Synthesis and characterization of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), mercury(II), ruthenium(III), rhodium(III), platinum(IV) and gold(III) complexes with 1-(2'-pyridyl)benzothiazole-2-thione

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A new ligand 1-(2'-pyridyl)benzothiazole-2-thione and its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Ru(III), Rh(III), Pt(IV) and Au(III) have been synthesized and characterized by elemental analysis, IR, 1H NMR, UV/Vis spectral data, molar conductance and magnetic susceptibility measurements. Conductivity measurement in DMSO show the non-ionic nature of Ru(III), Rh(III), Hg(II) and Au(III) complexes. The IR spectral studies reveal that the ligand is bidentate coordinating through the pyridine N-atom and thiono S-atom. An octahedral geometry has been proposed for all the complexes except that of Au(III) which has tentatively been assigned trigonal bipyramidal structure.

In the last few years there has been considerable interest in the synthesis and characterization of the metal complexes of ligands derived from pyridine and other heterocyclic molecules1-6 because of their biological significance. Pyridine and some of its derivatives, often found in several alkaloids, exhibit marked toxic properties. Pyridine hydrobromide is used, in small doses, as a sialogogue and diaphoretic and anthelmintic agents7. The pyridine complex of Pt(IV) has been shown recently to enhance the cytotoxicity as compared to the well known cisplatin8. Recently many pyridine based multidentate ligands9,10 have been synthesized and characterized. Very recently the preparation and characterization of some multidentate pyridine based ligands derived from indazole, pyridine-2-thiol and 2, 4, 6-pyrimidine-trione and several of their complexes with bivalent and trivalent transition metal ions11,12 has been reported. In the present paper, the synthesis and characterization of 1-(2'-pyridyl)benzothiazole-2-thione and its complexes with the title metal ions is reported.

Materials and Methods

2-Mercaptobenzothiazole (Koch Light), 2-bromopyridine (Aldrich) and sodium hydride (80% suspension in oil, BDH) were used as supplied. All metal chlorides Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II) (BDH, AR) and Ru(III), Rh(III), HAuCl4 and H2PtCl6 (Johnson Matthey) were used as received.

Preparation of the ligand

Sodium mercaptobenzothiazolide was formed by the reaction of 2-mercaptobenzothiazole (6.65 g, 4.0 mmol) with sodium hydride (2.95 g), in dry ethanol (150 ml). After the theoretical volume of hydrogen gas was evolved, the reaction was discontinued. On cooling to -5°C, a light yellow product was obtained which turned into a liquid at room temperature.

Sodium mercaptobenzothiazolide (2.0 g, 1.09 mmol) and 2-bromopyridine (1.20 ml, 1.02 mmol) were mixed together in dry ethanol (150 ml) and the reaction run at reflux for 4 h. The resulting solid was filtered, washed with ethanol and recrystallized from water. Yield 32%, m.pt. 180°C.

Preparation of the complexes

Ethanolic solutions of the ligand (20 ml, 2.05 mmol) and bivalent metal chlorides (1.02 mmol) (MnCl2, CoCl2, NiCl2, CuCl2, ZnCl2, HgCl2, HAuCl4 and H2PtCl6) in 1:2 molar ratios were mixed together and refluxed for ~6 h. A coloured precipitate was obtained which was filtered off, washed with ethanol and finally vacuum dried. Reactions were conducted in a similar man-
ner between the ligand (2.05 mmol) and trivalent 
metal chlorides (2.05 mmol) (CrCl₃, FeCl₃, RuCl₃, 
RhCl₃) and the products worked up as described 
above.

The elemental analysis was carried out using a 
Carlo Erba instrument at the RSIC, CDRI, Luck-
now. IR spectra (4000-200 cm⁻¹) in KBr and 
Nujol mulls, respectively were recorded with a 
Perkin-Elmer spectrophotometer model 621. ¹H 
NMR spectra in DMSO-d₆ were obtained on a 
Varian VXR-200 MHz NMR spectrometer. The 
conductance of the solution of the complexes in 
DMSO were measured at room temperature em-
ploying a Systronic 321 conductivity bridge. The 
complexes were analysed for metal and chlorine 
by standard procedures¹³,¹⁴. Magnetic susceptibi-
licity measurements were made on a vibrating sam-
ple magnetometer model 155 at room tempera-
ture.

