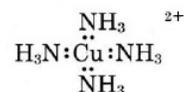


22.8: Coordination Compounds

A characteristic feature of the transition metals is their ability to form a group of compounds called **coordination compounds**, **complex compounds**, or sometimes simply **complexes**. A typical coordination compound is the intensely blue solid substance $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ which can be crystallized from solutions of CuSO_4 to which a very large excess of concentrated NH_3 has been added. These crystals contain two polyatomic ions, one of which is the sulfate ion, SO_4^{2-} , and the other of which is the **complex ion** $\text{Cu}(\text{NH}_3)_4^{2+}$ which is responsible for the blue color.

We can regard a complex ion such as $\text{Cu}(\text{NH}_3)_4^{2+}$ as being the result of the interaction of $:\text{NH}_3$ acting as a Lewis base with the Cu^{2+} ion acting as a Lewis acid. Each NH_3 molecule can be considered as donating a pair of electrons to a central Cu^{2+} , thus forming four **coordinate covalent (dative) bonds** to it:



Most coordination compounds contain a complex ion similar to $\text{Cu}(\text{NH}_3)_4^{2+}$. This ion can be either positively charged like $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, or it can be negatively charged like CoCl_6^{3-} . Neutral complexes like $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ are also known. All these species contain a *central metal* ion attached by coordinate covalent bonds to several **ligands**. These ligands are invariably Lewis bases. Some typical examples of ligands are H_2O , NH_3 , Cl^- , OH^- , CN^- , Br^- , and SCN^- . The number of ligands attached to the central metal ion is said to be its **coordination number** and is usually 2, 4, or 6. The group of ligands bonded to the metal taken collectively is said to constitute the metal's **coordination sphere**.

When writing the formula of a coordination compound containing complex ions, square brackets are usually used to enclose the coordination sphere. Examples are

- $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$
- $\text{K}_3[\text{Fe}(\text{CN})_6]$
- $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$

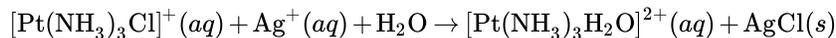
When such compounds are dissolved in H_2O , each of the ions present in the solid becomes an independent species with its own chemical and physical properties. Thus, when 1 mol $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ crystal is dissolved in H_2O the solution contains 1 mol $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion which can be recognized by its characteristic grayish-violet color and 3 mol Cl^- which can be detected by the precipitate of AgCl which forms when AgNO_3 is added to the solution.

Table 22.8.1: Observations on Complex Compounds Containing PtCl_2 , NH_3 , and KCl .

Compound	Molar Conductivity/A V^{-1} $\text{dm}^2 \text{mol}^{-1}$	Moles AgCl Precipitated per Mole Compound	Electrode to which Pt Migrates During Electrolysis
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	3.0	2 immediately	Cathode
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$	1.2	1 immediately; 1 after several hours	Cathode
$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$	~ 0	2 after several hours	Does not migrate
$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$	1.1	3 after several hours	Anode
$\text{K}_2[\text{PtCl}_4]$	2.8	4 after several hours	Anode

An even better example of how the various ions in a coordination compound can behave independently when dissolved in water is provided by the set of Pt(II) complexes shown in the table. The first of these compounds contains the complex ion $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and in each subsequent compound one of the NH_3 ligands in the coordination sphere of the Pt is replaced by a Cl^- ligand. As a result each compound contains a Pt complex of different composition and also of different charge, and when dissolved in H_2O , it shows just the conductivity and other properties we would expect from the given formula. When 1 mol $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ is dissolved in

H₂O, it furnishes 1 mol Pt(NH₃)₃Cl⁺ ions and 1 mol Cl⁻ ions. The strongest evidence for this is the molar conductivity of the salt (1.2 A V⁻¹ dm² mol⁻¹), which is very similar to that of other electrolytes like NaCl (1.3 A V⁻¹ dm² mol⁻¹) which also yield a +1 ion and a -1 ion in solution, but very different from that of electrolytes like MgCl₂ (2.5 A V⁻¹ dm² mol⁻¹) which yield one + 2 ion and two -1 ions in solution. The conductivity behavior also suggests that the Pt atom is part of a cation, since the Pt moves toward the cathode during electrolysis. The addition of AgNO₃ to the solution serves to confirm this picture. One mol AgCl is precipitated immediately, showing 1 mol free Cl⁻ ions. After a few hours a further mole of AgCl is precipitated, the Cl⁻ this time originating from the coordination sphere of the Pt atom due to the slow reaction



It is worth noting that in all these compounds, Pt has an oxidation number of + 2. Thus the combination of Pt with one NH₃ ligand and three Cl⁻ ligands yields an overall charge of 2(for Pt) - 3(for Cl) + 0(for NH₃) = -1. The ion is thus the anion [Pt(NH₃Cl₃]⁻ found in compound 4.

✓ Example 22.8.1: Oxidation State

What is the oxidation state of Pt in the compound Ca[Pt(NH₃)Cl₅]₂?

Solution

Since there are two complex ions for each Ca²⁺ ion, the charge on each must be -1. Adding the charge on each ligand, we obtain -5(for Cl⁻) + 0(for NH₃) = -5. If the oxidation number of Pt is *x*, then *x* - 5 must equal the total charge on the complex ion:

$$x - 5 = -1$$

or

$$x = +4$$

The compound in question is thus a Pt(IV) complex.

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