the multiplicity of Sn-Cl vibrations also suggests the possibility of chlorine atoms in cis positions around the tin atom. Dipole moment measurements have also confirmed such an arrangement for analogous compounds.

The authors are thankful to the Council of Scientific & Industrial Research, New Delhi, for the award of Junior Research Fellowship to one of them (M.K.). Thanks are also due to the International Lead and Zinc Research Organization, USA, for a gift of tetra pheny l lead and diphenyl lead dichloride.

**References**


**Chelates of Molybdenum Dioxydichloride with Substituted Thioureas & Ureas**

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Diamagnetic chelates of Mo(VI) with some N-aryl, N'-2-(4,5,6-monosubstituted-pyridyl)thioureas (RNH = SNHR) and N-aryl, N'-2-(4,5,6-monosubstituted-pyridyl) ureas (RNH = ONHR); where R = pyridyl, 5-nitro pyridyl, 4-methyl pyridyl and 6-methyl pyridyl groups and R' = -C,H₄, o-C,H(CH₃), p-C,H(CH₃) have been prepared. The complexes are of the type (MoO₃L)₂Cl₂, where L is a molecule of the bidentate ligand. The complexes have been characterized on the basis of elemental analysis, molar conductance in DMF, magnetic susceptibility measurements and infrared spectral studies. The infrared spectra of all the complexes show vC=O in the range 1690-1720 cm⁻¹, vC=S in the range 730-770 cm⁻¹ and v(C=O + C=N) in the range 1590-1630 cm⁻¹, indicating that C=O, C=S and heterocyclic ring nitrogen are coordinated to the central metal atom.

**Metal** complexes of substituted thioureas having a heterocyclic group as one of the substituents have been studied by many workers. However, a survey of the literature showed that no work has been done on the complexes of MoO₄Cl₂ with substituted thioureas having a heterocyclic group as one of the substituents. The present note describes the results of our studies on Mo(VI) dioxy dichloride complexes with some N-aryl, N'-2(4,5,6-monosubstituted pyridyl)thioureas and N-aryl, N'-2(4,5,6-monosubstituted pyridyl)ureas.

All the chemicals used were either BDH reagents of AR quality or E. Merck reagent of GR quality.

N-Aryl,N'-2(4,5,6-monosubstituted pyridyl)thioureas and N-aryl,N'-2(4,5,6-monosubstituted pyridyl)ureas — The ligands N-phenyl,N'-2(pyridyl)thiourea (PTU); N-phenyl,N'-2(pyridyl)urea (PU); N-phenyl,N'-2(5-nitro pyridyl)thiourea (PNTU); N-phenyl,N'-2(4-methylpyridyl)thiourea (P.4MeTU); N-phenyl,N'-2(6-methylpyridyl)thiourea (P.6MeTU); N-orthotolyl,N'-2(pyridyl)thiourea (o.TTU); N-ortho-tolyl,N'-2(5-nitro pyridyl)thiourea (o.TNTU); N-ortho-tolyl,N'-2(4-methylpyridyl)thiourea (o.T4MeTU); N-ortho-tolyl,N'-2(6-methylpyridyl)thiourea (o.T6MeTU); N-para-tolyl,N'-2(4-methylpyridyl)thiourea (p.4MeTU); N-para-tolyl,N'-2(5-nitro pyridyl)thiourea (p.TTU); N-para-tolyl,N'-2(6-nitro pyridyl)thiourea (p.T6MeTU); N-phenyl,N'-2(5-nitro pyridyl)urea (PNU); N-phenyl,N'-2(4-methylpyridyl)urea (P.4MeU); N-phenyl,N'-2(6-methylpyridyl)urea (P.6MeU), were prepared by a method similar to that suggested by Krishnaswami and Bhargava and were crystallized from hot ethanol.

MoO₄Cl₂ was prepared by Zado's method with slight modification. Excess of chlorine was removed by passing dry carbon dioxide. MoO₄Cl₂ was collected in dry receiver, and characterized on the basis of elemental analysis.

