Simple binary salts

When considering the structures of simple binary salts only a small number of types are important. The simplest are for crystals with formula MX and include NaCl, CsCl and ZnS where the CN of the anion and cation are the same and may be 6, 8 or 4.

Compounds with formulae of MX_2 or M_2X will have different CN's for the cation and anion. The most important of these are the fluorite and rutile structures.

For the MX case, one reason why a substance might favour one form over another is due to the geometry of the packing of the spheres. What is needed is to be able to maximise the interactions of oppositely-charged ions while at the same time minimise the interactions of similarly-charged ions. The larger the difference in the sizes of the ions affects the packing of the larger ions around the smaller ions. It is relatively easy to calculate the radius ratio (r+/r-) and from this determine the limits for the various CN's. For the ZnS type structure with CN 4:4 the radius ratio is predicted to be in the range 0.22 - 0.41 while for the NaCl type structure with CN 6:6 it is predicted that the radius ratio will be within the range of 0.41 - 0.73. For CsCl structures with CN 8:8, the radius ratio is expected to be greater than 0.73. The Table below shows the values for a number of alkali halides. Experimentally it is found that the only examples under normal conditions of temperature and pressure to adopt the CsCl structure are CsCl, CsBr and CsI whereas several other salts were predicted to have this structure based on their radius ratios.

Among the other factors that might influence the final structure is the interaction between ions in addition to the nearest neighbours. However the energies involved would not seem to be sufficient to alter the results as shown by the Madelung constants for NaCl and CsCl which are 1.74756 and 1.76267 respectively.

Radius ratio values for alkali halides

<table>
<thead>
<tr>
<th>X^- / M^+</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.44</td>
<td>0.70</td>
<td>0.98</td>
<td>0.92</td>
<td>0.81</td>
</tr>
<tr>
<td>Cl</td>
<td>0.33</td>
<td>0.52</td>
<td>0.73</td>
<td>0.82</td>
<td>0.93</td>
</tr>
<tr>
<td>Br</td>
<td>0.31</td>
<td>0.49</td>
<td>0.68</td>
<td>0.76</td>
<td>0.87</td>
</tr>
<tr>
<td>I</td>
<td>0.28</td>
<td>0.44</td>
<td>0.62</td>
<td>0.69</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Transition Metal Halides

The only stable pentahalide is VF_5, which is readily hydrolysed and a strong Lewis acid. In the solid state it exists as an
infinite chain polymer with c/s-bridging fluorides but in the vapour phase it has a trigonal-bipyramid monomeric structure. M.P. 19.5° and B.P. 48.3°C.

**Tetrahalides** are formed by Ti and V. The Ti tetrahalides are fairly unreactive in redox and halogenation chemistry, unlike the V compounds. VCl₄ and VBr₄ dissociate spontaneously under ambient conditions to VX₃ and X₂. They also tend to halogenate organic material.

All **trihalides** of the elements from Ti to Cr are known. Mn(III) and Co(III) are too oxidising to coexist with any halide except F- under ambient conditions, whereas Ti(III) and V(III) are moderately strongly reducing. Chromium(III) is fairly stable toward both reduction or oxidation. There is a marked tendency toward decreasing ionic character on passing from left to right across the period and from the fluorides to the heavier halides. Ferric chloride and bromide show essentially covalent behaviour such as low MPs and solubility in donor organic solvents.

Many trihalides can be prepared by direct combination of the elements. In those cases where direct combination gives a higher oxidation state, trihalides can be produced by either thermal dissociation, disproportionation of the higher halide or by reduction- for example TiCl₃ can be prepared by reduction of TiCl₄ with H₂ at high temperatures.

All these trihalides adopt structures in which the metal is six-coordinate, either octahedral or distorted octahedral. Many of the lattices are complicated, but can be represented as CrCl₃ or BiI₃ types. In some cases it becomes even more complicated since some salts exist in more than one form. For example, at low temperature (below 240K) CrCl₃ exists in the rhombohedral form mentioned above, but at room temperature it is monoclinic.

All the first row transition metal elements form **dihalides** with all the halogens, with the exceptions of TiF₂ and CuI₂. The instability of TiF₂ is probably due to easy disproportionation to Ti and TiF₃ whereas the oxidising power of Cu²⁺ (reducing power of I⁻) explains the lack of the copper salt. Anhydrous dihalides can generally be synthesised by reaction of the pure metal with hydrogen halide or, for labile metal ions, by dehydration of hydrated salts with a covalent halogen compound e.g. SOCl₂.

The difluorides commonly have rutile structures, for example MnF₂, the dichlorides CdCl₂ structures and the diiodides CdI₂ structures. Dibromides have either CdCl₂ or CdI₂ structures or both. Dihalides are all ionic and typically dissolve in water to give aquo complexes or mixed aquo-halo-complexes. The solutions of Ti(II), V(II) and Cr(II) are very strongly reducing. They react extremely rapidly with O₂, and Ti(II) even rapidly reduces water to liberate hydrogen. Solutions of Fe(II) undergo slow oxidation in air, but in acid or neutral solution Mn(II), Co(II), Ni(II), and Cu(II) are quite stable to oxygen.

Cul adopts the Zinc Blende cubic close packed structure.

---

**Contributors**

- [Prof. Robert J. Lancashire](mailto:Robert.J.Lancashire@uwi.edu) (The Department of Chemistry, University of the West Indies)