Manganese(II) Chloride & Thiocyanate Complexes with Some Potentially Bidentate Ligands

I S AHUJA
Chemistry Department, Banaras Hindu University, Varanasi 221 005

Received 11 June 1982; revised and accepted 14 October 1982

Coordination compounds formed by the interaction of manganese(II) chloride and thiocyanate with some potentially bidentate N, O donors—nicotinic acid, nicotinamide, N-methylnicotinamide, isonicotinamide, nicotinic acid N-oxide and 2-, 3- and 4-benzoylpyridines—have been isolated in the solid state. These have been characterized on the basis of their chemical analyses, room temperature magnetic moments, electronic and IR spectral measurements down to 200 cm⁻¹ in the solid state. Tentative stereochemistries have been assigned to the complexes.

The complexes prepared, their analytical data, room temperature magnetic moments, electronic spectral and ligand field parameters are listed in Table 1. All the ligands used in the present study—NA, NICA, NMeNICA, NAO, 2-BOP, 3-BOP and 4-BOP—possess two potential donor sites, (i) pyridine ring nitrogen, and (ii) amide oxygen in the case of NICA, NMeNICA, INCA; carbonyl oxygen in benzoylpyridines; or carboxyl oxygen in NA. NAO also possesses two donor sites (i) O-oxide oxygen, and (ii) carboxyl oxygen. Significant IR absorption bands due to the amide group are νNH, νCO and νCN. In amides¹ᵃ and other carboxyl¹ᵇ donors a significant negative shift of the carbonyl frequency takes place because of coordination through the carbonyl oxygen. The νNH, νCO and νCN of the uncoordinated NICA, NMeNICA and INCA remain either unperturbed or undergo slight positive shifts in the manganese(II) complexes studied here. These features clearly indicate that the amido group is inert towards coordination in these ligands. The carbonyl group vibrations of NA and NAO remain unperturbed in the IR spectra of the manganese(II) complexes thus excluding the possibility of (carboxyl) oxygen-to-metal coordination. The νCO in uncoordinated 3- and 4-benzoylpyridines remains either unperturbed or undergoes slight positive shift in the complexes thus suggesting that the carbonyl group is inert towards coordination. However, the pyridine ring vibrations occurring at ~990, 600 and 400 cm⁻¹ in the ligands undergo significant positive shifts in the complexes (except NAO). These features indicate conclusively that coordination of these ligands takes place via their pyridine ring nitrogen atoms only.¹ᶜ 2-Benzoylpyridine acts as a monodentate ligand (bonding via pyridine ring nitrogen) in the manganese(II) chloride complex. However, in the case of thiocyanate complex, it acts as a bidentate chelating ligand as is
by the fact that vNO in uncoordinated N-oxide spectrum of this complex. In uncoordinated evidence from the fact that vCO occurring at 1654 cm⁻¹ through the N-oxide oxygen only. This is indicated of the manganese(II) complex shows clearly that this complex suffers a marked negative shift in the manganese(II) attributed to a decrease in the ρ-bond character of the NO bond as a result of oxygen-to-metal coordination and is of the magnitude expected for complexes in which the N-oxide and negatively charged ligands (halides, NO₂⁻, etc.) constitute the first coordination sphere around the metal(II) ion.¹⁴ The 8 NO appearing at 845 cm⁻¹ in the IR spectrum of uncoordinated NAO is observed with similar intensity but it shifts slightly to lower energy side in the IR spectrum of the complex.¹⁴

