

## Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second Year)

Subject: Chemistry

Paper Code: CHC-104

Paper Title: Physical Chemistry and Inorganic Chemistry (Section B)

Unit: 1

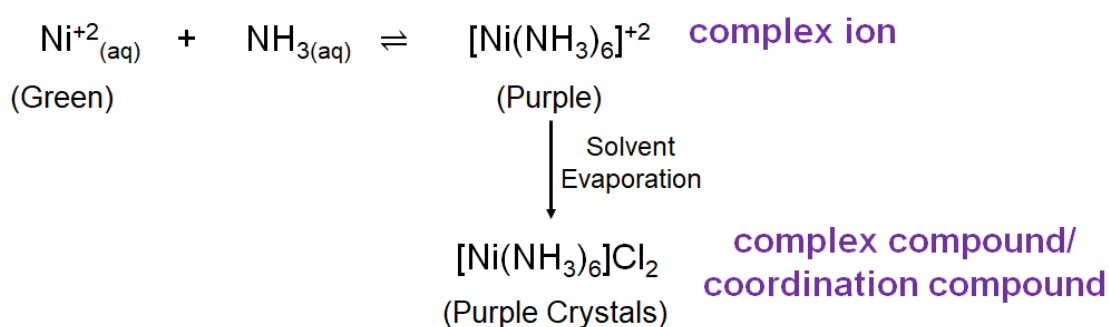
Module Name: Ability of 3d elements to form complexes and catalytic properties of 3d elements

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### Notes

#### Coordination Compounds



*Scheme 1: Reaction of  $\text{Ni}^{+2}$  ion with  $\text{NH}_3$  to give coordination compound,  $[\text{Ni}(\text{NH}_3)_6]^{+2}$ .*

(Refer Scheme.1) If aqueous  $\text{NH}_3$  added is to green coloured solution of  $\text{NiCl}_2$  then the green colour of the solution almost disappears and the solution acquires purple colour. This purple colour is because of formation of new ion with the formula  $[\text{Ni}(\text{NH}_3)_6]^{+2}$ , and this ion is called as **complex ion**. When aqueous  $\text{NH}_3$  is added to the solution of  $\text{NiCl}_2$ , each  $\text{Ni}^{+2}$  ion forms an intimate association with the six  $\text{NH}_3$  molecules.  $\text{Ni}^{+2}$  ion behaves as a Lewis acid and the  $\text{NH}_3$  molecules behaves as Lewis base giving its lone pair of electrons to  $\text{Ni}^{+2}$  ion to form a coordinate bond. Further if we evaporate the solvent we end up with purple crystals of compound with formula,  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ , and this compound is

called as **coordination compound** or **complex compound**. In this coordination compound the  $\text{NH}_3$  molecules are directly attached to  $\text{Ni}^{+2}$  ion through a coordinate bond whereas  $\text{Cl}^-$  ions are electrostatically associated with the complex ion. We can say that a complex compound is a combination of **Lewis acid** ( $\text{Ni}^{+2}$ ) with a number of **Lewis bases** ( $\text{NH}_3$ ). The geometry of the complex compound,  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  is octahedral (Refer figure.1), that is the  $\text{NH}_3$  molecules are arranged octahedrally (each  $\text{NH}_3$  is present at a vertex of an octahedron ) around  $\text{Ni}^{+2}$  ion.

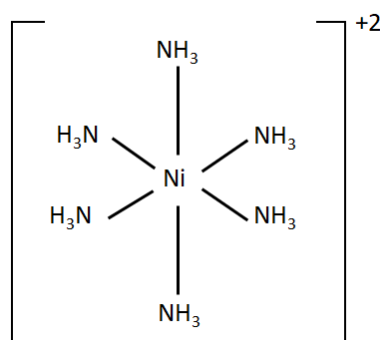
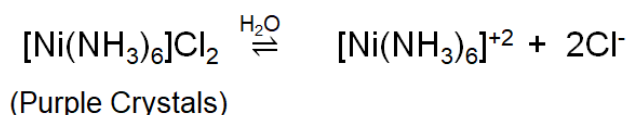


Figure 1. Octahedral geometry of  $[\text{Ni}(\text{NH}_3)_6]^{+2}$ .

If we dissolve the crystals of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  in water then it will ionise as per the equation show below:



When the crystals are dissolved in water there is no evidence for existence of free  $\text{Ni}^{+2}$  ions and  $\text{NH}_3$  molecules. This means mean that complex ion remains unaffected in the solution. As a matter of fact, the properties of complex ion are entirely different from that of free  $\text{Ni}^{+2}$  ion and  $\text{NH}_3$  molecules.

