Chem 309: Coordination Compounds (Part I)

INTRODUCTION:

The terms complex ion and coordination compound are frequently used very loosely.

In abroad sense any ion in which there is more than one atom may be called a complex ion. Also, any symmetrical arrangement of atoms about a central atom, in the construction of a molecule or ion, may be designated a coordination compound.

The class of complex (or coordination) compounds is one of the most important in inorganic chemistry. It includes a vast number of substances. Many complex compounds are of great practical value for biochemistry (hemoglobin, chlorophyll, many enzymes, and vitamins) and the chemical industry (metal complexonates, catalysts of oxidation and polymerization processes).

Some coordination compounds are rather simple in composition, such as ammonium ion, NH_4^+, complex cadmium chloride, $CdCl_4^{2-}$, and others, while others include hundreds and even thousands of atoms.

Complexes or coordination compounds are a kind of molecular or addition compounds. That is, Molecular or addition compounds are formed when stoichiometric amounts of two or more stable compounds; each capable of existing independently, join or unit together in definite

stoichiometric proportions. Carnallite, $KCl.MgCl_2.6H_2O$; potassium alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; tetramminecopper (II) sulfate monohydrate, $CuSO_4.4NH_3.H_2O$; and potassium ferrocyanide, $Fe(CN)_2.4KCN$, are familiar examples.

$KCl + MgCl_2 + 6H_2O \rightarrow KCl.MgCl_2.6H_2O$ (carnallite)

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$ (potassium alum)

$CuSO_4 + 4NH_3 + H_2O \rightarrow CuSO_4.4NH_3.H_2O$

(tetramminecopper (II) sulphate monohydrate)
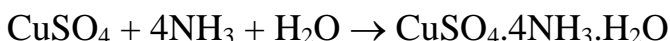
$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2.4KCN$ (potassium ferrocyanide)

Some of these substances maintain their identity as compounds only in the crystalline state and lose it when the crystal is dissolved or melted. i.e.:

These fall into two categories:

(1) Those which lose their identity in solution.

(2) Those which retain their identity in solution.

An aqueous solution of carnallite shows the properties of K^+, Mg^{2+}, and Cl^- ions, and so it behaves like a simple mixture of its three component ions in water. Potassium alum solutions similarly show the properties of K^+, Al^{3+}, and SO_4^{2-} ions. They are called **double salts** and exist only in the crystalline state.

The other two examples of addition compounds behave in a very different way from the double salts. That is, although potassium ferrocyanide may be prepared from potassium cyanide and iron (II) cyanide,

and can be formally written $Fe(CN)_2.4KCN$, its behavior is very different from that of a typical double salt, and so does tetramminecopper (II) sulphate monohydrate compound. When dissolved separately, they give little indication of the presence of Cu^{2+}, or Fe^{2+}, and CN^- ions, but instead give evidence(s) of the presence of more complicated structures corresponding to the formulations $[Cu(H_2O)_2(NH_3)_4]^{2+}$, the copproammonium ion, and $[Fe(CN)_6]^{4-}$, the ferrocyanide ion. These are complex ions and exist mainly as a single entity. Complex ions are indicated by square brackets. Molecular compounds of this type are called **complexes or coordination compounds.**

The distinction between double salts and complex compounds is not a sharp one, however. Some complexes, like the ferrocyanide ion and some of the ammonia complexes of cobalt (III) show only a very slight dissociation into their components. Others undergo much more extensive dissociation, and an almost continuous graduation in this property is found among various complexes, extending from the extremely stable ones down to the double salts. Even the double salts in aqueous solution may give not only hydrated ions, but appreciable concentrations of other complex species as well. The difference between a double salt and a complex compound, therefore, appears to be one of degree rather than of a more fundamental nature.

The presence of a complex ion or group may be detected in a variety of ways. Its chemical behavior is different in general from that of its components, and it may indicate its existence. If it is sufficiently stable with respect to dissociation and substitution it may pass intact through a series of operations, and separation and purification of compound containing it may be possible. Such properties as color, optical activity, absorption spectrum,

solubility behavior, magnetic susceptibility, reduction potential, transference behavior, X-ray pattern, and the like may also give evidence for the presence of a complex. Provided the complex can be isolated in the form of a pure compound, its composition can be determined by ordinary analytical methods. Even when the complex exists in solution but cannot be conveniently isolated, often its composition may by ascertained by one or more of a variety of special methods which have been developed.

The thermodynamic stability of a complex with respect to dissociation or substitution in a given environment is one of its important properties, as has been implied before.

An additional consideration of importance, here as well as in many other chemical systems, is the rate at which the complex proceeds toward equilibrium in such reactions. Great variability in this respect is observed among the reactions indifferent complexes. When, for example, a solution containing the tetramminecopper(II) ion, $[Cu(NH_3)_4]^{2+}$, is treated with excess hydrochloric acid, the complex is destroyed almost instantaneously, forming ammonium ion and (hydrated) copper (II) ion. When the hexamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$, is similarly treated, however, the complex appears to be unreactive, and persists almost indefinitely, even though removal of one or more ammonia molecules and replacement by water molecules are thermodynamically favored. Complexes reacting in such sluggish fashion are frequently said to be "**inert**", while those coming to equilibrium quite rapidly are described as "**labile**". The inertness or labiality of a complex, as well as its detection and characterization are often important.
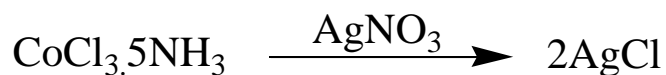
Used in a broad sense, the term "complex" applies to such ions as sulfate, nitrate, carbonate, perchlorate, and phosphate, as well as to ferrocyanide, tetramminecopper (II), and the like. In the present discussion, however, this term will be used in a more restricted sense to apply to such entities as $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, and $Pt(NH_3)_2Cl_2$. That is, most of the complex species to be considered here contain a metal atom or ion.

The earliest description of a complex in this narrower sense appeared near the beginning of the nineteenth century, and in the hundred years that followed a great many such components were prepared and characterized. Of special interest during this period were the complexes of cobalt (III), and platinum (II), and platinum (IV), which can be prepared in great variety, many of them being relatively inert. Some observations on a series of cobaltammines, in particular, provided an important part of the experimental foundation upon which Werner's coordination theory was based, and these are described in what follows.

If a solution containing cobalt (II) chloride and ammonium chloride is made strongly ammonical and treated for a time with a current of air, then made strongly acidic with hydrochloric acid, several products are obtained. Among them are a yellow crystalline compound having the formula $CoCl_3.6NH_3$, a beautiful purple solid of formula $CoCl_3.5NH_3$, and a green compound $CoCl_3.4NH_3$. Because of their colors these compounds were named respectively, luteocobalt chloride, purpureocobalt chloride, and praseocobalt chloride, but they are better called the hexammine-, pentammine-, and tetramminecobalt (III) chlorides. A fourth member in the

series is triamminecobalt (III) chloride, $CoCl_3.3NH_3$. A remarkable property of these cobaltammines is that the ammonia in them is not readily removed by acid. They are, for example, quite inert toward hydrochloric acid even when heated to boiling. Treatment with sodium or potassium hydroxide in the cold, moreover, does not precipitate the cobalt, although when the compounds are heated with these reagents they decompose with loss of ammonia. The term "**penetration complexes**" is sometimes applied to such relatively inert complexes to differentiate them from labile "**normal complexes**" such as tetramminecopper (II). The distinction is not a fundamental one, however.

All the ammine groups are inert in the compounds described before, but a very significant difference is found in the behavior of the chloride atoms. When a freshly prepared solution of the hexammine is acidified and treated in the cold with silver nitrate, all the chlorine is immediately precipitated. Under the same conditions only two thirds of the chlorine in the pentammine is precipitated, only one third in the tetramine, and none in the triammine.

$$CoCl_3.6NH_3 \xrightarrow{\text{AgNO}_3} 3AgCl$$

$$CoCl_3.5NH_3 \xrightarrow{\text{AgNO}_3} 2AgCl$$

$$CoCl_3.4NH_3 \xrightarrow{\text{AgNO}_3} 1AgCl$$

$$CoCl_3.3NH_3 \xrightarrow{\text{AgNO}_3} \text{none of AgCl}$$

Similar differences appear in some other reactions. For example, corresponding proportions of chlorides are lost as hydrogen chloride when these compounds are treated with concentrated sulfuric acid. In a similar series of iridium (III) complexes analogous behavior is observed. The reactions of $IrCl_3.6NH_3$, $IrCl_3.5NH_3$, and $IrCl_3.4NH_3$ with concentrated sulfuric acid, for example, result in the loss of all, two thirds, and one third of the chlorine, respectively, while $IrCl_3.3NH_3$ loses no hydrogen chloride under these conditions. This difference in behavior among the four types of ammines shown before is not limited to the chlorides.
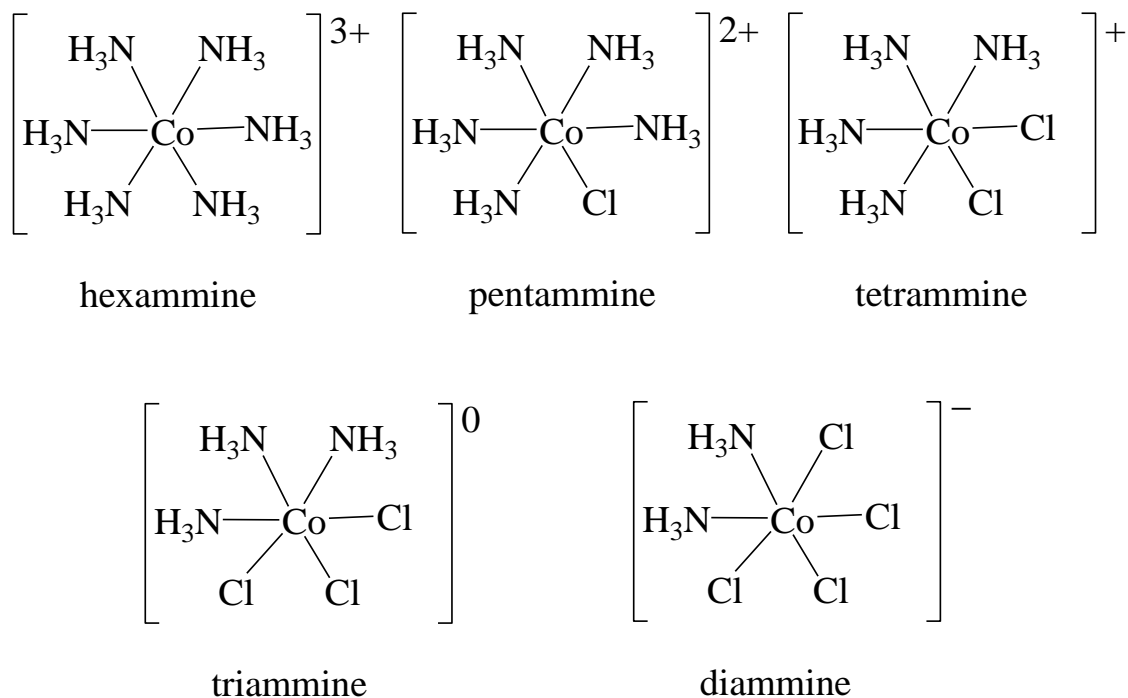
A series of hexammines of the type $CoX_3.6NH_3$ may be prepared, in which X represents a negative group such as nitrate or bromide. In these hexammines all three of the X groups show their characteristic ionic reactions. In the corresponding pentammines, $CoX_3.5NH_3$, however, only two of the X groups so behave, in $CoX_3.4NH_3$ only one, and in $CoX_3.3NH_3$, none. For example, $Co(NO_2)_3.3NH_3$ does not react with cold mineral acids to produce nitrous acid, in sharp contrast to the behavior of ionic nitrites. With regard to still lower ammines of these elements, containing fewer than three molecules of ammonia, it is significant that simple diammines of the type $MX_3.2NH_3$ are not obtained. Instead, such compounds as $KCo(NO_2)_4.2NH_3$ result, in which all four of the negative groups as well as the ammonia molecules are unreactive.