Results and Discussion

The formation of 1-(2'-pyridyl)benzothiazole-2-
thione takes place in two steps. In the first step 
the action of sodium hydride on 2-mercaptoben-
zothiazole results in the formation of sodium mer-
captobenzothiazolide which in the second step 
reacts with 2-bromopyridine. The characterization 
data are presented in Table 1. The complexes are 
quite stable towards heat and moisture and are in-
soluble in common organic solvents, except those 
of Ru(III), Rh(III), Hg(II) and Au(III) which are 
soluble in DMSO. The molar conductivities of 
these complexes in DMSO at room temperature 
displays non-ionic nature (Table 1).

The IR spectra of 1-(2'-pyridyl)benzothiazole-2-
thione is characterized by absorption bands at 
1610, 1595 and 1050 cm⁻¹ assignable to vC=N, vC=C and 
vC=S modes, respectively¹⁸. The strong bands at 
1610 and 1595 cm⁻¹ due to vC=N and vC=C 
of the ligand are shifted to lower region in the 
metal complexes indicating coordination through 
the nitrogen atom of the pyridine. Such negative 
shift of vC=N mode to lower frequency on com-
plexation may tentatively be attributed to lowering 
in the C=N bond order resulting from M-N bond 
formation¹⁸,¹⁹. A strong band at 1050 cm⁻¹ 
ascribed to vC=S is shifted to lower frequency 
(10-20 cm⁻¹) indicating the bonding of the metal 
ion through sulphur²⁰,²¹.

In addition, all the metal complexes 
show non-ligand bands in the far IR 
region (450-400 cm⁻¹) and (400-300 cm⁻¹) 
which are assigned to vM-N and vM-S modes, 
respectively. A new single band observed in 300-
200 cm⁻¹ region in the spectra of the complexes 
of bivalent metal ions is assigned to terminal 
vM-Cl mode²²,²³. In complexes of trivalent me-
tals, there are two bands in 300-200 cm⁻¹ range 
which are assigned to terminal and bridging M-Cl 
bands²⁴.

The ¹H NMR spectra of the ligand and its 
Ru(III), Rh(III) and Hg(II) complexes are compli-
cated and the assignments of chemical shifts were 
made on the pattern of the peak assignment given 
for similar compounds by Steel and Constable⁵. 
The downfield shift observed in all the aromatic 
protons indicate the coordination of nitrogen as 
well as sulphur atom of the ligand. The largest 
chemical shift observed for the protons at posi-
tion 6 and 4 of the pyridine also suggests coordi-
nation through the nitrogen atom of pyridine²⁵.

The Cr(III) complex shows three bands at 
16,200, 19,500 and 23,340 cm⁻¹ assignable to 
⁴T₁g(F)→⁴A₂g(F), ⁴T₂g(F)→⁴A₂g(F) and 
⁴T₁g(F)→⁴A₂g(F) transitions, respectively for an 
octahedral Cr(III) ion. The μₐₑffective value of 3.62 B.M. 
in the Cr(III) complex is slightly lower than that 
expected for an octahedral geometry. The μₐₑffective value 
of Mn(II) complex (5.65 B.M.) and the electronic 
spectral bands at 11,650, 20,530 and 22,350 
(DMSO) support an octahedral geometry around the 
Mn(II) ion. Three main bands are observed in the 
Fe(III) complex at 16,360, 18,900 and 25,450 
(DMSO) cm⁻¹ assignable to ⁴T₁g(G)→⁶A₁g, ⁴T₂g(G)→⁶A₁g.

[Chemical Structures and Figures]
Table 1—Characterization data of 1-(2'-pyridyl)benzothiazole-2-thione and its complexes