### Terminology for Coordination Compounds

Consider  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ ; (refer figure.2) in this complex compound  $\text{Ni}^{+2}$  ion is called as **central metal ion**, so central metal ion (or atom) is that ion which accepts the electron pair from neutral molecules or ions to form coordinate bonds,  $\text{NH}_3$  is called as **ligand**, so ligands are the neutral molecules or ions which donate lone pair of electrons to the central metal ion, Nitrogen is called as **donor**

**atom**, donor atom is that atom of the ligand which is attached to the central metal ion by donating its lone pair of electrons, the **coordination number** is 6 which is the total number of ligands coordinated to central metal ion, the central metal ion with all the ligands attached to it is called as **coordination sphere**, and the **charge on complex ion** is +2 here which is the algebraic sum of charge on central metal ion and all the ligands.

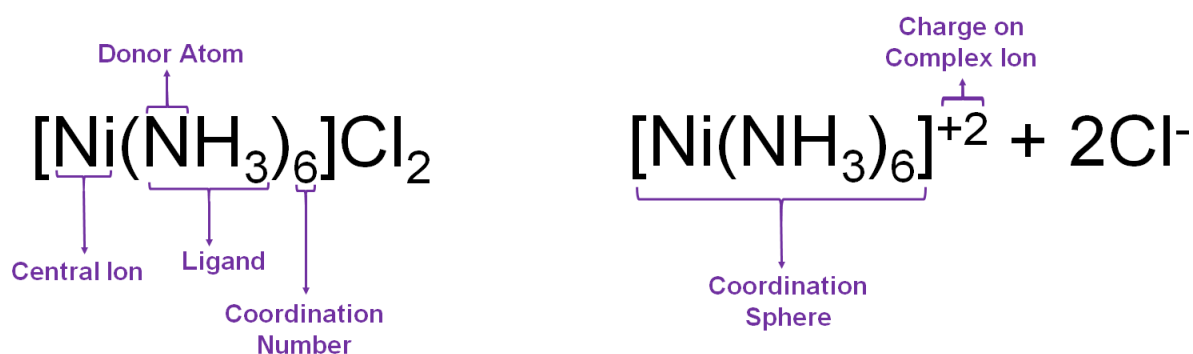
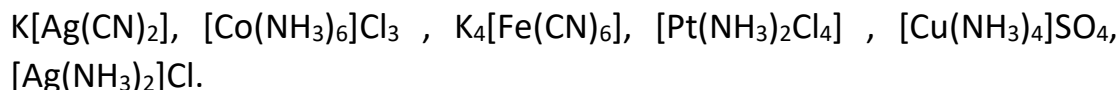


Figure 2. Terminology for coordination compounds.

A large number of coordination compounds of different types (geometry, coordination number, central metal ions, ligands etc.) are known, some of which are given below:



We come across some of the coordination compounds during our regular chemistry practical, for example,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  which has a deep blue colour is obtained when aqueous  $\text{NH}_3$  is added to a solution of  $\text{Cu}^{+2}$  ions, this test is used in qualitative analysis of copper.

### Importance of coordination compounds

It finds applications in **catalysis**, example: Zeigler-Natta catalyst which is a complex of Ti is used for manufacture of polyethene. Complex formation is used extensively in **analytical chemistry** for detection, estimation and separation of metal ions. Coordination compounds are also used in soil treatment, water softening, corrosion control, extraction of metal, electroplating etc. **Chlorophyll** which is a vital pigment in photosynthesis is a

magnesium complex and **haemoglobin** which carries  $O_2$  to animal cell is a complex of iron.

**Alfred Werner**, a Swiss chemist, was awarded the **Nobel Prize in Chemistry** in 1913 for his remarkable work in the field of **coordination chemistry**. Werner is rightly called the **father** of coordination chemistry.



*"File:Alfred Werner ETH-Bib Portr 09965.jpg" by ETH Zürich is licensed under CC BY-SA 3.0*

### Ability Of 3d (Transition) Elements to Form Coordination Compounds

Transition metal ions have a great tendency to form complexes, this is in contrast to s and p block elements due to two reasons:

1. They have **small size** and therefore they have higher positive charge density which facilitates the acceptance of lone pair of electrons from ligands
2. They have **vacant d orbitals of suitable energy** to accept lone pair of electrons to form coordination compounds.

### Stability of Coordination Compounds of 3d (Transition) Elements

Within a transition series the stability of the complexes increases with increasing atomic number and decreasing size of its atoms, this is because the positive charge density of metal ions increases with the decrease in size.

When the transition metal atom exhibit more than one oxidation state, the complex with higher oxidation state has greater stability. This can be again explained from the fact that the positive charge density increases with increase in oxidation state, example,  $[\text{Co}(\text{NH}_3)_4]^{3+}$  with  $\text{Co}^{3+}$  ion is stable, but  $\text{Co}^{2+}$  does not form stable complex with ammonia.

