CHAPTER 6


This chapter presents a comparison of the structures of all the polyiodides and tris-chelates reported in this thesis. A brief description of the different types of polyiodide anions formed, based on bond distances, angles and I...I contacts is given. Finally, the cation-anion packing in these complexes is discussed and comparisons are drawn.

6.1 Comparison of the Tris-Chelate Cations

A plot of metal-nitrogen (M-N) distances vs. N-M-N chelate angles for a series of such complexes is shown in Figure 6.1. The structural data are tabulated in Table 6.1. A correlation between increasing M-N distances and decreasing N-M-N angles is observed considering the average values. A large variation in M-N distances and N-M-N angles is observed in Cu$^{2+}$ complexes due to the statically Jahn-Teller distorted d$^9$ cation. The non-bonded N..N bite in these complexes is found to be nearly constant in the range of 2.6-2.7 A. The M-N distance varies because of the changing covalent radius of the metal ion forcing the N-M-N angle to alter in order to compensate for the inflexibility of the ligand bite (phen/bpy). Similar results were obtained for a series of phen complexes of transition metal ions studied earlier.$^1$
Figure 6.1  Plot of the metal - N (ligand) bond distances and bite angles (N-M-N) for the tris-chelates formed by bpy and phen. The symbols ++ and ± denote the observed ranges of bond distances and angles for a given ion, with the intersection corresponding to the average values. Numbers refer to serial numbers in Table 6.1.
Table 6.1 Structural data of the transition metal tris-chelate cations studied (* this work).

<table>
<thead>
<tr>
<th>SNo</th>
<th>Complex</th>
<th>M-N distances (Å), α‡</th>
<th>N-M-N angles (°)</th>
<th>Average valuest</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><a href="I%E2%82%83">Mn(phen)₃</a>₂ (1)</td>
<td>2.254, 2.263; 2.253, 2.245; (4°) 2.266, 2.223; (4°) 2.255, 2.245; (4°)</td>
<td>73.7, 73.0</td>
<td>2.259(3.6) Å, 73.7° (2.2)</td>
<td>*</td>
</tr>
<tr>
<td>2.</td>
<td><a href="I%E2%82%83">Mn(bpy)₃</a>₁.₅(I₈)₀.₂₅ (2)</td>
<td>2.294, 2.219; 2.230, 2.280; 2.233, 2.214; (13-25°)</td>
<td>73.4, 73.2, 73.6</td>
<td>2.245 Å, 73.4°</td>
<td>*</td>
</tr>
<tr>
<td>3.</td>
<td><a href="ClO%E2%82%84">Mn(bpy)₃</a>₂·0.5H₂O</td>
<td>2.098, 2.096; 2.094, 2.089; 2.084, 2.086; 2.091(3.6) Å, 79.5° (2.3)</td>
<td>79.2, 79.5, 79.8</td>
<td>2.090 Å, 79.4°</td>
<td>1</td>
</tr>
<tr>
<td>4.</td>
<td><a href="I%E2%82%83">Ni(phen)₃</a>₂·CH₃CN (3)</td>
<td>2.078, 2.090; 2.093, 2.078; 2.095, 2.106;</td>
<td>80.0, 79.4, 78.7</td>
<td>2.133(4.168) Å, 78.3° (1.25)</td>
<td>*</td>
</tr>
<tr>
<td>5.</td>
<td>[Ni(phen)₃][Mn(CO)]</td>
<td>2.327, 2.041; (22°) 2.031 x 2; (15°)</td>
<td>76.2, 80.3</td>
<td>2.134 Å, 77.5°</td>
<td>3</td>
</tr>
<tr>
<td>6.</td>
<td>[Cu(bpy)₃]I₈·CH₂Cl₂ (6)</td>
<td>2.450, 2.026; (31°) 2.034, 2.035; (11°) 2.030, 2.226; (14°)</td>
<td>73.9, 80.4, 78.2</td>
<td>2.134 Å, 77.5°</td>
<td>*</td>
</tr>
<tr>
<td>7.</td>
<td><a href="ClO%E2%82%84">Cu(bpy)₃</a>₂</td>
<td>2.34, 2.02; 2.06, 2.06; 2.32, 2.00;</td>
<td>76.6, 81.6, 77.2</td>
<td>2.13 Å, 78.5°</td>
<td>4</td>
</tr>
<tr>
<td>8.</td>
<td><a href="ClO%E2%82%84">Cu(phen)₃</a>₂</td>
<td>1.960, 1.956; (7°) 1.966, 1.974; (2°) 1.961, 1.950; (5°) 1.961(4.10) Å, 81.7° (2.2)</td>
<td>81.5, 81.9, 81.4</td>
<td>81.7° (2.2)</td>
<td>*</td>
</tr>
<tr>
<td>9.</td>
<td>[Fe(bpy)₃]I₉ (8)</td>
<td>1.977, 1.977; (9°) 1.977, 1.977; (9°) 1.977, 1.977; (9°)</td>
<td>81.8</td>
<td>81.8°</td>
<td>5</td>
</tr>
<tr>
<td>10.</td>
<td>[Fe(bpy)₃][NaFe(ox)₃]</td>
<td>1.971, 1.972; (9°)</td>
<td>81.9</td>
<td>81.9°</td>
<td>5</td>
</tr>
<tr>
<td>11.</td>
<td>[Fe(bpy)₃][LiCr(ox)₃]</td>
<td>2.254, 2.263; 2.253, 2.245; (4°) 2.266, 2.223; (4°) 2.255, 2.245; (4°)</td>
<td>73.7, 73.0</td>
<td>2.259(3.6) Å, 73.7° (2.2)</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Formula</td>
<td>M-N distances (Å)</td>
<td>Twists (°)</td>
<td>Complexes</td>
<td></td>
</tr>
<tr>
<td>---</td>
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<tr>
<td>12.</td>
<td>[bpyH]<a href="ClO%E2%82%84">Fe(III)(bpy)₃</a>₄</td>
<td>1.958, 1.959; 1.960, 1.960; 1.964, 1.967; (&lt;6°)</td>
<td>82.2, 82.3, 82.4; 1.961 Å, 82.3°</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td><a href="ClO%E2%82%84">Fe(phen)₃</a>₂·0.5H₂O</td>
<td>1.973, 1.982; 1.980, 1.981; 1.984, 1.965;</td>
<td>82.8, 83.0, 82.0; 1.978 Å, 82.6°</td>
<td>7</td>
<td></td>
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<tr>
<td>14.</td>
<td><a href="ClO%E2%82%84">Co(phen)₃</a>₂·H₂O</td>
<td>2.124, 2.138; 2.109, 2.138; 2.111, 2.142;</td>
<td>78.1, 78.5, 77.8; 2.127 Å, 78.1°</td>
<td>8</td>
<td></td>
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<tr>
<td>15.</td>
<td>[Zn(bpy)₃]I₁₂ (9)</td>
<td>2.136, 2.164; (8°) 2.162, 2.140; (13°) 2.188, 2.137; (15°)</td>
<td>76.3, 75.8, 76.5; 2.155(4.21) Å, 76.2° (3.4)</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td><a href="ClO%E2%82%84">Zn(bpy)₃</a>₂</td>
<td>2.172, 2.166; 2.135 × 2; (17°)</td>
<td>75.8, 77.2; 2.159 Å, 76.5°</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>[Zn(phen)₃]I₁₂ (10)</td>
<td>2.147, 2.188; 2.181, 2.187; 2.174, 2.144;</td>
<td>76.8, 76.8, 77.2; 2.170(4.20) Å, 76.9° (2.2)</td>
<td>*</td>
<td></td>
</tr>
</tbody>
</table>