Mo(VI) dioxy dichloride chelates — Molybdenum dioxy dichloride complexes were precipitated from ethereal solution when 500 ml of the ligand solution (0.002M) were added drop by drop with constant stirring to 200 ml of a solution of MoO₄Cl₂ (0.002M). During the course of reaction the temperature was maintained below 10°. Excess of ligand was removed by washing several times with ether. The complexes so obtained were dried in vacuo and characterized on the basis of their melting points and elemental analyses (Table 1). Molybdenum was estimated as lead molybdate and sulphur was estimated as barium sulphate by fusing the complexes with a 1:1 mixture of sodium peroxide and sodium carbonate, extracting the melt with water.
NOTES

Table 1 — Colour, Melting Point and Analytical Data of the Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Colour</th>
<th>Found (Calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₂Cl₂ (AmPy)₂</td>
<td>110-12</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (Am.4MePy)₂</td>
<td>187-200</td>
<td>White</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (PTU)₂</td>
<td>140</td>
<td>Blue</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (PU)₂</td>
<td>127</td>
<td>Light yellow</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (PNTU)₂</td>
<td>165</td>
<td>Light blue</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (P₄MeTU)₂</td>
<td>96</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (P₆MeTU)₂</td>
<td>178</td>
<td>Light blue</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (o.TTU)₂</td>
<td>132</td>
<td>Greenish blue</td>
<td></td>
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<tr>
<td>MoO₂Cl₂ (o.TNTU)₂</td>
<td>170</td>
<td>Yellowish blue</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (o.T₄MeTU)₂</td>
<td>123</td>
<td>Light yellow</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (o.T₆MeTU)₂</td>
<td>158</td>
<td>Greenish yellow</td>
<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (p.TTU)₂</td>
<td>150-52</td>
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</tr>
<tr>
<td>MoO₂Cl₂ (p.TNTU)₂</td>
<td>172-74</td>
<td>do</td>
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<tr>
<td>MoO₂Cl₂ (p.T₄MeTU)₂</td>
<td>153-54</td>
<td>do</td>
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<tr>
<td>MoO₂Cl₂ (p.T₆MeTU)₂</td>
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<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (PNU)₂</td>
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<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (P₄MeU)₂</td>
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<td></td>
</tr>
<tr>
<td>MoO₂Cl₂ (P₆MeU)₂</td>
<td>176</td>
<td>Yellow</td>
<td></td>
</tr>
</tbody>
</table>

Mo | S | Cl
---|---|---
24-52 | — | 18-24
(24-80) | (18-35) |
21-68 | — | 16-15
(22-07) | (16-32) |
13-88 | 9-19 | 10-28
(13-77) | (9-18) | (10-19) |
15-52 | — | 11-52
(15-36) | (11-36) |
12-93 | 8-66 | 9-53
(12-82) | (8-55) | (9-48) |
14-23 | 9-54 | 10-53
(14-02) | (9-34) | (10-36) |
14-15 | 9-44 | 9-96
(14-02) | (9-34) | (10-36) |
12-58 | 8-39 | 9-28
(12-39) | (8-26) | (9-16) |
13-75 | 9-96 | 9-72
(13-48) | (9-80) | (9-96) |
13-80 | 9-00 | 9-70
(13-48) | (9-80) | (9-96) |
14-22 | 9-53 | 10-48
(14-02) | (9-34) | (10-36) |
12-57 | 8-40 | 9-28
(12-39) | (8-26) | (9-16) |
13-76 | 9-17 | 9-73
(13-48) | (8-98) | (9-96) |
13-76 | 9-17 | 9-73
(13-48) | (8-98) | (9-96) |
13-58 | — | 10-02
(13-43) | — | (9-93) |
14-85 | — | 10-99
(14-70) | — | (10-87) |
14-84 | — | 10-99
(14-70) | — | (10-87) |

