22.11: Transitional Metal Ions in Aqueous Solutions

We often write transition-metal ions in aqueous solution with symbols such as Cr^{3+}, Cu^{2+}, and Fe^{3+} as though they were monatomic, but this is far from being the case. These ions are actually hydrated in solution and can be regarded as complex ions. Thus, for example, the grayish-violet color of many chromium(III) salts when dissolved in H_2O is due to the species $[Cr(H_2O)_6]^{3+}$ rather than to a bare Cr^{3+} ion. The same color is evident in many crystalline solids such as $[Cr(H_2O)_6]Cl_3$ which are known to contain the Cr^{3+} ion surrounded octahedrally by six H_2O molecules. In much the same way the blue color of many solutions of copper(II) salts can be attributed to the species $[Cu(H_2O)_4]^{2+}$ and the pale violet color of some solutions of iron(III) salts to the $[Fe(H_2O)_6]^{3+}$ ion. Because $[Fe(H_2O)_6]^{3+}$ is capable of donating a proton, the conjugate base, $[Fe(H_2O)_5OH]^{2+}$ is generally present when Fe^{3+} is dissolved in water. This imparts a yellow color to the solution. Figure 22.11.1 shows examples of colored ion complexes in aqueous solution.

$[Cr(H_2O)_6]^{3+}$ $[Cu(H_2O)_4]^{2+}$ $[Fe(H_2O)_5OH]^{2+}$ $[Co(H_2O)_6]^{2+}$
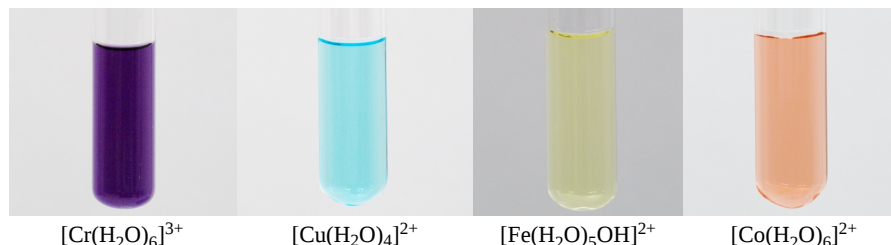
Figure 22.11.1 Examples of colored aqueous transition metal complexes

Not all salts of transition-metal ions yield the hydrated ion when dissolved in H_2O. Figure 22.11.2 compares three aqueous copper complexes. When $CuCl_2$ is dissolved in H_2O, a beautiful green color due mainly to the complex $[CuCl_2(H_2O)_2]$ is produced. This is obviously different from the sky-blue color of $[Cu(H_2O)_4]^{2+}$ which is obtained when Copper(II) sulfate or copper(II) nitrate are dissolved. This is because the Cl^- ion is a stronger Lewis base with respect to the Cu^{2+} ion than is H_2O. Thus, if there is a competition between H_2O and Cl^- to bond as a ligand to Cu^{2+}, the Cl^- ion will usually win out over the H_2O.

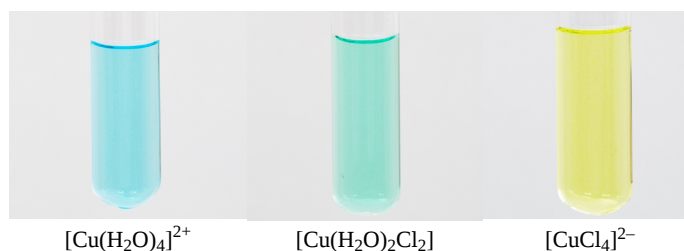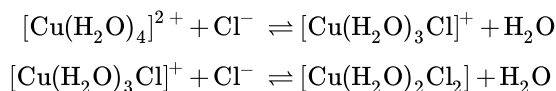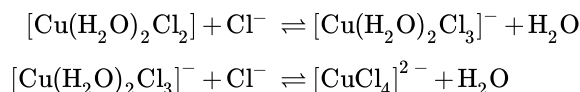$[Cu(H_2O)_4]^{2+}$ $[Cu(H_2O)_2Cl_2]$ $[CuCl_4]^{2-}$

Figure 22.11.2 The Different Colored Copper Chloride Complexes

The superior strength of the Cl^- as a Lewis base is easily demonstrated by adding Cl^- ions to a sky-blue solution of copper(II) sulfate. A green color immediately appears due to the formation of chloro complexes:

$$[Cu(H_2O)_4]^{2+} + Cl^- \rightleftharpoons [Cu(H_2O)_3Cl]^+ + H_2O$$

$$[Cu(H_2O)_3Cl]^+ + Cl^- \rightleftharpoons [Cu(H_2O)_2Cl_2] + H_2O$$

Green Complexes

If a large excess of Cl^- ion is added, the solution changes color again from green to yellow. This is because of even further displacement of H_2O ligands by Cl^- ligands:

$$[Cu(H_2O)_2Cl_2] + Cl^- \rightleftharpoons [Cu(H_2O)_2Cl_3]^- + H_2O$$

$$[Cu(H_2O)_2Cl_3]^- + Cl^- \rightleftharpoons [CuCl_4]^{2-} + H_2O$$

Yellow Complexes

Under favorable circumstances yellow crystals of salts like $Cs_2[CuCl_4]$, containing the complex ion $CuCl_4^{2-}$ can be obtained from these solutions.