†: The two M-N distances formed with each ligand (bpy/phen) are grouped. The twist angle a, observed for bpy ligand is given in paranthesis. †: The two standard deviations in paranthesis are calculated as: σ²[(Å)] = Σ(δイ/δΠ)²si² and σ²mean = Σ(xi-Jt)²/(n-1), respectively.

While phen is a rigid planar ligand, coordinated bpy shows considerable deviation from planarity, with interplanar angle between the two pyridine rings (a) ranging from 0 to 22°. Both the ligands coordinate in a symmetrical fashion with the two Mα-N bond distances equal within about 0.02 Å. However, Cu(II) complexes are exceptional in this regard. Due to Jahn-Teller distortion, two of the three ligand molecules in a tris-chelate adopt highly unsymmetrical coordination mode with Cu-N bond distances differing by as much as 0.4 Å. The Cu(II) complex ion in 6 has a C₂ symmetry while the Mn(II), Ni(II) and Fe(II) complex ions (in 1, 2, 3 and 8) closely approach D₃ symmetry. The Zn(II) complexes in 9 and 10 deviate more strongly from trigonal symmetry (the Zn-N bond length differences = 0.02 - 0.05 Å for 9, 0.01 - 0.04 Å, for 10, a = 8 - 15° for 9.).
6.2 Structure and Bonding in the Polyiodide Anions

