Coordination Compounds

Coordination Compound:

a compound in which a central metal ion is attached to a group of surrounding molecules or ions by coordinate covalent bonds.

Central metal ion + n Ligands → Complex

Central metal ion always transition element
has empty orbital

Ligands : ions or molecules have donor atom
(has lone electron pairs)

An introduction to complex ions with an explanation of what ligands are and how they bond to the central metal ion.

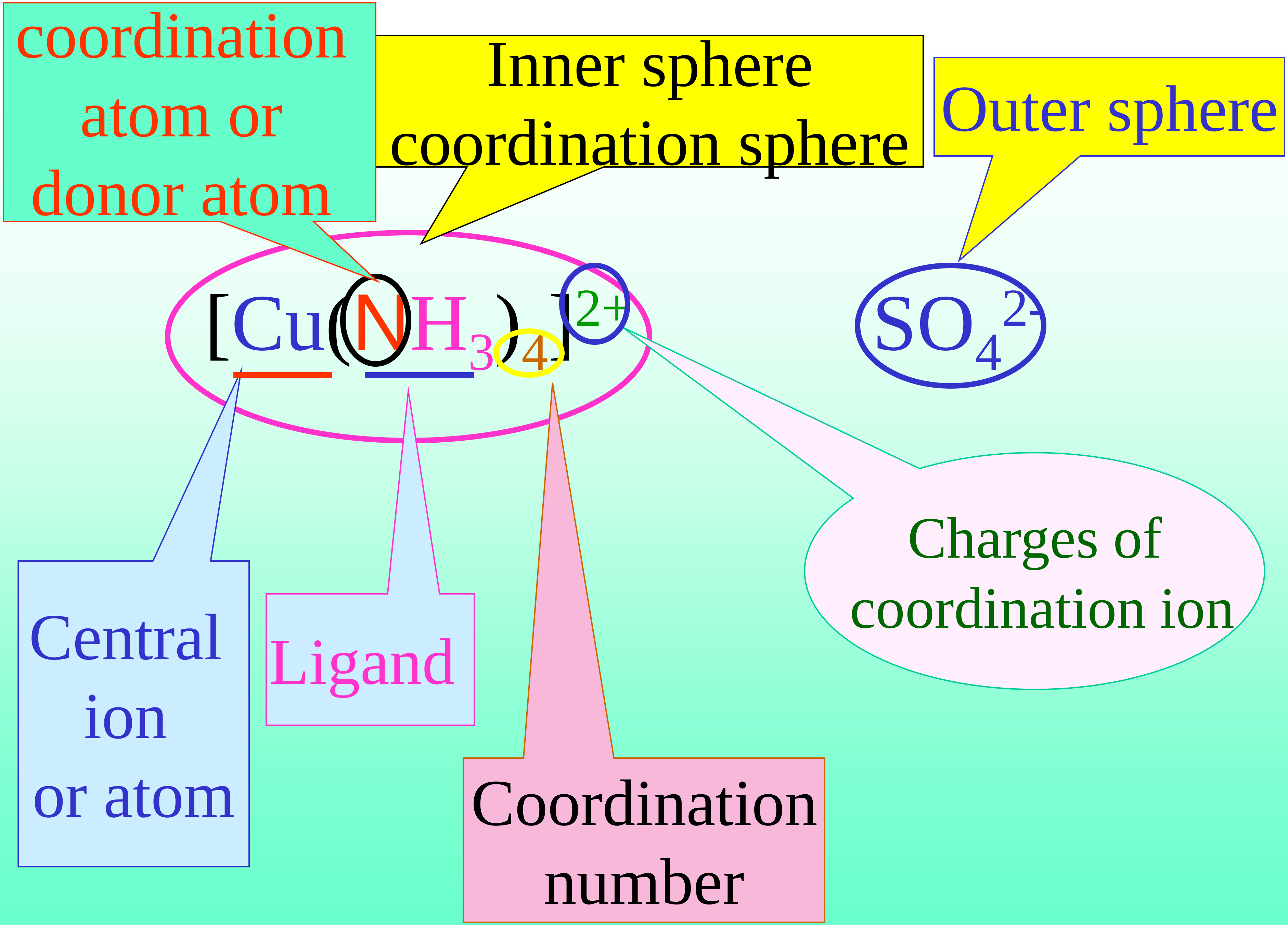
complex ion

- central metal ion
  - *transition metals* (*but not all)*
- ligands *(anions or polar molecules*)