and then neutralizing with dilute HCl, when BaSO₄ precipitated. Chlorine was estimated as silver chloride by Piria and Schiff’s method. All the complexes are coloured and decompose or melt with decomposition. These are easily decomposed by mineral acids. A solution of complexes in chloroform when treated with silver nitrate solution precipitated chlorine quantitatively. This observation and the observed molar conductances of the complexes (143-187 ohm^-1 cm² mol⁻¹) in DMF suggest ionic nature of the chlorine present in the complexes. Analytical results indicate the MoO₂Cl₂: ligand ratio as 1:2 which corresponds to the general empirical formula MoO₂.L₂.Cl₂. Very low solubility of the complexes (in suitable solvent like benzene, nitrobenzene) precluded their molecular weight determination. The complexes were found to be diamagnetic with susceptibilities varying from -0.67 x 10⁻⁶ to -0.88 x 10⁻⁶ gauss.

In the infrared spectra* (KBr) of the substituted thioureas, bands appearing at 720 and 1060 have been assigned to the vC=S and v(N=C=N+C=S) modes respectively. In Mo(VI) complexes these bands are reduced in intensity. The band at 730 is important in characterization of metal-sulphur bonds. On complexation, this band is reported to split and shift to lower wavelengths. As proposed by Stewart*, the band at 1600 was assigned to v(NH₂) rocking. However, Yamaguchi et al., while studying the metal complexes of methyl thio-urea assigned this band to be due to a combination of symmetric C—N stretching, NH₂ rocking and C=S stretching modes. They found that the band appeared with reduced intensity in the complexes. In the present complexes, both the bands either disappeared or were present with reduced intensities. This showed that vC=S mode also contributes to the band appearing at 1060 as proposed by Yamaguchi.

The lowering of C=O frequencies in the N-aryl, N'-2(4,5,6-monosubstituted pyridyl)urea complexes, seems to be a more reliable indication of the formation of the metal-oxygen bond. The band appearing at 1600 has been assigned to v(C=C+ C=N) modes, this band has been reported to shift in the case of coordinated pyridyl nitrogen. In the Mo(VI) complexes the v(C=C+ C=N) frequencies increase by 3-40 which indicates that the ring nitrogen is also involved in the bond formation. The ring nitrogen as one of the coordination site is further confirmed from the infrared spectra of 2-aminopyridine (AmPy), 2- amino-4-methylpyridine (Am-4MePy) and their metal chelates where we have

*IR band positions in cm⁻¹.
observed an increase in the frequency and decrease in the intensity of the above band. It has also been observed that in all these complexes a lowering in $v_{\text{Mo-O}}$ vibration (960 in MoO$_2$Cl$_2$ and 752-950 in complexes) occurs which may be ascribed to chelation.

MoO$_2$Cl$_2$ has been assigned a tetrahedral structure by H. A. Skinner$^{18}$. It seems probable that on complexation with N-aryl.N'-2(4,5,6-monosubstituted pyridyl)thiourea and N-aryl.N'-2(4,5,6-monosubstituted pyridyl)ureas, the coordination number increases to six and a complex compound with distorted octahedral structure is formed having $d^5sp^3$ hybridization. Chelation with these bidentate ligands and the displacement of chlorine atoms to outside the coordination sphere further confirms the observation of Griffith and Wichtins$^1$ that in MoO$_2$Cl$_2$ chlorine atoms are present in cis position.

The authors are thankful to the authorities of BITS, Pilani for providing necessary facilities and to the UGC, New Delhi for the award of a fellowship to one of them (K.L.M.).