**Stereochemistry of chloride complexes**—All the 1:2 manganese(II) chloride complexes with NA, NICA, N-MeNICA, NAO, INCA, 3-BOP and 4-BOP have room temperature magnetic moments in the range 5.90—6.15 B.M. (Table 1) and show a band at 220 cm⁻¹ in the far IR region which is assigned to vMn-Cl mode involving bridging chlorines in the chlorine-bridged polymeric octahedral structures for the complexes. The band at 240 cm⁻¹ in the Mn(2-BOP)₂Cl₂(EtOH)₂ complex is assigned to vMn-Cl mode which is consistent with terminal Mn-Cl bonds and a monomeric, six-coordinate structure with an octahedral environment around Mn(II) of two nitrogen atoms from pyridine ring nitrogen bonded 2-BOP molecules, two terminal chlorines and two oxygen atoms from ethanol molecules. In the case of nicotinic acid N-oxide, IR spectrum of the manganese(II) complex shows clearly that this ligand acts as a monodentate ligand and is bonded through its N-oxide oxygen only. This is indicated by the fact that vNO in uncoordinated N-oxide suffers a marked negative shift in the manganese(II) chloride-NAO complex. This lowering of vNO is attributed to a decrease in the ρ-bond character of the NO bond as a result of oxygen-to-metal coordination and is of the magnitude expected for complexes in which the N-oxide and negatively charged ligands (halides, NO₂⁻, etc.) constitute the first coordination sphere around the metal(II) ion. The 8 NO appearing at 845 cm⁻¹ in the IR spectrum of uncoordinated NAO is observed with similar intensity but it shifts slightly to lower energy side in the IR spectrum of the complex.

**Stereochemistry of thiocyanate complexes**—Manganese(II) thiocyanate gave a 1:2 complex with 2-BOP, 1:4 complexes with 3-and 4-BOP, but it did not react with NA, NICA, INCA, N-MeNICA and NAO under similar conditions. Magnetic moment values and the electronic spectral measurements indicate (Table 1) that all these complexes have high-spin octahedral structures. IR spectra indicate a significant positive shift of the pyridine ring vibrations which is consistent with coordination through the pyridine ring nitrogen by all the benzoylpyridines. In addition to coordination through the pyridine ring nitrogen atom, the 2-BOP is coordinated through its carbonyl oxygen also as is evident from the negative shift of the vCO in the 2-BOP complex. IR bands due to thiocyanato groups suggest the exclusive presence of terminally N-bonded NCS groups in all these complexes. Based on the magnetic moment, electronic and IR spectral evidences, the following tentative stereochemistries are suggested for the complexes: (i) six-coordinate monomeric structure with an octahedral environment of two oxygen atoms (from two benzoylpyridine molecules) and four nitrogen atoms (two from 2-BOP molecules and two from terminally N-bonded NCS groups) around the metal(II) ions. The 8 NO appearing at 845 cm⁻¹ in the IR spectrum of uncoordinated NAO is observed with similar intensity but it shifts slightly to lower energy side in the IR spectrum of the complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calc), %</th>
<th>Mn</th>
<th>Anion</th>
<th>N</th>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
<th>v₄</th>
<th>D₀</th>
<th>β</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(NA)₂Cl₂</td>
<td>(14.88) (19.00)</td>
<td>7.60</td>
<td>6.00</td>
<td>18180</td>
<td>22990</td>
<td>849</td>
<td>0.79</td>
<td>758</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(NICA)₂Cl₂</td>
<td>(14.85) (19.00)</td>
<td>3.14</td>
<td>6.10</td>
<td>18690</td>
<td>23530</td>
<td>26310</td>
<td>974</td>
<td>0.81</td>
<td>779</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(N-MeNICA)₂Cl₂</td>
<td>(13.90) (17.90)</td>
<td>8.12</td>
<td>6.12</td>
<td>18690</td>
<td>23800</td>
<td>957</td>
<td>0.81</td>
<td>779</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(INCA)₂Cl₂</td>
<td>(14.83) (19.01)</td>
<td>5.20</td>
<td>6.10</td>
<td>18870</td>
<td>23530</td>
<td>927</td>
<td>0.82</td>
<td>786</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(NAO)₂Cl₂</td>
<td>(13.72) (17.67)</td>
<td>6.93</td>
<td>5.90</td>
<td>19040</td>
<td>20000</td>
<td>25000</td>
<td>982</td>
<td>0.93</td>
<td>893</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(2-BOP)₂Cl₂(EtOH)₂</td>
<td>(9.48) (12.10)</td>
<td>4.72</td>
<td>6.12</td>
<td>18480</td>
<td>20105</td>
<td>25000</td>
<td>1017</td>
<td>0.93</td>
<td>892</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(3-BOP)₂Cl₂</td>
<td>(11.20) (14.53)</td>
<td>5.71</td>
<td>5.95</td>
<td>18690</td>
<td>23530</td>
<td>26300</td>
<td>934</td>
<td>0.87</td>
<td>835</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(4-BOP)₂Cl₂</td>
<td>(11.10) (14.50)</td>
<td>5.72</td>
<td>6.00</td>
<td>18690</td>
<td>21500</td>
<td>25640</td>
<td>1050</td>
<td>0.95</td>
<td>912</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(2-BOP)₂(NCS)₂</td>
<td>(10.31) (21.80)</td>
<td>10.54</td>
<td>6.11</td>
<td>21770</td>
<td>22600</td>
<td>26300</td>
<td>923</td>
<td>0.96</td>
<td>921</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(3-BOP)₂(NCS)₂</td>
<td>(6.12) (12.90)</td>
<td>9.30</td>
<td>6.00</td>
<td>25640</td>
<td>26630</td>
<td>984</td>
<td>0.93</td>
<td>911</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(4-BOP)₂(NCS)₂</td>
<td>(6.13) (13.10)</td>
<td>9.35</td>
<td>5.98</td>
<td>19230</td>
<td>21740</td>
<td>26310</td>
<td>886</td>
<td>0.81</td>
<td>777</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1—Analytical Data, Magnetic Moments and Electronic Spectral Data (cm⁻¹)