Ligands and Donor atom

- Ligands: ions or molecules that is bound directly to the metal atom. e.g. NH_3, CN^-, H_2O, Cl^-, I^-
- Donor atom: the atom in a ligand that is bound directly to the metal atom , has lone electron pairs.

e.g. C, N, O, S, F, Cl, Br, I



coordination atom or donor atom

Inner sphere coordination sphere

Outer sphere

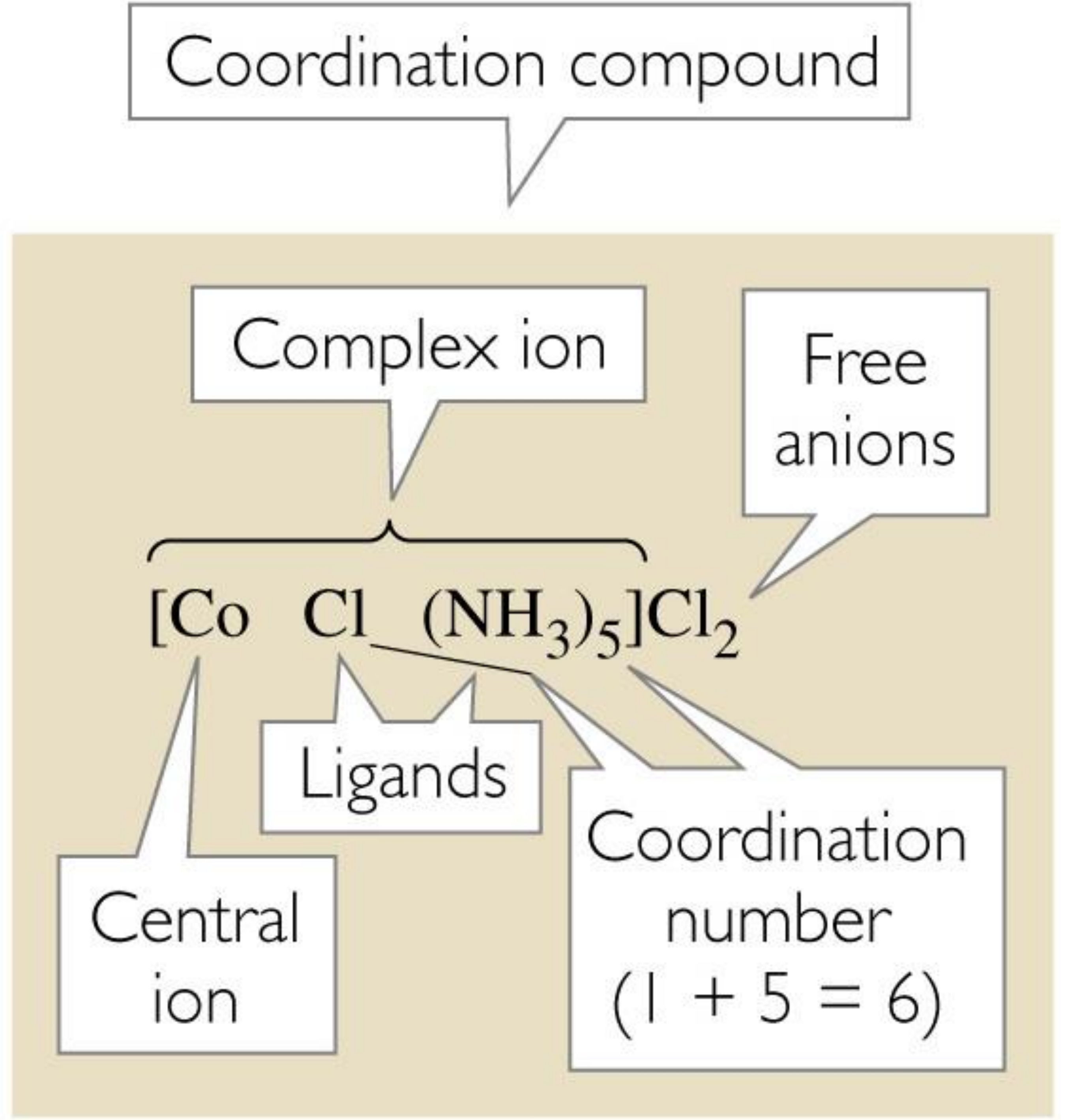
$[Cu(NH_3)_4]^{2+}$ SO_4^{2-}

Central ion or atom

Ligand

Coordination number

Charges of coordination ion



Coordination compound

Complex ion

Free anions

$[\mathbf{Co\ Cl\ (NH_3)_5}]\mathbf{Cl_2}$

Central ion

Ligands

Coordination number (1 + 5 = 6)

