Metal Complexes of Pyridine-2-carboxaldehyde Thiosemicarbazone

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Complexes of pyridine-2-carboxaldehyde thiosemicarbazone (HPAT) with Cu(II), Ni(II), Zn(II), Cd(II), Hg(II), Co(III), Fe(III), Ru(III), In(III) and Al(III) have been prepared and characterized through chemical analyses, electronic and infrared spectral studies and magnetic and conductance measurements. The ligand shows three types of coordination behaviour. In the complexes [Cu(HPAT)Br₂], [Ni(HPAT)₂(NO₃)₂C₂H₅OH], [Zn(HPAT)Cl₂]C₂H₅OH, [Cd(HPAT)Cl₂] and [Hg(HPAT)Cl₂]C₂H₅OH it acts as a neutral tridentate ligand coordinating through the ring nitrogen, azomethine nitrogen and the sulphur atom, while in [Co(HPAT)₂BF₄ and [Fe(HPAT)₂Cl₆ it behaves as a monobasic tridentate ligand coordinating through the same donor atoms. In the complexes [Ru(HPAT)Cl₃], [In(HPAT)₂Cl₃]Cl and [Al(HPAT)₂Cl₃] it acts as a bidentate ligand coordinating only through the ring nitrogen and azomethine nitrogen. Monomeric octahedral or dimeric chlorine-bridged, approximately octahedral structures are proposed for these complexes.

Thiosemicarbazones have versatile pharmacological activities1,2 and this activity increases manifold when the thiosemicarbazones are complexed with metals3. The present paper describes the synthesis and characterization of some new metal complexes of pyridine-2-carboxaldehyde thiosemicarbazone, herein after abbreviated as HPAT (I). The antifungal activity of HPAT and a few of its complexes has already been reported4.

HPAT, a spectrophotometric reagent for metal ions5,6, is reported to behave as a neutral unidentate ligand, coordinating through its sulphur atom in complexes such as [CoCl(DH₂)₃(HPAT)] (DH₂ = dimethylglyoxime)7 and as a monobasic tridentate ligand in cobalt(III) complexes of the type [Co(PAT)₂]X (X = Br⁻, I⁻, NO₃⁻ClO₄⁻) where it coordinates through the nitrogen of the pyridine ring, nitrogen of the hydrazine residue and the sulphur atom8,9. Preparation of the hydrated complex [Ni(HPAT)₂]Cl₂C₂H₅O in which HPAT acts as a neutral tridentate ligand has also been reported but no spectral characterization was attempted7. The results of present investigations, reveal, yet another mode of coordination for this ligand, i.e. it behaves as a bidentate ligand coordinating through the two nitrogen atoms only.

Materials and Methods
HPAT(I) was prepared by the method previously reported4. Its complexes with Cu(II), Ni(II), Zn(II), Cd(II), Hg(II), Co(III), Fe(III), Ru(III), In(III) and Al(III) were prepared by mixing a hot solution of the respective anhydrous metal salt (0.01 M) in absolute ethanol with a hot saturated solution of the ligand (0.01) in the same solvent. The complexes, which separated out immediately; were filtered, washed with ethanol and dried in vacuo.

Infrared spectra of the ligand and its complexes were recorded on a Perkin-Elmer 621 infrared spectrophotometer in the 4000-200 cm⁻¹ region as nujol and hexachlorobutadiene mulls or as KBr pellets. Electronic spectra of the ligand and the complexes were recorded in the 12.5-5.0 kK region on a SPECORD UV VIS. spectrophotometer. Diffuse reflectance spectra were recorded in 33.3 to 5 kK region on a UNICAM SP 700A UV and visible spectrophotometer. Magnetic susceptibilities of the complexes were determined by Gouy's method at room temperature using mercury tetrathiocyanatocobaltate(II) as a standard. The experimental magnetic susceptibility was corrected for diamagnetism. Conductivity measurements were carried out with Toshniwal Cl-01/-02A type conductivity bridge on freshly prepared 10⁻³ M solutions of the complexes at 25°C.