Evident from the far IR region which is assigned to vNO occurring at 1654 cm⁻¹ in uncoordinated 2-BOP shifts to 1615 cm⁻¹ in the spectrum of this complex.

Because of the additional stability of the half-filled d-shell, Mn(II) generally forms high-spin complexes which have an orbitally degenerate (6S) ground state. A spin-only magnetic moment of 5.92 B.M. is expected for Mn(II) ion which will be independent of the temperature and of the stereochemistry.¹⁷ The observed room temperature magnetic moment values (5.90—6.15 B.M.) in the Mn(II) complexes studied
here are consistent with the presence of five unpaired spins and hence these are all high-spin complexes.

In the case of Mn(II) complexes the intensities of the electronic transitions from the ground state \( ^6S \) to the states of four-fold multiplicity are rather weak, and since Mn(II) has a \( d^5 \) configuration the same type of energy level diagram applies whether the metal ion is in a tetrahedral or an octahedral environment. Out of the six electronic spectral bands of Mn(H\(_2\)O)\(_6\)\(^{2+}\) ion, only four (Table 1) could be observed in the electronic spectra of the manganese(II) complexes studied here. The observed bands representing the corresponding transitions and energies in terms of Racah parameters are:\(^{18}\)

\[
\begin{align*}
^6A_{1g} &\rightarrow ^4T_{1g}(4G), (10B + 5C) \sim 20000 \text{ cm}^{-1}, \\
&\rightarrow ^4E_g, ^4A_{1g}(4G), (10B + 5C) \sim 24000 \text{ cm}^{-1}, \\
&\rightarrow ^4E_g(4D), (17B + 5C) \sim 27500 \text{ cm}^{-1}, \\
&\rightarrow ^4T_{1g}(4P) (7B + 7C) \sim 33000 \text{ cm}^{-1}.
\end{align*}
\]

The observed electronic spectra of practically all the manganese(II) complexes studied are almost identical. The energies of \(^6A_{1g} \rightarrow ^4E_g(4D)\) and \(^6A_{1g} \rightarrow ^4E_g, ^4A_{1g}(4G)\) transitions are independent of \( D_0 \) and depend\(^{19}\) only on \( B \) and \( C \), and hence these have been used to calculate the values for the parameters \( B \) and \( C \). The \( D_0 \) values could be evaluated using the transition \(^6A_{1g} \rightarrow ^4E_g(4G)\) with the help of the plot of transition energies versus \( D_0 \) as given by Orgel\(^{20}\). The electronic spectra and ligand field parameters of all the manganese(II) complexes reported herein are consistent with octahedral environments around the manganese(II) ions.

The tentative stereochemistries and the isomorphous nature of the present manganese(II) complexes have been derived from a comparison of their magnetic moment values, electronic spectral data, ligand field parameters and coordinated metal-anion IR modes with those of compounds of established structures. However, unambiguous characterization of these compounds should be based on complete crystal structure determinations.

The author expresses his sincere thanks to Prof. B. M. Shukla, Head of the Chemistry Department, B. H. U., Varanasi for providing facilities and to Shri C. L. Yadava for helpful discussions.

References