The features of coordination ion

- Contains a complicated ion - coordination ion

  $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^{+}$, $[Fe(CN)_6]^{4-}$

- Metal ion bonded with other ion or molecule by coordination bond

Charges of coordination ion:

Charges of coordination ion =
the sum of charges of central ion and ligands

e.g. $K_3[Fe(CN)_6]$ Fe^{3+}

$[Fe(H_2O)_6]Cl_3$ Fe^{3+}

$K_4[Fe(CN)_6]$ Fe^{2+}

Coordination number

- Coordination number: the number of donor atoms surrounding the central metal atom in a complex ion. Commonly, it is 2, 4 ,5 or 6

  For : $\mathbf{[Cu(NH_3)_4]\ SO_4}$, $[Fe(CN)_6]^{4-}$

  Coordination number = ligand number

What are the oxidation numbers of the central metal in the complexes below?

- $K_3[FeF_6]$

- $Na_2[Ni(CN)_4]$

Coordination Compounds

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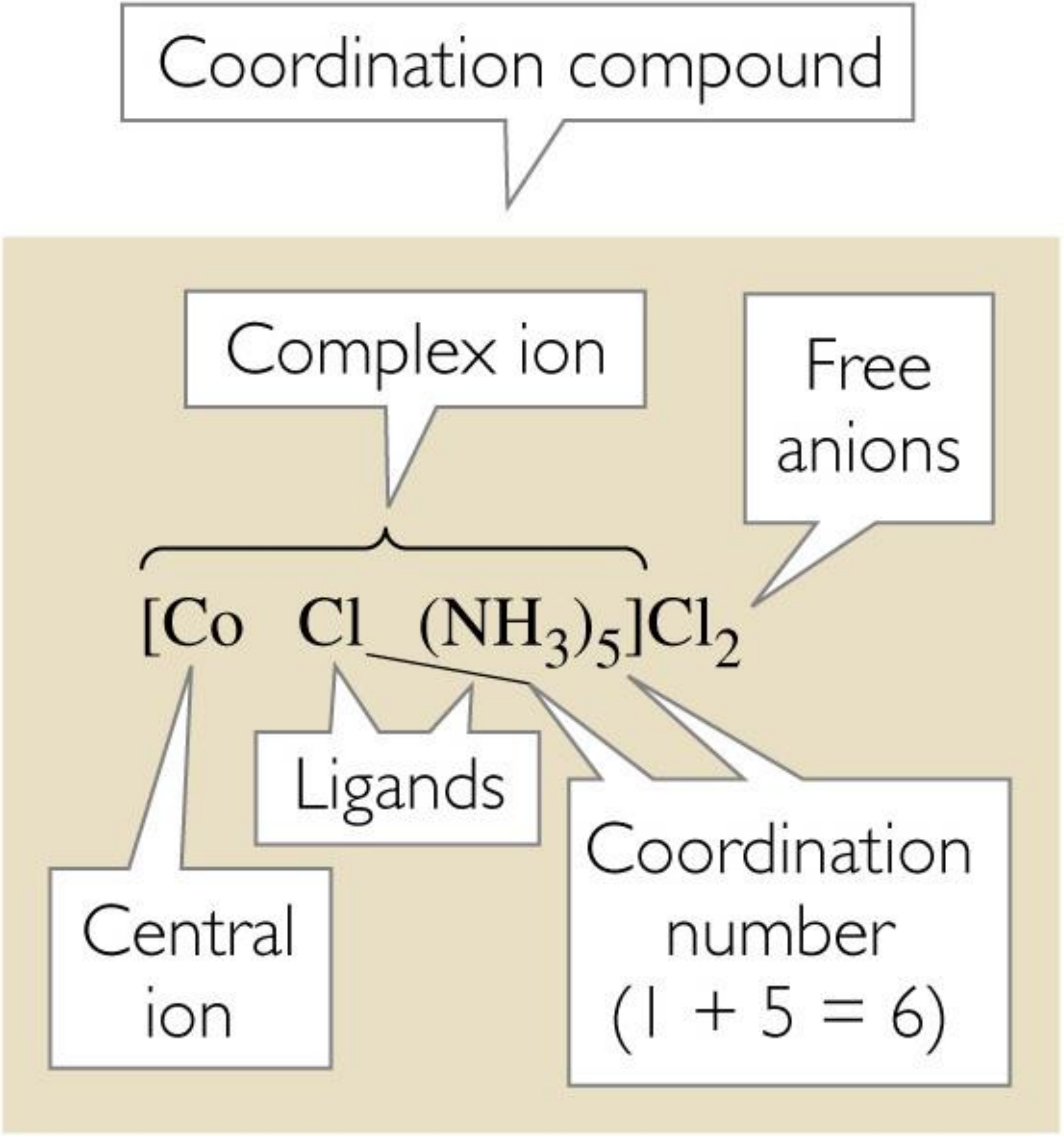