Werner's theory of coordination compounds:

The significance of the facts outlined before in relation to the structures of the cobaltammines and similar substances was first pointed out by Alfred Werner, whose brilliantly conceived researches, published between about 1893 and 1918, provided a rational explanation of the composition and behavior of these compounds. In this monumental contribution to the subject Werner described the preparation of a considerable number of new compounds, demonstrated and explained the existence of various types of isomerism, and established the fundamental structures of a great many complexes. He broadened the concepts of valence which had been held previously, and in so doing prepared the way for the modern application of electron theory in the field. So important was Werner's contribution that he was awarded the Nobel Prize in chemistry, and coordination compounds of the kind under discussion are often called "Werner complexes".
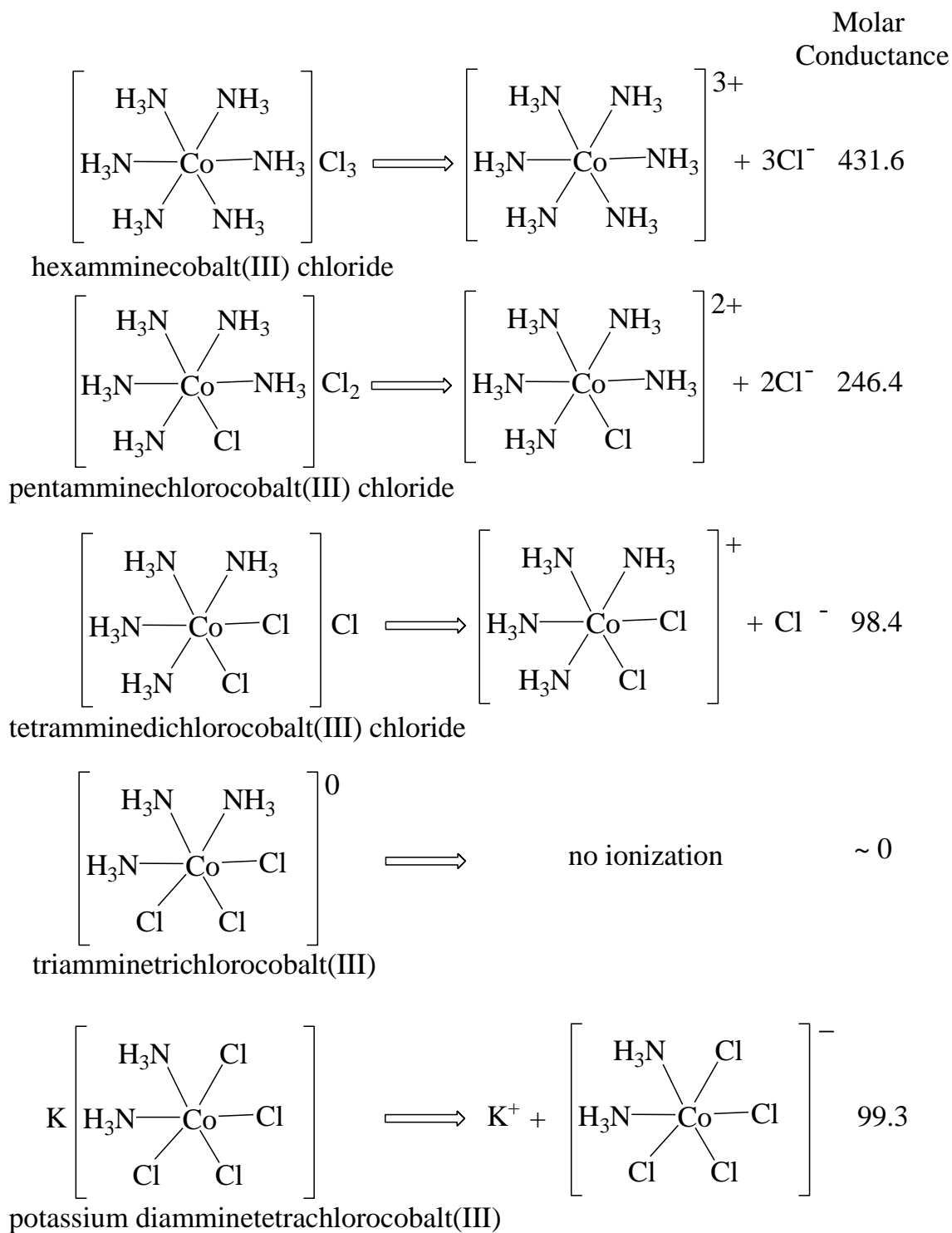
It will be noted that in each member of the cobaltammine series there are six relatively unreactive groups in the molecule besides the metal ion. In the hexammines these are the six ammonia molecules; in the pentammines they include the five ammonia molecules and one negative group, and so on. Werner assumed that these six groups were directly and individually bonded to the metal atom, giving rise to such complexes as those represented by the structural formulas shown in what follow. Thus in each of these compounds, according to Werner, there exists around the central metal atom an inner coordination sphere consisting of the six groups written inside the brackets, which are directly and more or less firmly attached to the metal atom.

Coordinated groups are often called **ligands**. They can be either ions (usually negative, although not always) or certain neutral molecules.

$$\left[\begin{array}{c} H_3N \quad\quad NH_3 \\ H_3N\!-\!Co\!-\!NH_3 \\ H_3N \quad\quad NH_3 \end{array}\right]^{3+} \left[\begin{array}{c} H_3N \quad\quad NH_3 \\ H_3N\!-\!Co\!-\!NH_3 \\ H_3N \quad\quad Cl \end{array}\right]^{2+} \left[\begin{array}{c} H_3N \quad\quad NH_3 \\ H_3N\!-\!Co\!-\!Cl \\ H_3N \quad\quad Cl \end{array}\right]^{+}$$

<div style="text-align:center">hexammine   pentammine   tetrammine</div>

$$\left[\begin{array}{c} H_3N \quad\quad NH_3 \\ H_3N\!-\!Co\!-\!Cl \\ Cl \quad\quad Cl \end{array}\right]^{0} \left[\begin{array}{c} H_3N \quad\quad Cl \\ H_3N\!-\!Co\!-\!Cl \\ Cl \quad\quad Cl \end{array}\right]^{-}$$

<div style="text-align:center">triammine   diammine</div>

In the hexammine complex shown there are six electrically neutral ammonia groups bonded to the central atom; cobalt (III), and the complex ion is, of course, a tri positive ion. The corresponding compound must then contain an equivalent number of negative groups, which are not, of course, a part of the inner coordination sphere, but are quite outside it, and in general maintain their ionic character in the compound. In hexamminecobalt(III) chloride, $Co(NH_3)_6$ Cl_3, for example, all three of the chlorides are of this nature. In the corresponding pentammine, $Co(NH_3)_5$ Cl Cl_2, however, only two of the chlorides are ionic since the third is a part of the inner coordination sphere, and so, tetrammine, $Co(NH_3)_4$ Cl_2 Cl, has one ionic chloride whereas the other two chlorides are in the inner coordination

sphere. The triammine, $Co(NH_3)_3Cl_3$, contains no ionic chloride since all three are within the inner coordination sphere: here the complex is electrically neutral and constitutes the complete molecule.

Molar
Conductance

hexamminecobalt(III) chloride 431.6

pentamminechlorocobalt(III) chloride 246.4

tetramminedichlorocobalt(III) chloride 98.4

triamminetrichlorocobalt(III) .... no ionization .... ~ 0

potassium diamminetetrachlorocobalt(III) 99.3

Both conductivity measurements and freezing-point depressions have been employed to give information concerning the number of ions actually furnished in aqueous solution by coordination compounds of the type discussed before.

Before are given the structures and modes of ionization postulated by the Werner coordination theory for a representative series of cobalt (III) ammines. The measured molar conductance values of approximately 0.001 N solutions at 25° C are included. For comparison, the molar conductance values of some simple salts under the same conditions may be kept in mind: LiCl, 112.4; $MgCl_2$, 248.2; $LaCl_3$, 411.0.

It is evident that the observed values of molar conductance are consistent with the mode of ionization proposed by Werner. An analogous series of platinum (IV) ammines shows a similar variation in molar conductance with progressive substitution of negative ligands for ammonia molecules. In these compounds, too, the results indicate the presence of six ligands within the coordination sphere, the residual charge of the complex varying with the number of negative ligands coordinated to the tetra positive platinum. Differences in valence type are shown also with a series of complex compounds of platinum (II), although here only four ligands are coordinated to the metal atom.

In the following Table are listed two representative series of platinum complex compounds, together with the corresponding molar conductance values of their solutions. In each formula, the groups shown inside the

brackets with the metal are those assumed to be present as ligands within the coordination sphere.

Table: Molar conductance values of some platinum (IV) and platinum (II) complex compounds.

Name	Formula	*Molar Conductance
Hexammineplatinum(IV) chloride	$[Pt(NH_3)_6]Cl_4$	522.9
Dichlorotetrammineplatinum(IV) chloride	$[Pt(NH_3)_4Cl_2]Cl_2$	228
Trichlorotriammineplatinum(IV) chloride	$[Pt(NH_3)_3Cl_3]Cl$	96.8
Tetrachlorodiammineplatinum(IV) chloride	$[Pt(NH_3)_2Cl_4]$	0
Potassium pentachloroammineplatinate (IV)	$K[Pt(NH_3)Cl_5]$	108.5
Potassium hexachloroplatinate (IV)	$K_2[PtCl_6]$	256
Tetrammineplatinum(II) chloride	$[Pt(NH_3)_4]Cl_2$	260
Chlorotriammineplatinum(II) chloride	$[Pt(NH_3)_3Cl]Cl$	115.8
Dichlorodiammineplatinum(II)	$[Pt(NH_3)_2Cl_2]$	0
Potassium trichloroammineplatinate (II)	$K[Pt(NH_3)Cl_3]$	106.8
Potassium tetrachloroplatinate (II)	$K_2[PtCl_4]$	267

* Molar conductance values of 0.001 N solutions at 25°

A striking fact brought out by these observations is that there appears to be a definite number of positions within the coordination sphere of each central atom which are available for occupancy by suitable ligands, whether these be neutral or charged.