Results and Discussion
The analytical data together with the composition of the complexes are given in Table I. A detailed analysis of the infrared spectra of the complexes reveals that the ligand behaves differently depending on the metal ions. For instance, in the case of Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes it behaves as a neutral tridentate ligand coordinating through the ring nitrogen, azomethine nitrogen and the sulphur atom (type-I). In the complexes with Co(III) and Fe(III) HPAT behaves...
Table I—Analytical Data of the Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal</th>
<th>Halogen</th>
<th>Found (%)</th>
<th>(Calc.)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [Cu(HPAT)Br₂]</td>
<td>15.70</td>
<td>39.41</td>
<td>8.13</td>
<td>20.32</td>
</tr>
<tr>
<td>2. [Ni(HPAT)₂(NO₃)₂C₂H₄OH</td>
<td>9.73</td>
<td>—</td>
<td>10.81</td>
<td>32.50</td>
</tr>
<tr>
<td>3. [Zn(HPAT)Cl₂]C₂H₄OH</td>
<td>17.90</td>
<td>20.14</td>
<td>8.71</td>
<td>29.80</td>
</tr>
<tr>
<td>4. [Cd(HPAT)Cl₂]</td>
<td>29.90</td>
<td>18.65</td>
<td>8.48</td>
<td>22.80</td>
</tr>
<tr>
<td>5. [Hg(HPAT)Cl₂]C₂H₄OH</td>
<td>40.00</td>
<td>13.67</td>
<td>6.25</td>
<td>—</td>
</tr>
<tr>
<td>6. [Co(HPAT)₂]BF₄⁻</td>
<td>12.61</td>
<td>—</td>
<td>13.46</td>
<td>36.35</td>
</tr>
<tr>
<td>7. [Fe(HPAT)₂]Cl₂</td>
<td>12.51</td>
<td>7.64</td>
<td>13.64</td>
<td>37.30</td>
</tr>
<tr>
<td>9. [In(HPAT)Cl₃]Cl</td>
<td>20.08</td>
<td>18.21</td>
<td>10.92</td>
<td>29.14</td>
</tr>
<tr>
<td>10. [Al(HPAT)₃]Cl₃</td>
<td>3.03</td>
<td>15.50</td>
<td>14.30</td>
<td>38.64</td>
</tr>
</tbody>
</table>

as a tridentate monobasic acid (type-2) and in the complexes with Ru(III), In(III) and Al(III) it acts as a neutral bidentate ligand coordinating only through the nitrogen of the pyridine ring and the nitrogen of the azomethine group (type-3).

The infrared spectrum of HPAT exhibits three bands at 3450, 3425 and 3140 cm⁻¹ attributable to νNH. These bands occur in the same region or are shifted to higher frequencies in all the complexes showing that NH₂ is not participating in coordination. This is also supported by a shift to higher frequencies of the NH₂ band which appears at 1613 cm⁻¹ in the free ligand. The free ligand band of medium intensity at 1600 cm⁻¹, assignable to νC=N, is shifted to higher wavenumbers in the spectra of all the complexes and in certain cases merges with the pyridine ring vibration which appears at about 1600 cm⁻¹ in the complexes, indicating that the nitrogen of the azomethine group is coordinated to the metal ions.¹²

In the spectrum of HPAT, seven prominent bands due to pyridine ring vibrations are observed at 1586, 1559, 1465, 1432, 1000, 620 and 422 cm⁻¹. The first four are due to νC=C and νC=N modes, the 1000 cm⁻¹ band is due to ring breathing and the last two due to ring deformation. In the spectra of all the complexes the first four bands are either shifted to higher wavenumbers (Δν = 10-15 cm⁻¹) or remain unshifted. The ring breathing vibration is shifted to 1015-1025 cm⁻¹ and ring deformation modes to 630 and 430 cm⁻¹ regions, indicating participation of pyridine ring nitrogen in coordination to the metal atom in all the complexes.¹³

The strong band at 815 cm⁻¹ in HPAT due to νC=S is shifted to lower wavenumber region and appears at 800 cm⁻¹ with very low intensity in type-1 complexes but disappears completely in type-2 complexes. The two free ligand bands at 1105 and 1081 cm⁻¹ which have been assigned to a combination of νCS and νNCN, respectively, either appear with a very weak intensity or disappear altogether in the spectra of the complexes. In the type-3 (Ru(III), In(III) and Al(III)) complexes all the above three bands shift to higher frequencies and appear in the regions of 825-832, 1110-1120 and 1080-1090 cm⁻¹ respectively. The shift to higher frequencies of the three bands, in particular the 815 cm⁻¹ band without any change in intensity, testifies to the fact that sulphur atom is not coordinating to the metal in the type-3, Ru(III), In(III) and Al(III), complexes.

**Type-1: Complexes with HPAT as a neutral tridentate ligand**

Copper(II) complex, [Cu(HPAT)Br₂], behaves as a non-electrolyte in dimethylformamide with μₑₑₑ = 1.79 B.M. The diffused reflectance spectrum of the complex exhibits two bands at 22.73 and 15.73 kK; whereas the solution spectrum in DMF displays bands at 23.6 (ε = 1.0 × 10⁴) and 15.6 kK (ε = 1.7 × 10³). The intense absorption at 22.73 kK is assumed to be a charge transfer band. The broad band envelope centred at 15.73 kK may be identified with x²-y² ← x², x²-y² ← xy and x²-y² ← xz, yz transitions usually expected in six-coordinated tetragonal copper(II) complexes.¹⁵ Penta-coordination is ruled out due to the absence of a band in the 11.0 to 9.0 kK region.
dimeric halogen-bridged, six-coordinated structure is therefore suggested, to the copper(II) complex.

