

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4\text{Fe}(\text{CN})_6$, do not dissociate into Fe^{2+} and CN^- ions.

$\text{CoCl}_2 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination *polyhedra*. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions

Q.2 Definitions of Some Important Terms Pertaining to Coordination Compounds

(a) **Coordination entity**

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[\text{CoCl}_3(\text{NH}_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[\text{Ni}(\text{CO})_4]$, $[\text{PtCl}_2(\text{NH}_3)_2]$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$.

(b) **Central atom/ion**

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[\text{NiCl}_2(\text{H}_2\text{O})_4]$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are Ni^{2+} , Co^{3+} and Fe^{3+} , respectively. These central atoms/ions are also referred to as **Lewis acids**.

(c) **Ligands**

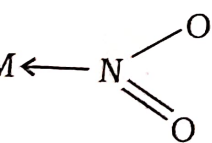
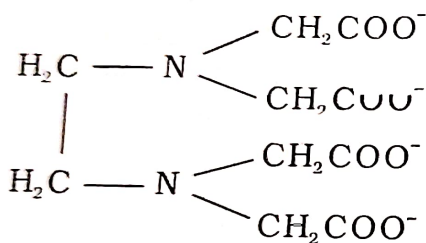
The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules, such as proteins.

When a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be **unidentate**.

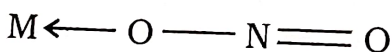
When a ligand can bind through two donor atoms as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1,2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion (EDTA^{4-}) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands (for reasons see Section 9.8).

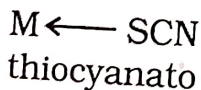
Ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.



nitrito-N



nitrito-O



thiocyanato



isothiocyanato

(d) **Coordination number**

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[\text{PtCl}_6]^{2-}$ and $[\text{Ni}(\text{NH}_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $\text{C}_2\text{O}_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.