This characteristic number Werner called the **coordination number** of the particular atom or ion. Cobalt (III), iridium (III), and platinum (IV), for

example, possess a coordination number of six in their complexes. In platinum (II) compounds the coordination number is four. Indeed, six and four are by far the most common coordination numbers, although examples of all coordination numbers from two to eight are known.

The characteristic coordination number of the central atom in a complex differs, in general, from the numerical value of its oxidation state, as is seen in the examples given before.

To account for the discrepancy between the number of bonds actually established by the central atom and the number that would correspond to its oxidation state alone, Werner postulated the existence of an "auxiliary valence" in addition to the ordinary or "**principal valence**". Thus, in $[Pt(NH_3)_6]Cl_4$ the platinum was considered to use six such auxiliary valences to bind the ammonia molecules, while in $K_2[PtCl_6]$ it uses only two, the remaining four chlorine atoms being held by "principal valences".

In terms of the electron theory of valence, the binding between the central metal atom and the attached ligands is to a considerable extent covalent, although the strength and polarity of these bonds may show wide variation. Those bonds which arise from the use of the so-called auxiliary valences are, according to the Lewis theory, coordinate covalent bonds, in which both electrons in the shared pair are contributed by the ligand. In $[Pt(NH_3)_6]^{4+}$, for example, all six ammonia molecules are regarded as being held by bonds of this type, each ammonia molecule having contributed its unshared pair of electrons for this purpose.

On the other hand, $[PtCl_6]^{2-}$ may be considered formally to comprise two chloride ions bonded in this fashion and four neutral chlorine atoms each bond by an ordinary covalent bond in which one electron was contributed by the chlorine atom and one by the platinum atom. These formal distinctions are sometimes represented graphically in structural formulas by the use of arrows, *or dotted lines*, to denote coordinate covalent bonds, whereas solid lines represent the principal, *or main,* bonds as shown bellow.
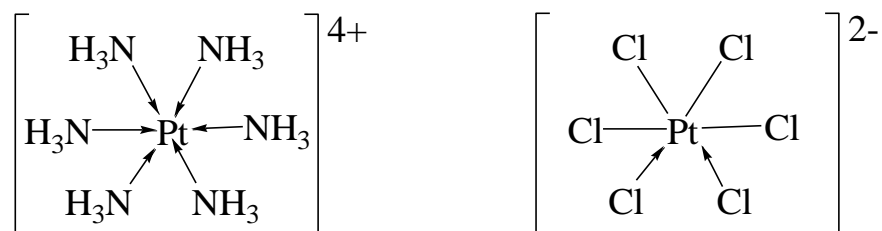
On behave conclusion of what Werner suggested, it is mentioned that in complexes there are two different sorts of valency:

(1) Primary or ionizable valence that is so-called main or principal valence

(2) Secondary or non-ionizable valence that is so-called auxiliary valence.

Having established the number of secondary valencies (that is the coordination number) in the studied complexes, Werner attempted to find the shape of these complexes. For example, consider a platinum (IV) complex in which the coordination number of the central atom is six, the possible arrangement or structure is a planar hexagon, a trigonal prism, or an octahedron as shown hereafter.
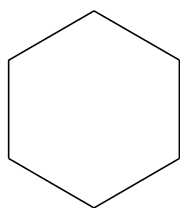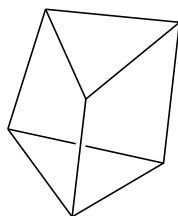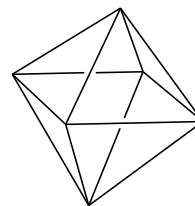
Planar hexagon   Trigonal prism   Octahedron

Werner found how many isomeric forms of various complexes could be prepared in the laboratory, and compared this with the theoretical number for each of the possible shapes as shown in the following Table.

Table: Number of Isomers

Complex	Experimental Observation	Planar hexagon	Trigonal prism	Octahedron
MX_6	*1*	1	1	1
MX_5Y	*1*	1	1	1
MX_4Y_2	*2*	3	3	2
MX_3Y_3	*2*	3	3	2

The results strongly suggested that the shape was octahedral. This is not absolute proof of the shape, since the correct experimental conditions for preparing all the isomers may not have been found, but the shape is now known to be octahedral for the complexes having the coordination number six of their central atom.

Werner theory can be summarized in the following points:

1- According to Werner's theory, atoms in complexes may display not only the usual "main" or "primary" valence (*solid lines in structural formulas*), but also an "additional" or "secondary" or auxiliary valence (*dotted lines or arrows*).

2- The secondary valencies are saturated when the complex compounds are formed. While the main valencies of metal cations are saturated only by negatively charged ions, the secondary ones may also be saturated by neutral molecules.

3- Each complex ion contains a central atom surrounded by coordinated ions and molecules.

4- Every complex is characterized by its "coordination number" which indicates the number of atoms, ions, or molecules that may surround the central atom. The coordination number may be high or low. For example, the coordination number of silver in $[Ag(NH_3)_2]OH$ is *two*, that of aluminium in $[Al(H_2O)_6]Cl_3$ is *six*, and that of lanthanum in $[La(H_2O)_9](NO_3)_3$ is *nine*. The coordination number in complexes of rare-earth elements may be as high as the *twelve*. Many central atoms form complexes with a variable coordination number. For instance, in the case of rare-earth elements, it may vary from *6* to *12*, and copper (II) is known to form complexes with coordination numbers equal to *4*, *5* and *6*.

5- The coordinated atoms (by way of both main and secondary valencies) are on the ***inner sphere*** of the complex compound. They are known as ***addends*** (or **ligands** according to the current nomenclature).

6- The central atom and the inner sphere constitute the *nucleus of the complex*, which is enclosed in brackets in written formulas: $[Ag(NH_3)_2]^+$. The nucleus of a complex may be *neutral* or *charged positively* as well as *negatively*, for example:

$$\begin{bmatrix} Cl & NH_3 \\ Cl{-}Co{\cdots}NH_3 \\ Cl & NH_3 \end{bmatrix}^0 \quad \begin{bmatrix} Cl & Cl \\ Cl{-}Pt{\cdots}Cl \\ Cl & Cl \end{bmatrix}^{2-} \quad \begin{bmatrix} H_3N & NH_3 \\ Cu \\ H_3N & NH_3 \end{bmatrix}^{2+}$$
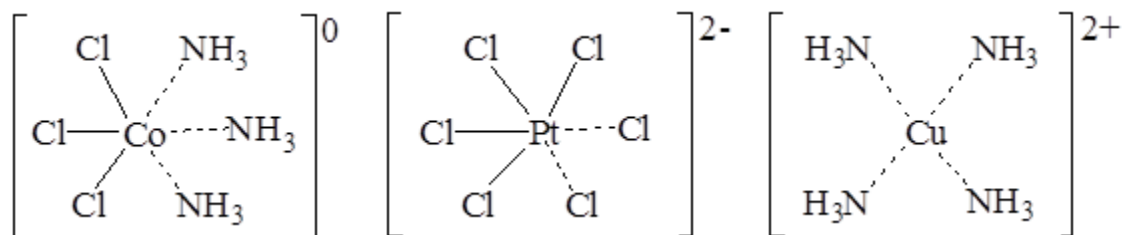
7- If the nucleus of a complex is charged, the complex has an *outer sphere* because a charged complex (or rather its nucleus) may attract oppositely charged ions:

$$\begin{bmatrix} H_3N & NH_3 \\ H_3N{\cdots}Co{\cdots}NH_3 \\ H_3N & NH \end{bmatrix}^{3+} \quad 3\,Cl^-$$
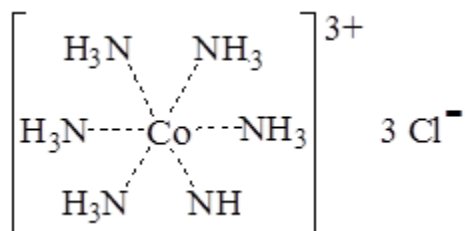
8- The linkage between the nucleus of a complex and its outer sphere is *ionic*, therefore, the complex dissociates in solution into several ions: the nucleus and the outer sphere ions:

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$
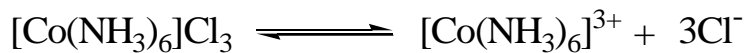
Thus, **[Co(NH₃)₆]Cl₃** gives away four ions in an aqueous solution. Such dissociation does not seem to affect the nucleus of the complex which it does not undergo dissociation but to an insignificant degree determined by the "*stability constant*".

9- The central atom is usually a *cation* (Co^{3+} , Fe^{3+} , Ag^+ , etc.) or less commonly, an *anion* (e.g., O^{2-} in beryllium oxyacetate, $[[O^{2-}]Be_4(CH_3COO)_6]^0$). Sometimes, the central atoms are formally *uncharged particles*: $[Ni(CO)_4]$, $[Cr(C_6H_6)_2]$, and so on.

10- The main and secondary valencies according to Werner in the nuclei of the complexes do not differ either in strength or in nature. In particular, all of the four hydrogen atoms in the NH_4^+ ion are identical in position and the strength of their linkage with the central atom, and in the complex $[PtCl_6]^{2-}$ all of the six chlorine atoms are similar in their structural role and properties.

11- The strength of the bond between the central atom or ion and the ligands, arising due to secondary valency, may be even greater than that of the main bond existing before the complex was formed. For example, in the complex $[Co(NH_3)_6]Cl_3$ resulting from the reaction $CoCl_3 + 6NH_3 \rightarrow$, the chloride ions linked with Co^{3+} by way of the main valency are easily detached by the complex as it dissolves in water and are detectable in solution after addition of $AgNO_3$, for example, to the latter, whereas the NH_3 molecules coordinated in $[Co(NH_3)_6]^{3+}$ are not neutralized by strong acids even if a highly acidic medium is created in solution. Quite the

opposite may occur, however, $[Co(NH_3)_4]^{2+}$ stops to exist in an acidic medium:

Werner's theory has made it possible to systematize the available data

$$[Co(NH_3)_4]^{2+} \ + \ 4H^+ \ \rightleftharpoons \ Co^{2+} \ + \ 4NH_4^+$$
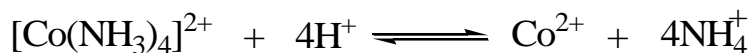
concerning complex compounds and to embark upon methodical search for new compounds.