Nickel(II) complex, [Ni(HPAT)3] (NO3)2C2H3OH behaves as a 1:2 electrolyte in water and nitromethane with $\mu_{eff} = 2.86$ B.M.. The very strong ligand band at 1360 cm$^{-1}$ appears as a strong and broad band in the region 1390-1300 cm$^{-1}$ in the Ni(II) complex probably due to the overlap of the ligand bands and the band due to the nitrate$^{-}$ ion$^{17}$. The presence of a medium intensity band at 822 cm$^{-1}$ also supports the ionic nature of the nitrate$^{-}$. The electronic spectrum of this complex displays three spin allowed transitions at 11.91 $^{3}T_{2g} \rightarrow ^{3}A_{2g}$ 18.18 ($^{2}T_{1g}(F) \rightarrow ^{3}A_{2g}$) and 25.0 kK ($^{3}T_{1g}(P) \rightarrow ^{3}A_{2g}$)$^{18}$. The spectral, magnetic and conductance measurements thus support six-coordination for Ni$^{2+}$. Since the ligand is tridentate in these complexes, they would involve non-planar ligands.

Zinc(II) and Cd(II) complexes, viz [Zn(HPAT)Cl2] C2H3OH and [Cd(HPAT)Cl2] are non-electrolytes (molar conductance, $\Lambda_M = 7.11$ and 6.20 ohm$^{-1}$cm$^2$mol$^{-1}$ respectively in DMSO). Mercury(II) complex, [Hg(HPAT)Cl2] C2H3OH, is a non-electrolyte in DMF ($\Lambda_M = 3.2$ ohm$^{-1}$cm$^2$mol$^{-1}$). Since the ligand is tridentate in these complexes, they could be either five-coordinate monomers or six-coordinate dimers with a structure similar to that of the Cu(II) complex. Lack of additional evidence precludes a distinction between these possibilities.

Type-2: Complexes with HPAT as a monobasic tridentate ligand

Cobalt(III) and Fe(III) complexes, [Co(HPAT)2]BF4 and [Fe(HPAT)2]Cl, respectively belong to this category. The infrared spectrum of the Co(III) complex displays a strong, broad band in 1130-920 cm$^{-1}$ region due to the ferric nitrate$^{-}$ ion$^{19}$. This is in accordance with the molar conductance data in acetonitrile ($\Lambda_M = 131.0$ ohm$^{-1}$ cm$^2$mol$^{-1}$). The complex is diamagnetic indicating that cobalt is present in +3 oxidation state. The electronic spectrum of the complex exhibits two absorption bands at 21.0 and 26.10 kK due to the transitions $^{1}T_{1g} \rightarrow ^{1}A_{1g}$ and $^{1}T_{2g} \rightarrow ^{1}A_{1g}$, respectively$^{20}$. These data are very much like those reported for other Co(III) complexes and are consistent with the assignment of an octahedral geometry to the Co(III) complex.

The measured $\mu_{eff}$ of 2.2 B.M. for the complex [Fe(HPAT)2]Cl, suggests that it might be octahedral$^{21}$. The electronic spectrum exhibits three bands at 22.0, 17.2 and 11.1 kK. The molar conductance of the complex in water indicates it to be a 1:1 electrolyte. In view of the above observations, both the Co(III) and Fe(III) complexes can be assigned a cis-octahedral structure in which two tridentate ligand molecules coordinate to the metal ion in two equatorial planes at right angles to one another.

Type 3: Complexes with HPAT as a neutral bidentate ligand

Ruthenium(III) complex, [Ru(HPAT)Cl3], is insoluble in almost all the common organic solvents and has $\mu_{eff} = 1.3$ B.M., which is considerably lower than the value expected for one unpaired electron. This might be due to the high values of spin-orbit coupling constants in the heavier transition elements which often lead to very low magnetic moments or due to metal-metal interaction. The electronic spectrum of the complex displays three bands at 17.5, 20.0 and 25.6 kK. The 17.5 kK band may be attributed to the lowest spin allowed $d$-$d$ transition $^{2}T_{1g} \rightarrow ^{2}A_{2g}$. Since the ligand is bidentate in this complex, coordinating through N(pyridine) and N(hydrazine), a chlorine-bridged structure is suggested.

The bright yellow In(III) complex, [In(HPAT)Cl2]Cl, behaves as a 1:1 electrolyte in methanol ($\Lambda_M = 104$ ohm$^{-1}$cm$^2$mol$^{-1}$). The pale yellow Al(III) complex, [Al(HPAT)Cl3] behaves as a 1:3 electrolyte in methanol ($\Lambda_M = 302.5$ ohm$^{-1}$cm$^2$mol$^{-1}$). Since the ligand is bidentate the metal in both these complexes should be six-coordinated.

References