Coordination compound

Complex ion

Free anions

$[\mathrm{Co}\ \ \mathrm{Cl}\ \ (\mathrm{NH_3})_5]\mathrm{Cl_2}$

Ligands

Central ion

Coordination number (1 + 5 = 6)

Ligands

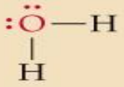
- Depending on the number of donor atoms present in the molecule or ion, ligands can be classified as：

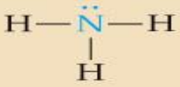
monodentate： (H_2O: :NH_3)

bi dentate： （$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ ）

polydentate： (EDTA)

Monodentate ligands

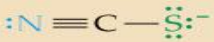

Water


Ammonia


Chloride ion

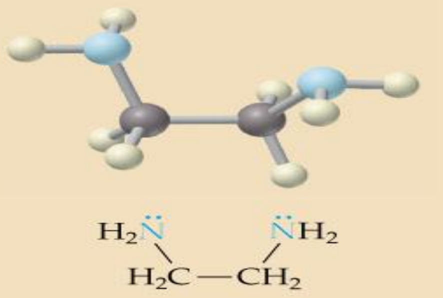

Cyanide ion

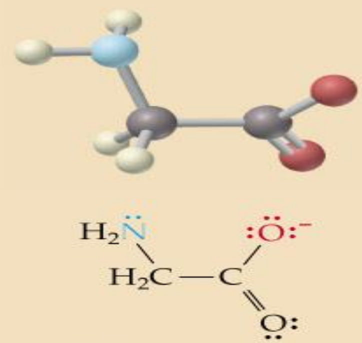

Carbon monoxide

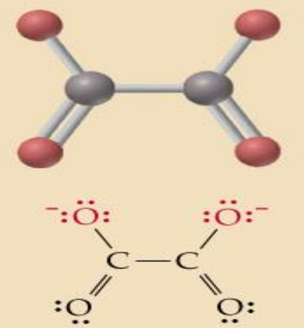

Thiocyanate ion


Hydroxide ion

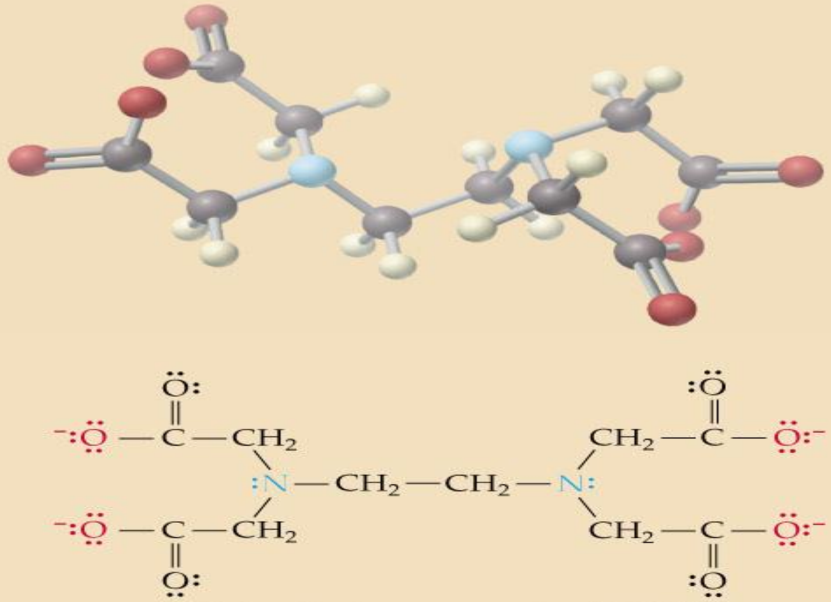
Bidentate ligands


Ethylenediamine (en)