Limitations of the Werner's theory:

Werner and his contemporaries could not provide a valid explanation of the nature of secondary valencies as well as the factors responsible for coordination of the central ion with a particular number of addends.

However, Werner's ideas and the theories elaborated by his contemporaries Lewis and Sidgwick, according to which chemical bonding involves electron pairs, have led concepts of coordinate (donor-acceptor) bonding resulting from donation of an electron pair by the ligand to the metal ion.

Coordinate, or Donor – Acceptor, Bonding

Lewis and Sidgwick completed what Werner did concerning explanation of the nature of the bond between the ligand and the central metal.

They assumed that coordinate bonding usually arises when particles exhibiting the properties of a donor and an acceptor enter into interaction.

The properties of an acceptor are displayed by atoms, ions, or molecules characterized by **electrophilic** (or, in other words, *electronophilic*) behavior – that is, having a tendency to *attach electrons*. Such properties are most often observed in atoms or ions with an *incomplete electron shell*.

The properties of a donor are displayed by atoms, ions or molecules characterized by **nucleuphilic** behavior – that is, having the tendency to *give electrons* (or, in other words, the tendency of attaching the nucleus of positive charges). Such properties are most often observed in atoms or ions with *unshared electrons in the outer shell*.

Unlike the ordinary covalent two-electron bond which forms as a result of overlapping of the electron orbitals belonging to both partners, in coordinate (donor-acceptor) bonding the electron pair is given away *only by the donor*. The other partner, who is the acceptor, must provide a *vacant orbital* for this electron pair. The result is a molecular orbital covalent coordination or, has become common to say, donor-acceptor nature.

Many examples can be given to illustrate donor-acceptor bonding in inorganic chemistry. The interaction between ammonia (NH_3) and boron trifluoride (BF_3) is a representative example for that kind of bonding. Ammonia is the donor because it has the ability to give away a pair of unshared electron, and boron trifluoride acts as the acceptor since the boron atom has a vacant orbital, that is one of the three 2p orbitals, and these vacant orbitals can accommodate the electron pair providing with the donor.

$$NH_3 + BF_3 \rightarrow \quad H_3N \rightarrow BF_3 \ \ \text{or} \ \ H_3N^+ \rightarrow {}^-BF_3$$
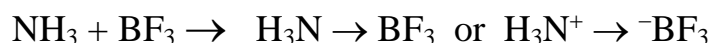
An important distinction of donor-acceptor bonding from the ordinary covalent one is not only *its origin* but also, and mainly, its *ionic nature*. Indeed, since the donor supplies both electrons, as a consequence of donor-acceptor bonding the acceptor receives a certain negative charge, while the donor receives a positive charge.

Therefore, donor-acceptor bonds are usually indicated by an arrow directed from the donor to the acceptor; in addition, the positive and negative charges resulting from donor-acceptor bonding are also indicated.

Just as in the case of covalent bonding, coordinate bonds may be of the $\sigma-$ or $\pi-$type.

The notions of "complex" and "coordination" compounds have been evolved in parallel and are often treated as identical, which is easy to understand if it is remembered that a complex is *the result* of coordination of

the central ion with addends (or ligands) and obeys the postulates of the coordination theories (Werner's theory, the donor-acceptor bonding theory, theory of the valence bonds, etc.).

At the same time, it should be borne in mind that coordinate or donor-acceptor bonding is not the only factor responsible for coordination of ligands with the central ion. For instance, the contribution of the electrostatic forces in the complex formation, whereas this contribution in some times even more important than that of covalent coordinate interaction.

The nature of the linkage in complex ions and coordination compounds:

The previous discussion may have left the impression that the components of complex ions and compounds are held together only by covalent or coordinate covalent bonds. This is far from true, inasmuch as many complexes are formed without the donor–acceptor sharing of electrons. Such ions or compounds result from electrostatic forces between their constituents. Therefore it is possible to classify complex compounds rather loosely into those resulting from electrostatic forces and those held together by coordinate covalent bonds.

i- Complexes resulting from electrostatic forces between constituents:

A large group of complexes contain ion-dipole bond. Those hydrated ions which are isoelectronic with the inert gases contain bonds of this type. For example, the ions $Mg(H_2O)_6^{++}$ and $Al(H_2O)_6^{3+}$ result from the electrostatic attraction between the positively charged cations and the electric-dipole charges within the water molecules. Water molecule possesses an angular structure in which the two hydrogen atoms are on the same side of the oxygen atom and the resulting structure produces a permanent dipole moment. This molecule may be visualized as being triangular in shape oxygen forming an apex to the triangle, and may be represented diagrammatically as:

$$\overset{-}{O}$$
$$H \quad + \quad H$$
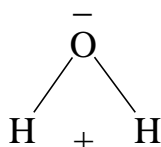
Because of their polar nature, water molecules may be oriented and attracted by ions in water solutions. Positive ions are usually smaller than negative ions; therefore cations attract and bind water molecules more tightly to themselves than do anions. The number of water molecules attached to a cation is called its coordination number, and this number is determined by the size of the cation. The hydrated aluminum ion is indicated symbolically as thus:
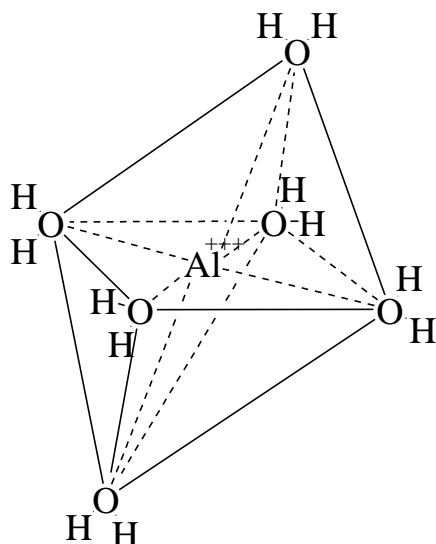
ii- Complexes resulting from the formation of coordinate bonds:

The coordinate bond is called the *semi polar bond* because such a bond appears to be partly ionic and partly covalent. This bond may be considered as consisting of an electron pair as in a covalent linkage, but the electron pair is furnished, according to the Sidgwick theory, by one atom or ion in a donor-acceptor relationship. Ions which are isoelectronic with the inert gases do not form the "Werner type" complexes with their characteristic coordinate linkage. Instead these ions may form hydrates due to electrostatic

forces, and there is little evidence that the coupling in such compounds is brought about by the completion of incomplete electronic orbitals.

Ions of the transition elements have a tendency toward the formation of complexes containing coordinate bonds, and these complexes are apparently more stable than those formed by electrostatic forces. As a general rule the radii of the transitional metal cations are less than the radii of those cations which are isoelectronic with the inert gases. This may account, in part, for the greater stability of the transition-ion complexes. An examination of the electronic orbitals of the first transition elements, with atomic numbers 21 to 30, shows that these elements, with the exception of copper and zinc, have incomplete *3d* orbitals, which are progressively filled in passing through the range of these elements. In general an atom or ion entering into chemical reaction tends to add a sufficient number of electrons to fill incomplete orbitals, within spatial limitations. Ions of the transition elements may accept electrons in pairs from donor atoms.

The formation of complex ions by coordinate bonds appears to follow two general rules:

a- The central ion tends to accept electrons to fill incomplete stable orbitals, and each completed orbital contains a pair of electrons of opposite spins.

b- The central ion tends to accept sufficient coordinated molecules or ions to produce a symmetrical structure of molecules packed around the central ion. This structure may be planar, tetrahedral, octahedral, or cubic.

Effective Atomic Number:

Coordinate bonds are formed between the ligands and the central metal ion in a complex; that is, a ligand donates an electron pair to the metal ion.

Coordination compounds are formed very readily by the *trans*ition metals since they have vacant *d* orbitals which they can accommodate donated electron pairs.

The number of coordinate bonds which they can be formed depends largely on the number of vacant orbitals of suitable energy.

The effective atomic number rule states that "when forming a complex, ligands are added until the total number of electrons on the central metal atom or ion plus the electron pairs donated by the ligands become the same as the number of electrons in the next inert gas". In turn, by means of EAN rule, one can predict the number of ligands required to form a complex with a certain metal ion.

Consider $K_4[Fe(CN)_6]$, potassium hexacyanoferrate(II) as a typical representative example: An iron atom has 26 electrons, so the central metal ion Fe^{2+} has 24 electrons. The next inert gas Kr, Krypton, has 36 electrons, so 12 electrons, six pairs, are needed to attain the 36 electron configuration. The electron pairs from six CN^- ligands raises the effective atomic number (EAN) of Fe^{2+} in the complex $[Fe(CN)_6]^{4-}$ to $24 + (6 \times 2) = 36$.

The following table includes further examples of the EAN:

Table: Effective Atomic Numbers of Some Metals in Complexes

Atom	Atomic Number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN	Inert gas
Fe	26	$[Fe(CN)_6]^{4-}$	2	12	36	Krypton
Co	27	$[Co(NH_3)_6]^{3+}$	3	12	36	Krypton
Ni	28	$[Ni(CO)_4]$	0	8	36	Krypton
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36	Krypton
Pd	46	$[Pd(NH_3)_6]^{4+}$	4	12	54	Xenon
Pt	78	$[PtCl_6]^{2-}$	4	12	86	Radon
Cr	24	$[Cr(NH_3)_6]^{3+}$	3	12	33	
Fe	26	$[Fe(CN)_6]^{3-}$	3	12	35	
Ni	28	$[Ni(NH_3)_6]^{2+}$	2	12	38	
Pd	46	$[PdCl_4]^{2-}$	2	8	52	
Pt	78	$[Pt(NH_3)_4]^{2+}$	2	8	84	

Although the **EAN** rule correctly predicts the number of ligands in a large number of complexes there are a significant number of exceptions where the EAN is not quit that of an inert gas.

The tendency to attain an inert gas configuration is a significant factor but not a necessary condition for complex formation, because it is also necessary to produce a symmetrical structure (tetrahedral, square-planar, and octahedral) irrespective of the number of electrons involved.

Nomenclature of Coordination Compounds

Just as there are rules for naming simple inorganic and organic compounds, coordination compounds are named according to an established system.

The **I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry (**IUPAC**) published rules for the systematic naming of coordination compounds in 1957. For example, the following compounds are named according to the rules outlined below.

COMPOUND	*SYSTEMATIC NAME*
$[Ni(H_2O)_6]SO_4$	Hexaaquonickel(II) sulfate
$[Cr(en)_2(CN)_2]Cl$	Dicyanobis(ethylenediamine)chromium(III) chloride
$K[Pt(NH_3)Cl_3]$	Potassium amminetrichloroplatinate(II)

As reading through the rules, notice how they apply to these examples.