The structures of polyiodide anions formed with tris-chelate cations are collected in Figure 6.2. The cations \([\text{Mn(phen)}_3]^2^+, [\text{Ni(phen)}_3]^2^+\) and \([\text{Mn(bpy)}_3]^2^+\) prefer \(I_3^-\) as the counter-anion (Figure 6.2a,b,c). In the highly symmetrical complex, \([\text{Mn(phen)}_3](I_3)_2\) (1), the two triiodide anions occur in linear and symmetric form, having two different I-I distances and no I..I contacts between them. But in \([\text{Ni(phen)}_3](I_3)_2\cdot\text{CH}_3\text{CN}\) (3), the change of metal atom and the slight decrease in the metallic radius results in the change of anion shapes to slightly bent and unsymmetrical triiodides and also having end-to-end van der Waals contacts between four anions. Similarly, the change of ligand from phen to less rigid bpy in 1, resulted in complex 2, \([\text{Mn(bpy)}_3](I_3)_{15}(I_8)_{0.25}\), which also has two types of triiodides. One of them is linear asymmetrical, while the other is disordered about the inversion centre. The rest of the charge is balanced by linear infinite polyiodide chains of the type \((I_8)^{2^-}\). The chain is disordered and is difficult to divide into smaller fragments of \(I_3^-\) and \(I_2\) based on bond distances, as can be done in other cases. Although infinite chains of \(I_8^{2^-}\) are not known yet, the occurrence of a nearly linear dimer of \(I_8^{2^-}\) \((I_{16}^{4^-})\) has been reported once.\(^\text{10}\)

In \([\text{Cu(bpy)}_3](I_8)\cdot\text{CH}_2\text{Cl}_2\) (6), the anion \(I_8^{2^-}\) has a commonly occurring centrosymmetric Z-shape of the type \(I_3^-\cdotI_2\cdotI_3^-\). But the difference here is that the unit is non-planar (Figure 6.2d). Non-planar \(I_8^{2^-}\) have been reported in a few examples wherein, the anion is forced to become non-planar by the cationic environment, resulting in the elongation and distortion of one of the \(I_3^-\cdotI_2\) bonds. In 6, there is no elongation of the bond and there is a uniform distortion making the two \(I_3^-\) arms nearly orthogonal. The anions have weak van der Waals contacts between \(I_8^{2^-}\) units at the \(I_3^-\cdotI_2\) junction, leading to formation of a loose network of the anions.
Figure 6.2 Polyiodide anions formed with transition metal tris-chelate cations:

(a) $I_3^-$ in 1; (b) $I_3^-$, $(I_8^{2-})_n$ in 2; (c) $I_3^-$ in 3; (d) $I_8^{2-}$ in 6; (e) $(I_{18}^{4-})_n$ in 8(f);
$I_{12}^{2-}$ in 9 and (g) $I_{24}^{4-}$ in 10.
The network forming centrosymmetric $\text{I}_{18}^{4-}$ (Figure 6.2e) made up of $\text{I}_3^-$ and $\text{I}_2$ molecules, is a new anion occurring in $[\text{Fe(bpy)}_3]\text{I}_9$ (8). The $\text{I}_{12}^{2-}$ anion in 9 is formed by an $\text{I}_2$ unit bridged between two bent $\text{I}_5^-$ units. One of the $\text{I}_5^-$ here is symmetrical ($\text{I}_2\text{I}^-$), while the other is asymmetrical ($\text{I}_3^-$). The $\text{I}..\text{I}$ contacts lead to the formation of a close network.

The $\text{I}_{12}^{2-}$ anion in $[\text{Zn(phen)}_3]\text{I}_{12}$ (10), has a new shape, that of a dimeric 24-membered ring formed by end-to-end connection of two $\text{I}_{12}^{2-}$ units (Figure 6.2g). The shape of the ring is like the number '8', so as to fit two $[\text{Zn(phen)}_3]^{2+}$ cations inside the ring. These rings are connected to each other by $\text{I}..\text{I}$ contacts at three adjacent iodines on the ring.

6.3 Cation - Anion Packing

6.3 (a) Cationic arrangement. An interesting study of these polyiodide salts of metal complex cations, is the arrangement of the divalent cations in the crystal lattice. A careful look at the packing in all the complexes, revealed similarities in the packing of some of the cations.

The $[\text{Mn(bpy)}_3]^{2+}$ cations in 2, are arranged in a nearly-planar hexagonal-like layers stacked parallel to form hexagonal-like (honey-comb) channels along the c-axis. These channels are filled with infinite chains of $\text{I}^2^-$. Just as hexagonal layers of carbon stack as layers of $\text{abab}$. type in graphite, the planar hexagonal layers of cations of 1, form $\text{abcabc}$... stacking layers along c-axis direction (Figure 6.3).