### Catalytic Properties of 3d (Transition) Elements

A **catalyst** speeds up a chemical reaction without undergoing a permanent chemical change by providing alternating pathway with **lower activation energy** (refer figure.3).

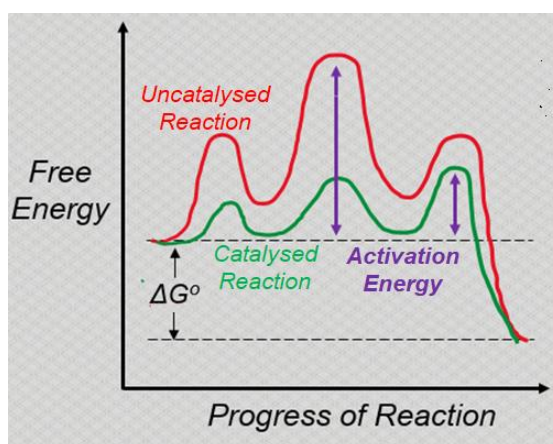
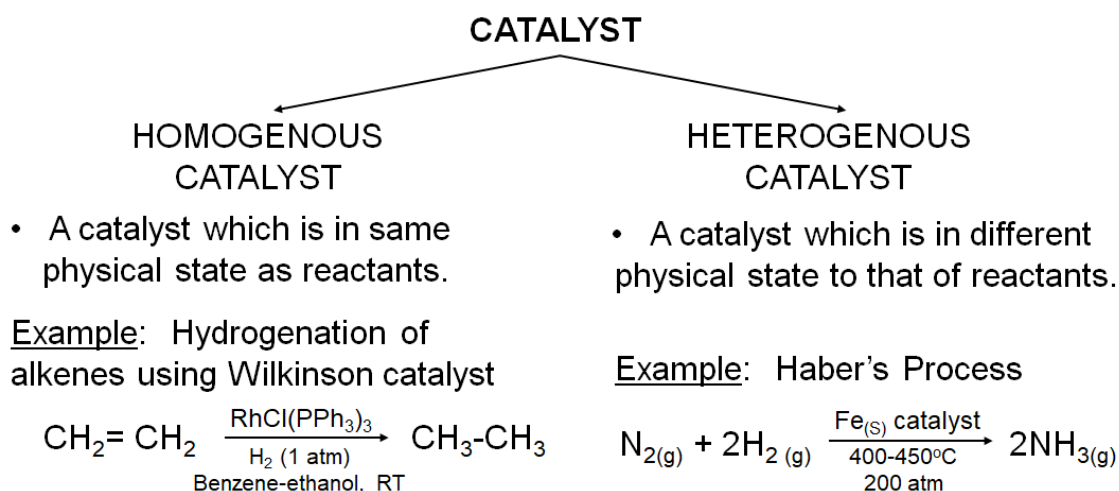


Figure 2. Pathway for a catalysed and uncatalyzed chemical reaction.

Catalysts can be classified into two types, homogenous catalyst and heterogenous catalyst(Refer Scheme. 2).



Scheme 2. Classification of catalysts.

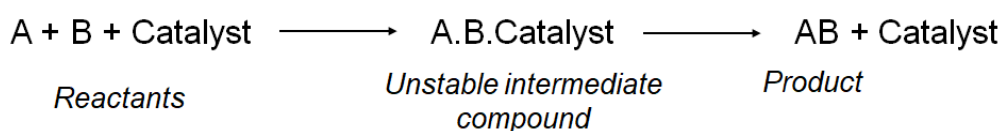
Many **transition elements** and their compounds are used as **catalysts** in the laboratory and in industries, for example:

- Hydrogenation of alkenes using Wilkinson's catalyst (complex of Rh ).
- Zeigler-Natta catalyst (complex of Ti) is used for the manufacture of polythene.
- Fenten's reagent ( $\text{FeSO}_4 + \text{H}_2\text{O}_2$ ) is used for oxidation of alcohols to aldehydes.
- Zinc chromite is used in the synthesis of methyl alcohol.
- Finely divided iron and molybdenum are used in the manufacture of ammonia (Haber's process).
- Finely divided nickel and palladium are used in the manufacture of Vanaspati as well as hydrogenation reaction in the laboratory.

### Mechanism for Homogenous Catalysis

According to Intermediate Compound Formation Theory of Catalysis:

Transition metals can have **variable oxidation states** and this allows them to form **unstable intermediate** compounds with reactants. These intermediate compounds immediately **decompose** to give final product and regenerate the catalyst.



### Mechanism for Heterogenous Catalysis

According to Adsorption Theory:

The finely divided transition metals and their compounds provide large surface area for adsorption of reactants. The adsorbed reactants react faster due to their closer contact on the surface of the catalyst to give product.