1. The names of coordination complexes are written as *single words*, built from the names of the ligands, prefixes to indicate how many ligands are present, and a name for the central metal.

2. If the coordination complex is ionic, that consists of two (or more) ions, one of which is the nucleus of this complex: the positive ion is named first, followed (*after a space*) by the name of the negative ion, regardless of which is the complex ion.

3. When giving the name of the complex ion or molecule, the ligands are named first, followed by the name of the metal.

4. Coordinated groups (ligands) are listed in the following order: negative ligands, neutral ligands and then positive ligands.

5. Negative ligands end with the suffix –*o*, for example CN^- cyan*o*, Cl^- chlor*o*, NO_2^- nitr*o*, and OH^- hydrox*o*. If there are several negative ligands present, these are listed alphabetically.

6. Neutral ligands have no special ending, e.g. NH_3 *ammine* (not amine or amino), H_2O *aquo*, CO *carbonyl*, NO *nitrosyl*, and hydrocarbons end in –*yl*, for example *phenyl* and *methyl*. If several neutral ligands are present, these are listed as follow: H_2O then NH_3 then any others alphabetically.

7. Positive groups end in –*ium*, e.g. $NH_2–NH_3^+$ hydrazin*ium*.

8. Greek prefixes (*di-, tri-, tetra-, penta-, hexa-*) are used to indicate the number of ligands of a given type (of the same type) attached to the central ion; if there is only one ligand, the prefix *mono-* is not used.

9. When the name of the ligand includes a number, e.g. dipyridyl or ethylenediamine then the name of the ligand is placed in parentheses (brackets) and the prefixes *bis-*, *tris-*, and *tetrakis-* are used instead of *di-*, *tri-*, and *tetra-*.

10. The oxidation state of the central metal atom is given by a Roman numeral enclosed in parentheses immediately following the name of the metal.

11. If the complex ion has a net negative charge, the ending –*ate* is added to the stem (end) of the name of the metal. But complex positive ions and neutral molecules have no special ending.

12. If the complex contains two or more metal atoms, it is termed "*polynuclear*". The ligands that link the two metal atoms are called "*bridge groups*" and are separated from the rest of the complex by hyphens and denoted by the prefix μ.

13. If any lattice components such as water or solvent of crystallization are present, these follow the name, and are preceded by the number of these groups in *Arabic* numerals.

These rules are illustrated by the following examples:

COMPOUNDS	*SYSTEMATIC NAMES*
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(II) chloride
$[Co(NH_3)_5Cl]^{2+}$	Chloropentamminecobalt(III) ion
$[Co(NH_3)_4SO_4]NO_3$	Sulphatotetramminecobalt(III) nitrate
$[Co(NH_3)_3(NO_2)_3]$	Trinitrotriamminecobalt(III)
$[Co(NH_3)_3NO_2.Cl.CN]$	Chlorocyanonitrotriamminecobalt(III)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine)chromium(III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
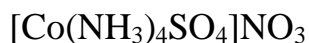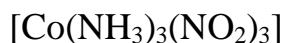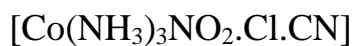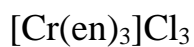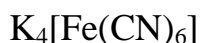
[Pt(py)₄][PtCl₄]   Tetrapyridineplatinum(II)tetrachloroplatinate(II)

$[(NH_3)_5Co.NH.Co(NH_3)_5](NO_3)_5$ Decammine-μ-amidodicobalt(III)

nitrate

$$\left[(en)_2Co \underset{OH}{\overset{NH_2}{\diamond}} Co(en)_2 \right] (SO_4)_2$$
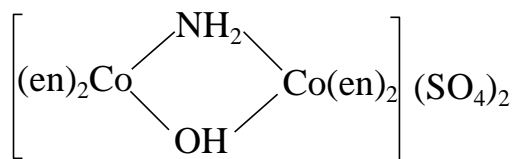
Tetrakis(ethylenediamine)-μ-amido-μ-hydroxo-dicobalt(III) sulphate

$$(CO)_3Fe \underset{CO}{\overset{CO}{\Longleftrightarrow}} Fe(CO)_3$$
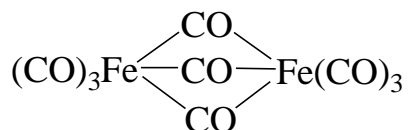
Tri-μ-carbonylbis(tricarbonyliron(III))

OR

Hexacarbonyltri-m-carbonyl-diiron(III)

$AlCl_3.(EtOH)_4$ Aluminum(III)chloride-4-ethanol.

Name the following complexes:

(a) $[Cu(NH_3)_4]SO_4$; (b) $K_2[CoCl_4]$;

(c) $Co(phen)_2Cl_2$; (d) $[Co(en)_2(H_2O)Cl]Cl_2$

=-=

The answer:

(a) $[Cu(NH_3)_4]SO_4$
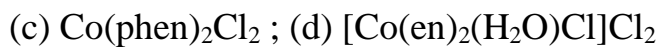
tetraamminecopper(II) sulfate

(b) $K_2[CoCl_4]$
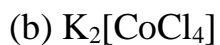
potassium tetrachlorocobaltate(II)

(c) $Co(phen)_2Cl_2$
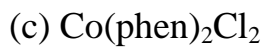
dichlorobis(phenanthroline)cobalt(II)

(d) $[Co(en)_2(H_2O)Cl]Cl_2$
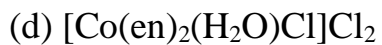
chlorobis(ethylenediamine)aquocobalt(III) chloride

Types of Ligands

Some specific examples of ligands in various complexes have been mentioned before. It is found that a great variety of chemical entities, both ions and neutral molecules, may serve in this capacity. Since, as has been pointed out, the ligands are very commonly attached to the coordination center by coordinate covalent bonds, it is not surprising that the groups which can function as ligands are, with few exceptions, those which possess one or more unshared pairs of electrons in the valence shell, and which can act as electron-pair donors.

In a large proportion of such ligands the actual donor atom is nitrogen, phosphorus, arsenic, oxygen, or sulfur atom, or a halide or sulfide ion, each possessing at least one unshared pair of electrons. Carbon in most of its combinations has no unshared electrons in its valence shell, and does not, in general, act as a donor atom. However, in the complexes of carbon monoxide, cyanide ion, and isonitriles the carbon atom is directly attached to the metal. In these ligands, of course, the carbon atom does have an unshared pair of electrons; moreover, the multiple bonds in these groups may make possible an additional stabilizing effect. Complexes of such unsaturated hydrocarbons as ethylene and cyclopentadiene with certain metal ions ban be obtained, too, but the bonding is of a somewhat different nature from that just described.

According the number of bonds between ligand and the central metal atom ligands can be classified into the following two main classes:

1. Monodentate ligands:

Monodentate is a Latin word: *mono* means "one" and *dentate* means toothed that is derived from *dens*; dens = tooth. This indicates that monodentate ligand is capable of forming only a single bond to the central metal atom.

The followings are some of the representative monodentate ligands:

Halide ions:
$$F^- \quad Cl^- \quad Br^- \quad I^-$$

The anions of various oxo acids:
$$NO_3^- \quad NO_2^- \quad RCO_2^-, \quad SO_4^{2-}$$

Neutral molecules in which the donor atoms are usually N or O:
$$NH_3 \quad RNH_2 \quad H_2O \quad MeOH \quad CH_3CN$$

The simplest role that each of these ligands can play is that of an electron-pair donor to a single metal atom.

2. Polydentate Ligands: (Multidentate ligands or Chelates):

Polydentate ligands are also called **Chelates** (from Greek *chela*, meaning "*claw*", because the ligand attaches to the central atom like a *pincers*).

Although the first chelate was recognized and described by Werner, the development of chelate chemistry has taken place almost entirely within recent years. However, chelation is nothing more than a special form of complex formations and what has being said concerning simple complexing applies equally well to chelate formation.

A chelate possesses complexes of a cyclic structure arising from the union of a metal ion with an organic or inorganic ring. Usually chelate rings contain five or six members, including the metal ion. Chelation may arise by the formation of covalent linkages, or coordinate bonds, or by a combination of the two. In fact the nature of the linkages has been used as a basis for the classification of chelate compounds.

Covalent bonding is produced by the replacement of a proton (H^+) in an organic group. Functional groups of this type are sometimes called acidic groups because of the fact that hydrogen may be replaced from them. The most common examples of these groups are – COOH (carboxyl), –SO_3H (sulfonic), –OH (enolic hydroxyl), and =NOH (oxime).

Coordinate linkages, without the replacement of hydrogen, are formed by the donation of an electron pair. The most common functional groups of this category which contain donor atoms are –NH_2 (primary, secondary, and tertiary amines), =NOH (oxime), –OH (alcoholic hydroxyl), =CO (carbonyl), and –S– (thioether).

According to the number of attachments (*chelates*) to the central metal atom *Polydentate ligands* can be classified. The followings represent some of the different *Polydentate ligands*:
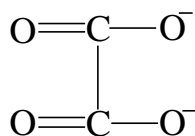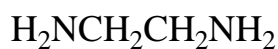
Bidentate Ligands:
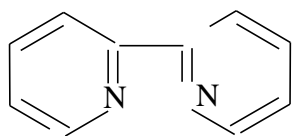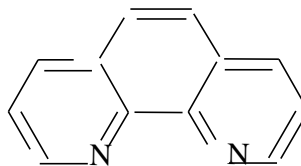
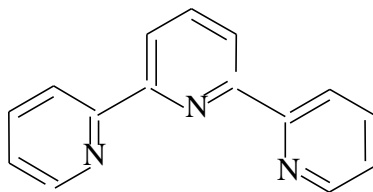2,2'-bipyridine, bipy   1,10-phenanthroline, phen

$H_2NCH_2CH_2NH_2$
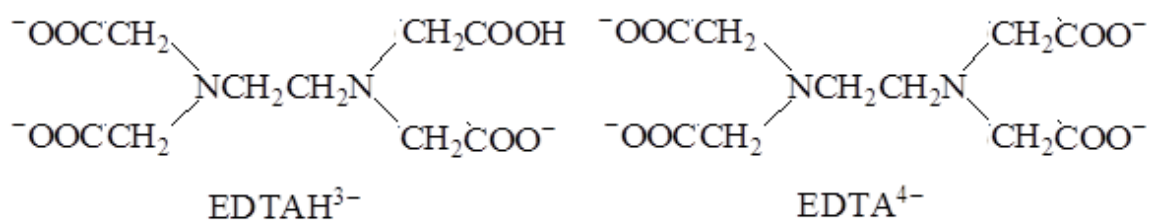
Oxalate ion, ox   Ethylenedimine, en

Tridentate Ligands:

Terpyridine, terpy

$H_2N-CH_2-CH_2-N-CH_2-CH_2-NH_2$
             |
             H
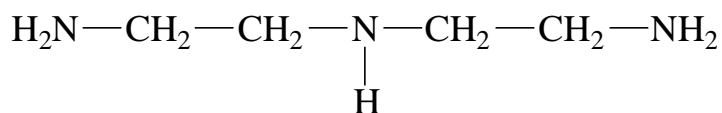
Diethylenetriamine, dien

Quadridentate Ligands:

$$^-OOC - CH_2 - NH - CH_2 - CH_2 - NH - CH_2 - COO^-$$
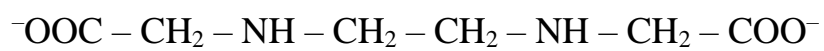
Ethylenediamineacetate ion

Penta- and Hexa-dentate Ligands:

$$^-OOCCH_2 \diagdown \qquad\qquad \diagup CH_2COOH \qquad ^-OOCCH_2 \diagdown \qquad\qquad \diagup CH_2COO^-$$
$$NCH_2CH_2N \qquad\qquad\qquad\qquad NCH_2CH_2N$$
$$^-OOCCH_2 \diagup \qquad\qquad \diagdown CH_2COO^- \qquad ^-OOCCH_2 \diagup \qquad\qquad \diagdown CH_2COO^-$$

EDTAH^{3-} EDTA^{4-}

Ethylediaminetetraacetate, EDTA

General Types of Complex Ions

All ions in aqueous solution may be regarded as complex ion. These ions may be hydrates, or the complexes may result from the union of a certain ion with other ions, atoms, or molecules.

