound(III) has principal absorption bands at 3400 m[$\nu$(NH)]; 2380 m [$\nu$(CN)]; 1640 m [$\delta$(NH$_2$)]; 1520 s [$\nu$(CN)]; 990 m [$\nu$(CS)]; 940 s [$\nu$(Mo = O)]; 850 w [$\nu$(CS)]; 475 m [$\delta$(NCS)]; 375 s [$\nu$(Mo = S$_{6e}$)]; 340 m [$\nu$(Mo = NCS)]. The bands at 2020 s, 850 w and 475 m indicate$^3-13$ that the thiocyanate group is coordinated through the nitrogen atom. The strong band at 940 cm$^{-1}$ suggests$^7$ the presence of MoO$_4^{2-}$ moiety. It is proposed that six coordination around molybdenum is completed by oxo, isothiocyanate and dithiocarbamate groups.

The nitrosyl complex(IV) is found to be diamagnetic and its electronic spectrum in methanol has absorption maxima at 475 (85.3) and 330 nm (10.210) which are assigned$^4$ to $\pi^*(NO)$ and internal ligand transitions respectively. The characteristic IR spectral bands along with the assignments are as follows: 3380 m[$\nu$(NH)]; 1745 s[$\nu_\text{as}$(NO)]; 1650 m [$\delta$(NH$_2$)]; 1630 s [$\nu$(NH$_2$)]; 1500 s [$\nu$(CN)]; 960 s [$\nu$(CS)]; 900 s [$\nu$(Mo - S)]; 840 w [$\nu$(NCS)]. Two strong bands occurring at 1745 and 1630 cm$^{-1}$ are attributed to $\nu$(NO) which suggest that NO groups are coordinated as NO$^+$ in cis configuration$^{6,14}$, with molybdenum in the formal oxidation state of zero. The $^1$H NMR spectrum of (III) in DMSO-$d_6$ has been recorded and the assignments are as follows: $\delta$ 3.20, 3.26 [NH$_2$ - CH$_2$ - ] and $\delta$ 3.34, 3.40, 3.44 [-NH - CH$_2$ - ]. The distinct peaks at $\delta$ 3.20, 3.26 and 3.34, 3.40, 3.46 suggest that the dithiocarbamate has the formulation NH$_2$CH$_2$CH$_2$NHCSS. If both the amine groups of ethylenediamine were converted into dithiocarbamate groups (SSNHCH$_2$CH$_2$NHCSS), then two -CH$_2$ - groups would be identical resulting in one signal. The resonance due to free NH$_2$ protons is observed at $\delta$ 1.50. The signal due to proton attached to the dithiocarbamate group (-NHCSS-) is not observed, which may probably be due to fast exchange of the proton with the solvent. The studies indicate that the six coordination around molybdenum is completed by the NO groups and the dithiocarbamate groups.

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