<table>
<thead>
<tr>
<th>Compound (colour, % yield)</th>
<th>m.p. (°C)</th>
<th>Found (Calcd), %</th>
<th>μ\text{eff} (B.M.)</th>
<th>QM (cm(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{12})H(</em>{8})N(_2)S(_2) (White, 32)</td>
<td>180</td>
<td>59.20 3.00 11.20 26.30</td>
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<tr>
<td>Cr(<em>2)(C(</em>{12})H(_{8})N(_2)S(_2))Cl(_6) (Green, 65)</td>
<td>300</td>
<td>35.92 1.92 6.94 15.80 26.62 12.65</td>
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<tr>
<td>Mn(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (White, 50)</td>
<td>280</td>
<td>46.60 2.12 9.32 20.82 11.32 8.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(<em>2)(C(</em>{12})H(_{8})N(_2)S(_2))Cl(_6) (Red, 52)</td>
<td>310</td>
<td>35.23 1.98 6.23 15.60 26.31 13.00</td>
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<td></td>
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<tr>
<td>Co(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (Pink, 62)</td>
<td>310</td>
<td>48.73 2.53 9.02 20.54 11.42 9.51</td>
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<tr>
<td>Ni(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (Light green, 55)</td>
<td>300</td>
<td>46.23 2.50 9.00 20.90 11.46 9.58</td>
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<td></td>
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<tr>
<td>Zn(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (White, 70)</td>
<td>310</td>
<td>46.90 2.32 8.63 20.32 11.97 10.42</td>
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<tr>
<td>Hg(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (White, 78)</td>
<td>290</td>
<td>37.86 2.10 7.36 9.26 16.58 26.92</td>
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<td></td>
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<tr>
<td>Rh(<em>2)(C(</em>{12})H(_{8})N(_2)S(_2))Cl(_6) (Brown, 63)</td>
<td>320</td>
<td>31.62 1.70 6.00 14.02 23.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(<em>2)(C(</em>{12})H(_{8})N(_2)S(_2))Cl(_6) (Black, 32)</td>
<td>270</td>
<td>31.90 1.82 6.20 14.71 23.20</td>
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<tr>
<td>Au(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (Reddish brown, 30)</td>
<td>230</td>
<td>26.60 1.40 5.02 11.90 19.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(C(<em>{12})H(</em>{8})N(_2)S(_2))Cl(_6) (Orange, 60)</td>
<td>310</td>
<td>25.89 1.40 4.61 11.00 22.03</td>
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</table>

and \(4A_{2g}(P) \rightarrow 6A_{1g}\) transitions for an octahedral geometry. The \(\mu_{\text{eff}}\) value is very close to that expected for an octahedral Fe(III) ion. There is a charge transfer band at 33,330 cm\(^{-1}\) in the Co(II) complex. The other bands at 15,260 and 21,300 cm\(^{-1}\) assigned to \(4T_{2g}(F)^{+} \rightarrow 4T_{1g}(F)^{-}\) and \(4T_{2g}(P)^{+} \rightarrow 4T_{1g}(F)\) transitions, respectively, are suggestive of an octahedral geometry for Co(II) complex. Besides the charge transfer band at 34,430 cm\(^{-1}\) in Ni(II) complex, there are three more bands consistent with an octahedral geometry for the Ni(II) ion. The \(\mu_{\text{eff}}\) value (2.98 B.M.) of this complex also supports the above geometry.

The electronic spectrum of Cu(II) complex shows two main bands at 13,500 and 20,630 cm\(^{-1}\) assigned to \(2A_{1g} \rightarrow 2B_{1g}\) and \(2E_{g} \rightarrow 2B_{1g}\) transitions, respectively. The \(\mu_{\text{eff}}\) value of 1.82 B.M. for this complex also supports the proposed octahedral structure. The \(\mu_{\text{eff}}\) values of 2.12 B.M. and 0.53 B.M. for Ru(III) and Rh(III) complexes as well as their electronic spectra are consistent with an octahedral geometry about these metal ions. Ru(III) complex displays only one band at 19,330 cm\(^{-1}\) corresponding to the \(2A_{2g} \rightarrow 2T_{2g}\) transition having an octahedral geometry. The Rh(III) complex exhibits four absorption bands at 11,530, 15,630, 18,950 and 20,350 cm\(^{-1}\) assigned to \(3T_{1g} \rightarrow 1A_{1g}, 3T_{2g} \rightarrow 1A_{1g}, 1T_{2g} \rightarrow 1A_{1g}\) and \(1T_{1g} \rightarrow 1A_{1g}\) transitions respectively. The absorption
bands in the electronic spectrum of Pt(IV) complex is observed at 17,400, 21,230 and 26,500 cm\(^{-1}\) with an intense charge transfer band at 33,330 cm\(^{-1}\) characteristic of an octahedral geometry around the metal ion\(^{28,29}\).

The complexes of Zn(II) and Hg(II) are diamagnetic. Although the evidence is insufficient to allow any definite conclusion regarding the geometry of these complexes, the analytical and IR spectral data indicate that the Zn(II) and Hg(II) complexes are presumably octahedral while Au(III) complex is trigonal bipyramidal in structure.

References