One broad classification of complex ions divides them into three general types:

1. ***Complex ions formed by the union of cations with inorganic molecules***:

Hydrated ions.   The majority of ions are hydrated to some extent in aqueous solutions. The followings represent the most familiar examples of these ions:
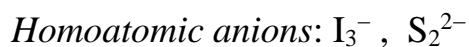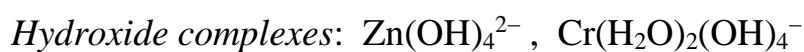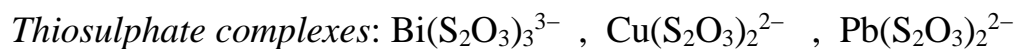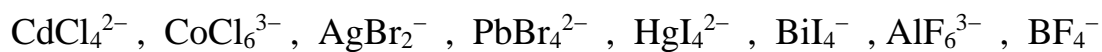
The hydronium ion H_3O^+, the hydrated chromic ion $Cr(H_2O)_6^{3+}$, and the hydrated beryllium ion $Be(H_2O)_4^{++}$.

Ammoniates: Many cations form coordination compounds with ammonia. Examples:

NH_4^+ , $Zn(NH_3)_4^{++}$, $Cu(NH_3)_4^{++}$, $Ni(NH_3)_6^{++}$, $Ag(NH_3)_2^+$, $Cd(NH_3)_4^{++}$, $Co(NH_3)_6^{++}$
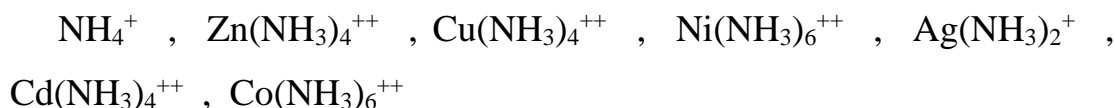
2. ***Complex ions formed by the union of cations with inorganic anions***:

Halide complexes: All halides form complexes meanwhile fluoride ion is the most effective complexing agent among the halides. A few of the most common examples are the followings:

$CdCl_4^{2-}$, $CoCl_6^{3-}$, $AgBr_2^-$, $PbBr_4^{2-}$, HgI_4^{2-} , BiI_4^- , AlF_6^{3-} , BF_4^-

Cyanide complexes: $Ag(CN)_2^-$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Ni(CN)_4^{2-}$

Thiocyanate complexes: $Ag(CNS)_2^-$, $Hg(CNS)_4^{2-}$

Thiosulphate complexes: $Bi(S_2O_3)_3^{3-}$, $Cu(S_2O_3)_2^{2-}$, $Pb(S_2O_3)_2^{2-}$

Sulfide complexes: $SnS_3^=$, HgS_2^{2-} , AsS_3^{3-}

Hydroxide complexes: $Zn(OH)_4^{2-}$, $Cr(H_2O)_2(OH)_4^-$

Homoatomic anions: I_3^- , S_2^{2-}

3. ***Complex ions formed by the union of cations with organic anions or molecules***:

Certain inorganic cations may form coordination compounds with specific organic ions or molecules. In what follows are some of representative examples:
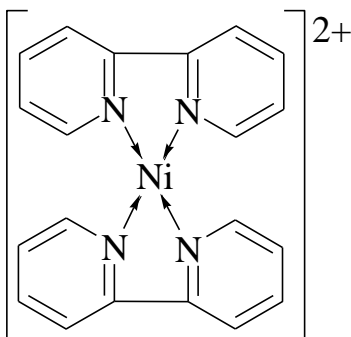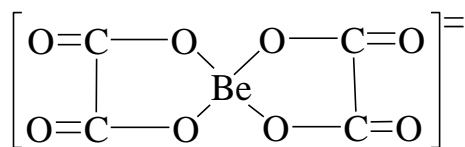
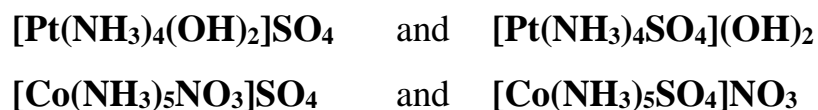## *Isomerism in Coordination Compounds*

The term isomerism generally means the existence of two or more chemical compounds with identical chemical compositions but with different properties. Compounds of this description are called *isomers*, and the structural difference which produces dissimilar properties is referred to as *isomerism*. The variety of chemical linkage and complexity of stereo chemical relationships which occur in coordination compounds are favorable to those structural arrangements which lead to isomerism.

In what follows is a description of various types of isomerism that have been predicted by the Werner theory:

1- *Ionization isomerism.*

Two coordination compounds which differ in the distribution of ions between those directly coordinated and counter-ions present in the crystal lattice. This means that two compounds have the same empirical formula, but containing different ionic groupings.

For example, the violet bromopentammine sulfate of cobalt with a formula of **[Co(NH$_3$)$_5$Br]SO$_4$** is an ionization isomer of the red sulfatopentammine bromide with the formula of **[Co(NH$_3$)$_5$SO$_4$]Br**. Both these complexes have the same empirical formula, but the first gives a precipitate of $BaSO_4$ with $BaCl_2$ and no precipitate with $AgNO_3$ and the second gives a precipitate of $AgBr$ with $AgNO_3$ and no precipitate with $BaCl_2$. Other illustrations of ionization isomerism are:

$$[Pt(NH_3)_4(OH)_2]SO_4 \quad \text{and} \quad [Pt(NH_3)_4SO_4](OH)_2$$

$$[Co(NH_3)_5NO_3]SO_4 \quad \text{and} \quad [Co(NH_3)_5SO_4]NO_3$$
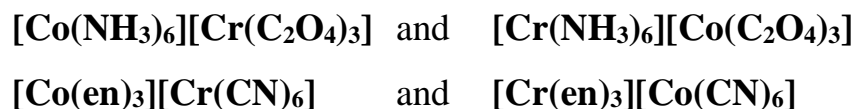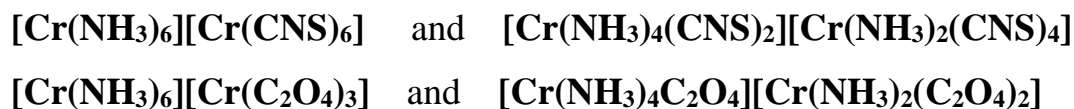
2- Coordination isomerism.

This type of isomerism may occur only when the cation and anion of a salt are both complexes, the two isomers differing in the distribution of ligands between the cation and anion. In the compounds

$$[Co(NH_3)_6][Cr(CN)_6] \quad \text{and} \quad [Cr(NH_3)_6][Co(CN)_6]$$

cobalt occurs in the cation of the first and in the anion of the second, whereas for chromium the situation is reversed. Other examples of the coordination isomerism are

$$[Co(NH_3)_6][Cr(C_2O_4)_3] \quad \text{and} \quad [Cr(NH_3)_6][Co(C_2O_4)_3]$$

$$[Co(en)_3][Cr(CN)_6] \quad \text{and} \quad [Cr(en)_3][Co(CN)_6]$$

Another form of the coordination isomerism may occur when the same metal appears in both cation and anion of two compounds in which there is a different distribution of donor components. Compounds exemplifying this arrangement are

$$[Cr(NH_3)_6][Cr(CNS)_6] \quad \text{and} \quad [Cr(NH_3)_4(CNS)_2][Cr(NH_3)_2(CNS)_4]$$

$$[Cr(NH_3)_6][Cr(C_2O_4)_3] \quad \text{and} \quad [Cr(NH_3)_4C_2O_4][Cr(NH_3)_2(C_2O_4)_2]$$

3- Polymerization isomerism

Actually, it is not isomerism, but it is included in this list because it represents an additional way in which an empirical formula may give incomplete information about the nature of the complex. That is, this term is used to describe compounds which have the same stoichiometric composition but whose molecular compositions are multiples of the simplest stoichiometric arrangement. For example, there are several compounds which have an empirical composition corresponding to $[Pt(NH_3)_2Cl_2]_n$. One of these compounds is yellow, sparingly soluble nonelectrolyte which may be prepared from solid tetrammineplatinum(II) chloride, $[Pt(NH_3)_4]Cl_2$, with loss of ammonia, by heating at 250 °C. Its formula is appropriately written $[Pt(NH_3)_2Cl_2]$. A second compound (Lagnus's green salt) is precipitated when solutions of tetrammineplatinum(II) chloride and tetrachloroplatinic acid are mixed, and therefore may be formulated $[Pt(NH_3)_4][PtCl_4]$. Other compounds of general formula $[Pt(NH_3)_2Cl_2]_n$ correspond to the formulas $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$, and $[Pt(NH_3)_3Cl]_2[PtCl_4]$.

Other compounds illustrating polymerization isomerism are

$[Cr(NH_3)_3(CNS)_2]$ and $[Cr(NH_3)_5CNS]_3[Cr(CNS)_6]_2$

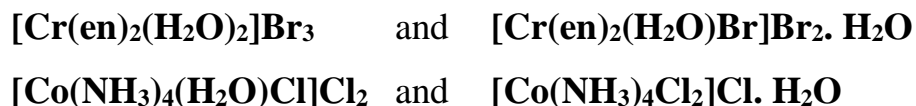## 4- Hydrate isomerism

For aqua complexes, the number of water molecules in the inner sphere does vary, and this variation results in the formation of hydrate isomerism.