The cations of $[\text{Ni(phen)}_3]([\text{I}_3^-]_2\cdot\text{CH}_3\text{CN}$ (3) and $[\text{Zn(phen)}_3]\text{I}_{12}$ (10) also adopt a packing similar to 2, forming parallel stacked roughly planar hexagonal-like layers (Figure 6.4).
Figure 6.3  Two views of the packing of metal ions: (a), (b) in 2; (c), (d) in graphite (coordinates taken from ORTEX program examples); (e), (f) in 1. (distances between atoms are given in A.)
Figure 6.4  Two views of the packing of metal ions: (a), (b) in 3; (c), (d) in 10.
(distances between atoms are given inÅ.)
Figure 6.5  Two views of the packing of metal ions: (a), (b) in 6; (c), (d) in 9.
(distances between atoms are given in Å.)
The $[\text{Cu(bpy)}_3]I_8$ (6) and $[\text{Zn(bpy)}_3]I_{12}$ (9) however, form 6-membered non-planar rings packed in layers (Figure 6.5).

The cations in $[\text{Fe(bpy)}_3]I_9$ (8) are aligned linear along c-axis direction. These aligned cations are parallel to the adjacent chains of cations forming a rhombic pattern when viewed normal to the ab-plane (Figure 6.6). Such aligned cations were also observed in $[\text{Cu(dafone)}_3]I_{12}$.11

![Figure 6.6](image_url)  
(a) Two views of the packing of metal ions in 8. (distances between atoms are given in Å.)
6.3 (b) Crystal packing. After a study of the cationic arrangement it is easier to understand the cation-anion packing in the polyiodide.

In \([\text{Mn(phen)}_3](\text{I}_3)_2(1), [\text{Mn(bpy)}_3](\text{I}_3)_{1.5}(\text{I}_8)^{0.25}\) (2), \([\text{Ni(phen)}_3](\text{I}_3)_2\cdot\text{CH}_3\text{CN} \) (3) and \([\text{Cu(bpy)}_3](\text{I}_8)\cdot\text{CH}_2\text{Cl}_2\) (6), a layered packing of cations and anions are observed (Figure 6.7, 6.8).

In the \(\text{Mn}^{2+}\) complexes 1 and 2, the cations pack in a more symmetric way, forcing the \(\text{I}_3^-\) to become linear and symmetric in 1, and forming hexagonal-like channels filled with polyiodide chains in 2 (Figure 6.7). The packing is less rigid in 3, leading to \(\text{I}_3^-\cdot\text{I}_3^-\) contacts and also formation of empty cavities. These cavities are occupied by disordered molecules of the solvent, \(\text{CH}_3\text{CN}\), used for recrystallisation of complex. In 6, layered packing of cation and anion along with loose network of centrosymmetric \(\text{I}_8^{2-}\) anions, leads to formation of large channels along c-axis direction. These channels are filled with disordered solvent molecules of \(\text{CH}_2\text{Cl}_2\). Thus, in complexes 3 and 6, there is an 'equal influence' of cation and anion on the crystal lattice formation.

![Figure 6.7](image)

**Figure 6.7** Cation-anion packing in polyiodides salts of metal complex cations: layered packing in (a) 1; (b) 2.
Figure 6.8  Cation-anion packing in polyiodides salts of metal complex cations: (a), (b) in 3; (c), (d) in 6.
The anionic networks are more dominating in the higher iodine content complexes of $[\text{Fe(bpy)}_3]\text{I}_9$ (8), $[\text{Zn(bpy)}_3]\text{I}_{12}$ (9) and $[\text{Zn(phen)}_3]\text{I}_{12}$ (10). In these, the cations are either sitting inside the compact anionic channels (8), or trapped inside thick anionic cages (9), or anionic rings (10) (Figure 6.9). Thus, the anionic network dominates over the cation packing arrangement in these complexes.

Figure 6.9  Cation-anion packing in polyiodides salts of metal complex cations: (a) in 8; (b) in 9; (c) in 10.
This is also reflected in their high crystal densities which range from 2.71 to 2.79 g ml$^{-1}$, while the other polyiodides have (1, 2, 3, 6) have densities ranging from 2.23 to 2.43 g ml$^{-1}$.

6.4 Conclusions

The polyiodide salts of Mn$^{2+}$ complex cations can be considered as symmetrical arrangement of cations accommodating counter-anions like I$_3^-$ in between the layers (See back cover).

The polyiodide salts of Fe$^{2+}$ and Zn$^{2+}$, on the other hand, are tris-chelate cations trapped inside the anionic polyiodide networks (See back cover).

The complexes [Ni(phen)$_3$](I$_3$)$_2$·CH$_3$CN and [Cu(bpy)$_3$I$_8$·CH$_2$Cl$_2$ lie in between the above two categories. The uniform cation-anion interactions leads to a nullification of lattice dominance and neutral solvent molecules fill the empty interstices.
References