Because they might very possibly form complexes with it, one must be careful about what ions are added to a solution containing hydrated transition-metal ions. Not only the chloride ions, but the other halide ions are liable to complex, and the same is true of species like NH_3 and CN^-. These ligands differ quite a lot in their affinity for a particular metal ion, but the rules governing this situation are not simple. One finds, for instance, that although NH_3 will complex very readily with Cu^{2+} it has little or no affinity for Fe^{3+}. In other words, a ligand which is a strong Lewis base with respect to one metal ion is not necessarily a strong base with respect to another. There are some ions, however, which almost always function as very weak Lewis bases. The perchlorate ion, ClO_4^- in particular, forms almost no complexes. The nitrate ion, NO_3^-, and sulfate ion, SO_4^{2-}, only occasionally form complexes.

The addition of ligands to a solution in order to form a highly colored complex is often used to detect the presence or absence of a given metal in solution. The deep blue color of $[Cu(NH_3)_4]^{2+}$ produced when excess NH_3 is added to solution of Cu(II) salts is a case in point. This can be seen in the following video, where a aqueous solution of ammonia is added to a copper sulfate solution:

The initial copper sulfate solution is sky blue, due to the $[Cu(H_2O)_4]^{2+}$ complex. When ammonia is added, a precipitate of $Cu(OH)_2(s)$ is formed. as it settles to the bottom, it can be seen that the remaining solution is a dark blue, due to the $[Cu(NH_3)_4]^{2+}$ complex formed by copper with ammonia.

Other well-known color reactions are the blood-red complex formed between Fe(III) ions and the thiocyanate ion, SCN^-, as well as the pink-red complex of Ni(II) with dimethylglyoxime.

While most of the reactions we have been describing are very fast and occur just as quickly as the solutions are mixed, this is not always the case. With certain types of complexes, ligand substitution is quite a slow process. For example, if Cl^- ions are added to a solution containing $[Cr(H_2O)_6]^{3+}$ ions, it is a few days before the grayish-violet color of the original ion is replaced by the green color of the chloro complexes $[Cr(H_2O_5)\,Cl]^{2+}$ and $[Cr(H_2O)_4\,Cl]^+$. Alternatively the solution may he heated, in which case the green color will usually appear within 10 min. The reaction

$$[Cr(H_2O)_6]^{3+} + Cl^- \rightarrow [Cr(H_2O)_5Cl]^{3+} + H_2O$$
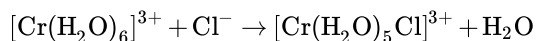
is thus a slow reaction with a high activation energy. Ligand substitution reactions of other Cr(III) complexes behave similarly. In consequence Cr(III) complexes are said to be **inert**, as opposed to a complex like $Fe(H_2O)_6^{3+}$ which swaps ligands very quickly and is said to be **labile**. Other examples of inert complexes are those of Co(III), Pt(IV), and Pt(II). Almost all the compounds which were used to establish the nature and the geometry of coordination compounds were inert rather than labile. There is very little point in trying to prepare cis and trans isomers of a labile complex, for example, because either will quickly react to form an equilibrium mixture of the cis and trans forms.

A final complication in dealing with aqueous solutions of transition-metal complexes is their acid-base behavior. Hydrated metal ions like $[Cr(H_2O)_6]^{3+}$ are capable of donating protons to water and acting as weak acids. Most hydrated ions with a charge of + 3, like Al^{3+} and Fe^{3+} behave similarly and are about as strong as acetic acid. The hydrated Hg(II) ion is also noticeably acidic in this way. Perhaps the most obvious of these cationic acids is the hydrated Fe(III) ion. When most Fe(III) salts are dissolved in water, the color of the solution is yellow or brown, though the $Fe(H2O)_6^{3+}$ ion itself is pale violet. The yellow color is due to the conjugate base produced by the loss of a proton. The equilibrium involved is

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+$$
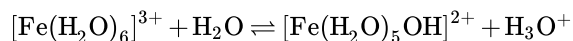
Pale violet Brown Complexes

If solutions of Fe(III) salts are acidified with perchloric acid or nitric acid, the brown base is protonated and the yellow color disappears from the solution entirely.