For example, there are three different hexahydrates (three hydrate isomers) of chromic chloride with an empirical formula of **CrCl$_3$.6H$_2$O**. All three differ in the number of water molecules in the coordination sphere.

[Cr(H$_2$O)$_6$]Cl$_3$ **[Cr(H$_2$O)$_5$Cl]Cl$_2$.H$_2$O**   **[Cr(H$_2$O)$_4$Cl$_2$]Cl.2H$_2$O**
     violet   green   green
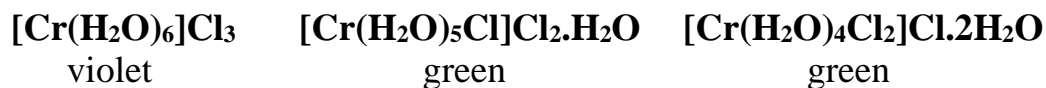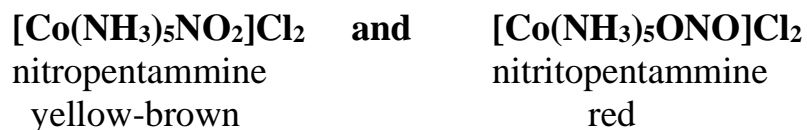
these compounds differ not only in color but also in their solubility. Also, as might be predicted from their formulas, silver nitrate can precipitate all the chlorine from the first isomer, two-thirds from the second, and only one-third from the third. Other hydrate isomers are
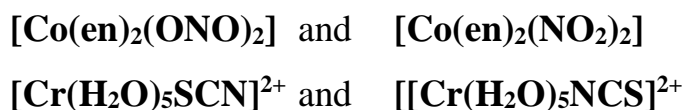
[Cr(en)$_2$(H$_2$O)$_2$]Br$_3$ and   **[Cr(en)$_2$(H$_2$O)Br]Br$_2$. H$_2$O**

[Co(NH$_3$)$_4$(H$_2$O)Cl]Cl$_2$ and   **[Co(NH$_3$)$_4$Cl$_2$]Cl. H$_2$O**

5- *Linkage isomerism (Salt isomerism)*

Isomerism of this type results from the ability of some ligands to coordinate in two or more ways to the central metal ion. Thus the NO$_2$ group may be attached as a nitro grouping with pentavalent nitrogen linking itself to the central atom directly through the nitrogen atom (**—NO$_2$**), or the group can be attached as a nitrito grouping with trivalent nitrogen linked to the central atom through an oxygen atom (**—ONO**).

Examples of isomeric forms resulting from these two modes of linkage are

[Co(NH$_3$)$_5$NO$_2$]Cl$_2$ **and**   **[Co(NH$_3$)$_5$ONO]Cl$_2$**
nitropentammine   nitritopentammine
    yellow-brown   red

Other compounds which illustrate linkage (salt) isomerism are

[Co(en)$_2$(ONO)$_2$]   and   **[Co(en)$_2$(NO$_2$)$_2$]**

[Cr(H$_2$O)$_5$SCN]$^{2+}$ and   **[[Cr(H$_2$O)$_5$NCS]$^{2+}$**

6- *Stereoisomerism (Geometrical isomerism)*

It is the most widely occurring and consequently the most important of any of the forms of isomerism. Stereoisomerism is a form of isomerism in which two substances of the same composition and constitution differ only in the relative positions in space assumed by certain of their constituent atoms or groups. This phenomenon is sometimes called ***geometrical*** isomerism, inasmuch as two isomers may possess the same geometrical figure but may differ only as to the points of attachment of coordinating groups.

Stereoisomerism of compounds with the coordination number of 6 or 4 is well known, and in many cases proof of the configurations of this stereoisomerism has been established. For the other coordination numbers no isomeric phenomena have as yet been observed to establish definite spatial structures.

The symmetrical arrangements of six coordinating groups about a central atom can be attained by the octahedral configuration, whereas four coordinated complexes are represented either by the square-planar configurations or by the tetrahedral ones.

a- *Stereoisomerism in Octahedral Complexes*:

For octahedral complexes of the **[ML$_6$]** form in which there is one ligand type, e.g. **[Co(NH$_3$)$_6$]$^{3+}$**, no isomerism are found. Also no isomerism is possible for the complexes of the form **[MA$_5$B]**; A and B represent two different ligands, e.g. **[Co(NH$_3$)$_5$Cl]$^{2+}$**. However, of those complexes of the type **[MA$_4$B$_2$]** and **[MA$_3$B$_3$]** two isomers are possible.

cis and *trans* isomers are examples of geometrical (stereo) isomerism. *Cis-trans* isomerism for the complexes of the formulas **[MA$_4$B$_2$]** and **[MA$_3$B$_3$]** may be exemplified by the followings

[Co(NH$_3$)$_4$Cl$_2$]$^+$ is a representative example for complexes of the formula **[MA$_4$B$_2$]**, that enhances geometrical "*cis-trans*" isomerism.

| *cis* | *trans* |
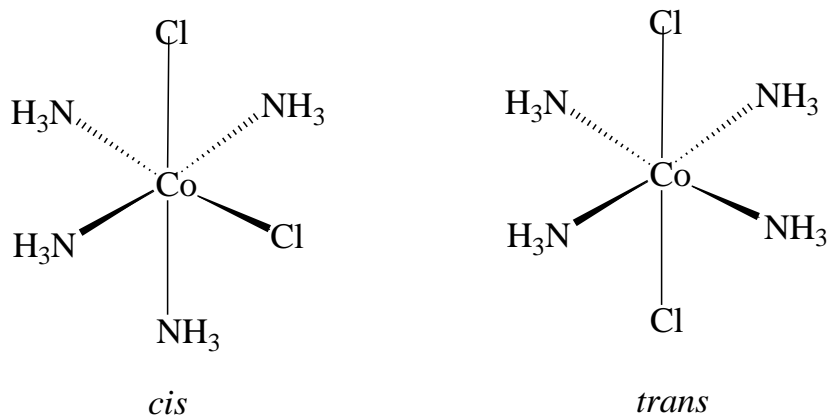
Isomeric configurations of [Co(NH$_3$)$_4$Cl$_2$]$^+$ complex ions

[Co(NH$_3$)$_3$(NO$_2$)$_3$] complex represents the isomeric configurations of complexes of the formula [MA$_3$B$_3$]
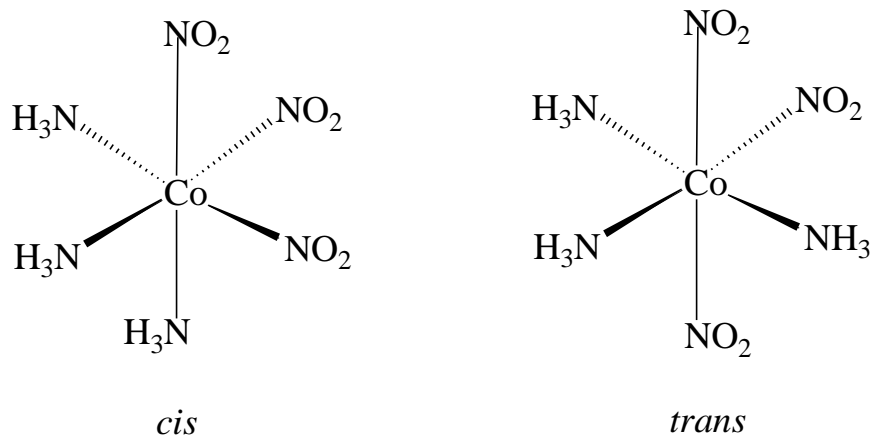
Isomeric configurations of [Co(NH$_3$)$_3$(NO$_2$)$_3$] complexes

b- Stereoisomerism in Square-planar Complexes

No stereoisomerism is possible for the square-planner structure for those complexes of the types [MA$_4$], [MA$_3$B], and [MAB$_3$], because all possible arrangements of components in each of these complexes are exactly the same.

In the case of materials of the type [MA$_2$B$_2$], *cis* and *trans* isomers exist. *cis* means "adjacent to" and *trans* means "on the opposite side of".

Diamminedichloroplatinum(II) complex; [Pt(NH$_3$)$_2$Cl$_2$], performs the geometrical isomerism. In the *cis* complex, the chloro groups are closer to

each other (on the same side of the square) than they are in the *trans* complex.
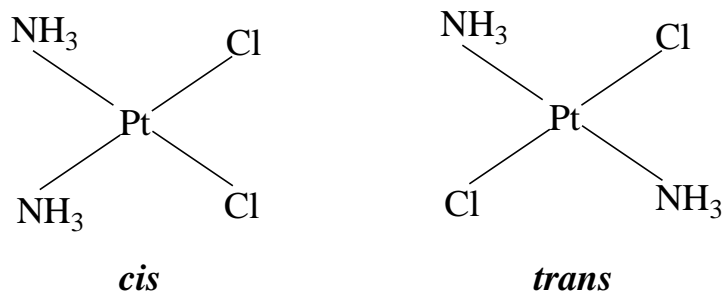
cis and *trans* isomers of diamminedichloroplatinium.

Note that, complexes of coordination number 4 that have tetrahedral structure do not exhibit geometrical isomerism because all ligands in the tetrahedral complex are adjacent to each other.

7- Optical Isomerism:

Optical isomerism arises when two compounds exist which have configurations of atoms or groups in space about the central atom such that one structure is the mirror image of the other. Thus, optical isomers have the same stoichiometry and the atom-to-atom bonding sequence, but they differ in the details of the arrangement of atoms in space. This phenomenon is also called **enantiomorphism**.

An optically active substance has the power of rotating the plane of polarized light *trans*mitted through it. The plane of the ray may be rotated to

the right, in which case the substance is called the ***dextrorotatory*** (*d*) form, or it may be rotated to the left, in which case the substance is designated as the ***levorotatory*** (*l*) form. The optical isomers are thus called *dextro* and *levo* isomers.

A single solution containing equal amounts of the two isomers does not rotate a plane of polarized light because the equal and opposite effects of the two isomers exactly cancel. This mixture is optically inactive, and it is so-called a ***racemic mixture***.

Now, begin by considering tetrahedral ML_4. If four different groups (ligands) are bound to a central metal atom, the molecule can exist in two forms that are mirror images of one another, but where one form cannot be superimposed on the other. In coordination chemistry there are no examples of stable complexes with a metal bonded tetrahedrally to four different types of ligands, so no optical isomerism can be existed for tetrahedral complexes.