References

Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) & Hg(II) with Schiff Base Derived from Benzoin & 1-Amino-2-naphthol-4-sulphonic Acid

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Complexes of Co(II), Ni(II) having the composition [MLB]$_x$(H$_2$O)$_y$ and those of Cu(II), Zn(II), Cd(II) and Hg(II) of the type [MLB]$_x$(H$_2$O)$_y$, where LH$_2$ is a tridentate Schiff base derived from benzoin and 1-amino-2-naphthol-4-sulphonic acid and B is H$_2$O, have been synthesized and characterized on the basis of analysis, conductance, magnetic susceptibility infra-red and electronic spectral studies. Co(II), Ni(II) complexes are presumably octahedral, those of Zn(II), Cd(II) and Hg(II) tetrahedral and Cu(II) planar.

IN continuation of our earlier investigations$^{1-3}$ on metal complexes with tridentate ligands including Schiff bases, the synthesis of a new tridentate Schiff base, derived from benzenol and 1-amino-2-naphthol-4-sulphonic acid and its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) are described in this note.

All the chemicals used were of AR grade.

The ligand was synthesized as follows: to a methanolic solution of benzenol (2.12 g) and 1-amino-2-naphthol-4-sulphonic acid (2.07 g) was added anhyd. sodium acetate (4 g). The mixture was refluxed for 1 hr on a water-bath. The hot solution was poured into ice cold water when a reddish-brown precipitate of the Schiff base separated out. It was filtered, washed with water, dried and recrystallized from rectified spirit, m.p. 115$^\circ$, yield 70%. It was analysed for C$_8$H$_{18}$NO$_5$S.

For the preparation of the complexes, ethanolic solutions of metallic chlorides were treated separately with ethanolic solution of the Schiff base in 1:1 ratio followed by dropwise addition of ammonia, when metal chelates separated out. These were filtered, washed with ethanol followed by ether and dried in vacuo. Their analytical and magnetic susceptibility data are recorded in Table 1.

Complexes reported in the present investigation have the composition [MLB]$_x$(H$_2$O)$_y$, where M = Co(II), Ni(II), and [MLB]$_x$(H$_2$O)$_y$, where M = Cu(II), Zn(II), Cd(II) and Hg(II); B is H$_2$O and LH$_2$ is the tridentate Schiff base. All the complexes have fairly low melting points and low conductance values in acetone medium point to their nonelectrolytic nature. Magnetic moment values show the presence of three, two and one unpaired electrons in the case of cobalt (5.1 B.M.), nickel (3.7 B.M.) and copper (1.8 B.M.) complexes respectively, indicating a spin-free octahedral configuration for the cobalt and nickel compounds. There is no significant shift in $v(C-O)$ of the ligand (1210 cm$^{-1}$) on complexation (1200 cm$^{-1}$). However, there is a significant shift in $v(C=O)$ of the ligand (1600 cm$^{-1}$) on complexation (1580 cm$^{-1}$). Further in the ligand v(O-H) appears at 3300 cm$^{-1}$ as a relatively sharp band (lowered due to hydrogen bonding). In the complexes a broad hump is observed around 3450 cm$^{-1}$ indicating

<table>
<thead>
<tr>
<th>Compd</th>
<th>Colour</th>
<th>Metal (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Req'd</td>
<td>Found</td>
</tr>
<tr>
<td>LH$_2$</td>
<td>Reddish-brown</td>
<td>---</td>
<td>3.07</td>
</tr>
<tr>
<td>[CoLH$_2$]</td>
<td>Pink</td>
<td>10.54</td>
<td>10.83</td>
</tr>
<tr>
<td>[NiLH$_2$]</td>
<td>Violet</td>
<td>10.62</td>
<td>10.94</td>
</tr>
<tr>
<td>[CuLH$_2$]</td>
<td>Blue</td>
<td>12.17</td>
<td>12.42</td>
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<tr>
<td>[ZnLH$_2$]</td>
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<td>12.55</td>
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</tr>
<tr>
<td>[CdLH$_2$]</td>
<td>Greyish-white</td>
<td>19.83</td>
<td>20.02</td>
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<tr>
<td>[HgLH$_2$]</td>
<td>Greyish-white</td>
<td>30.58</td>
<td>30.82</td>
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</table>