The situation is quit different with octahedral complexes. The *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium (III) geometric isomer exists in two forms that bear the same relationship to each other as left and right hands. They are non-superimposable mirror images of each other and are called optical isomers, or enantiomers, as shown in the following figure. (Note that, the other geometric isomers of the complex ion $[Cr(NH_3)_2(OH_2)_2Br_2]^+$ do not give up optical isomerism.)
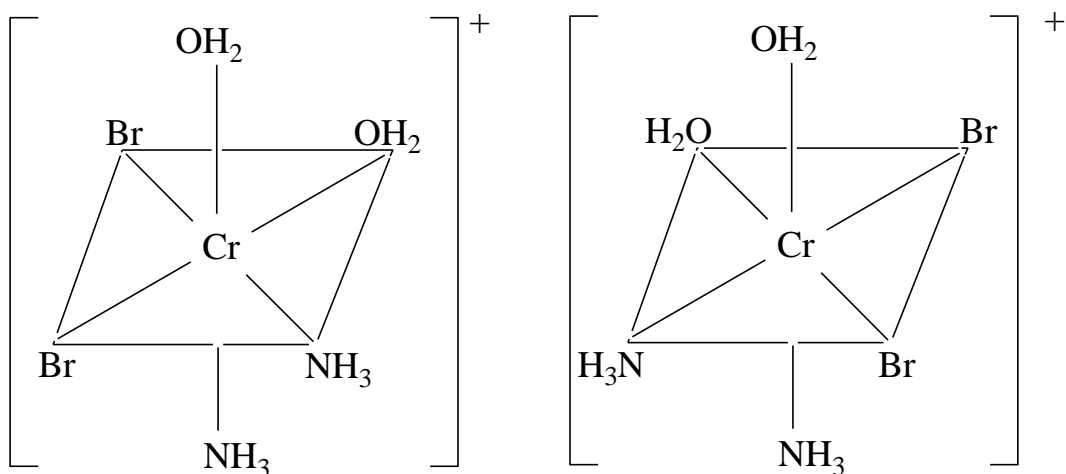
Optical isomers of cis-diammine-cis-diaqua-cis-dibromochromium(III) ion

Optical isomerism in octahedral structures is occurred also by the complexes of the types $[M(AA)_3]$, $[M(AA)_2B_2]$, and $[M(AA)_2BC]$, in which AA represents a symmetrical bidentate ligand like ethylenediamine or the oxalate ion. An example of a pair of optical isomers is shown bellow:
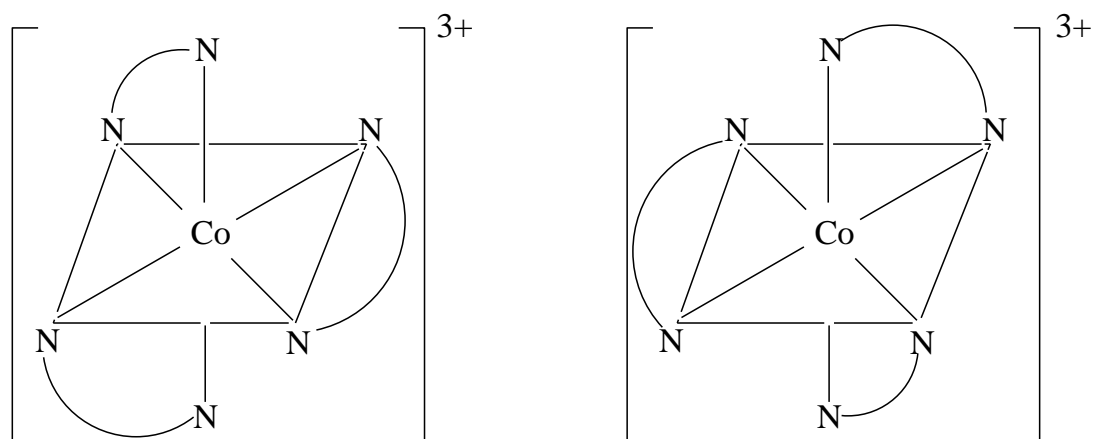

Λ-tris(ethylenediamine)cobalt(III) ion   Δ-tris(ethylenediamine)cobalt(III) ion

Λ (lambda) = levo, and Δ (delta) = dextro

Coordination complexes in Biology

    Coordination complexes, particularly chelates, play fundamental roles in the biochemistry of both plants and animals. At least nine transition elements– vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and molybdenum– are essential in trace amounts to life.

    Three of the many biologically important substances that are simultaneously coordination complexes are *hemoglobin*, in which Fe is chelated, *chlorophyll*, in which Mg is chelated, and *vitamin B₁₂*, in which Co is chelated.

**Porphine**   **Heme**
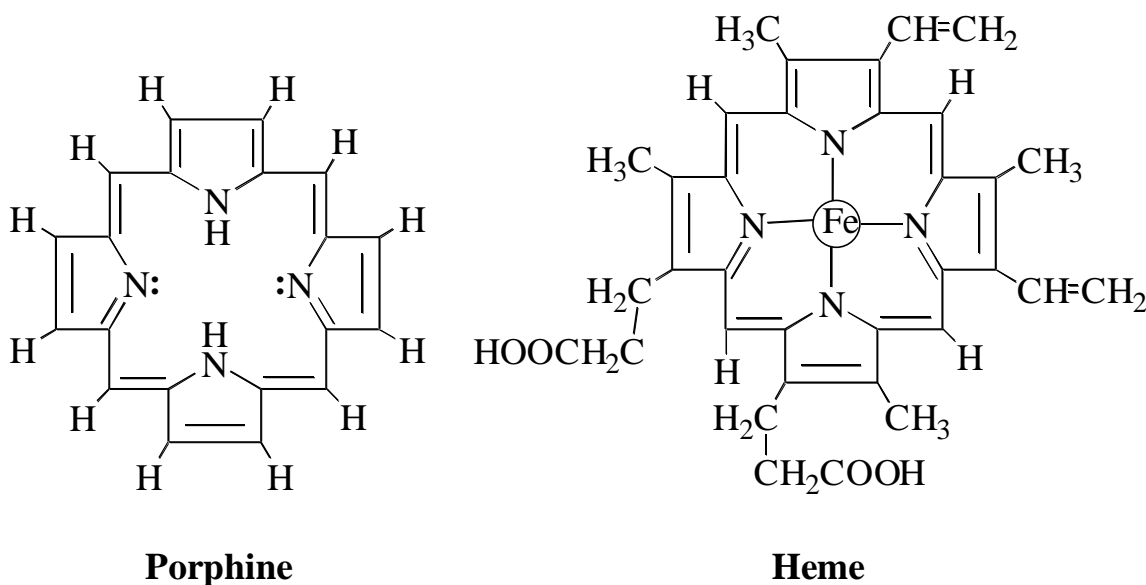
    Several of the most important complexes are based on the organic compound *porphine*, which has the approximately planar structure shown above. Donation of the two acidic (N-bound) hydrogen ions from porphine

to some base leaves (porphine)$^{2-}$, which has four nitrogen atoms ready to bind to a metal ion M^{2+} and form a chelate structure. This tetra dentate ligand, modified by the addition of several side groups, gives a complex with Fe^{2+} ions called **heme**, as shown above.

The absorption of light by heme is responsible for the red color of blood. In hemoglobin, the compound that transports oxygen in the blood, the fifth coordination site of the iron (II) ion binds **globin** (a high-molar-mass protein), and the sixth is occupied by water or molecular oxygen. In case of carbon monoxide poisoning, CO molecules occupy the sixth coordination site and block the binding and transport of oxygen. Hemoglobin has a complex structure that contains four such heme groups.

Photosynthesis depends on the properties of chlorophyll, which contains a derivative of the porphine molecule with different side groups and with a magnesium ion at its center, as shown in the figure. The aqueous Mg^{2+} ion does not absorb light in the visible region of the spectrum, but chlorophyll, in which Mg^{2+} is chelated, does. Absorption of light by this complex provides the energy to carry out photosynthesis, producing **glucose** (a sugar) from water and carbon dioxide:

$$6\ CO_2(g) + 6\ H_2O(l) \rightarrow 6\ O_2(g) + C_6H_{12}O_6(aq)$$
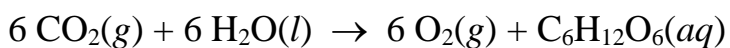
The appearance of chlorophyll and related substances in the early biological history of the earth provided a way for the energy of the sun to drive the above reaction, which is nonspontaneous. The accumulation of O_2 about two billion years ago profoundly changed the nature of the atmosphere

from a reducing environment (dominated by CO_2, CH_4, and NH_3) to an oxidizing environment (dominated by oxygen). The harvesting of the sun's energy using chlorophyll led to life as we know it on earth.

Vitamin B_{12} is a naturally occurring compound that is useful in the treatment of pernicious anemia and other diseases. The structure of vitamin B_{12} has certain similarities to that of heme and chlorophyll. Again, a metal ion is coordinated by a planar tetradentate ligand, with two other donors completing the coordination octahedron by occupying *trans* position. In vitamin B_{12}, the metal ion is cobalt and the planar ring is not porphine but *corrin*, as shown in the figure.

In the human body, enzymes derived from vitamin B_{12} accelerate a range of important reactions, including those producing red blood cells.
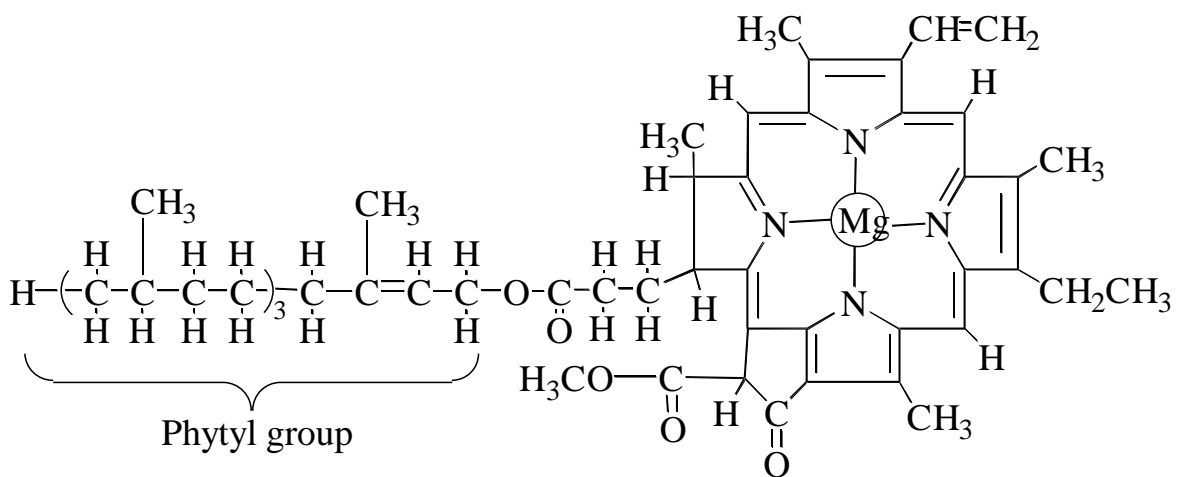
The structure of Chlorophyll *a*, $C_{55}H_{72}MgN_4O_5$.

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