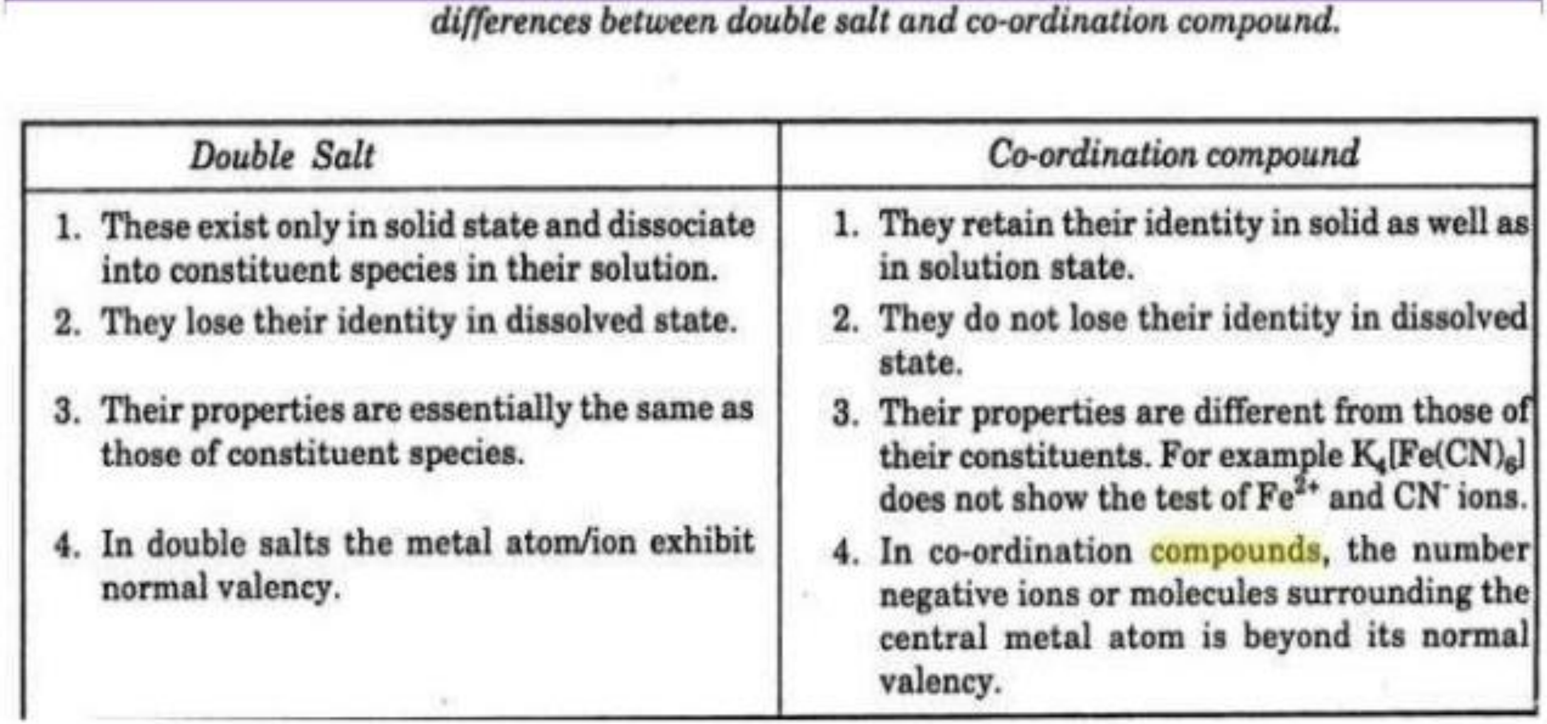

Glycinate ion (gly⁻)


Oxalate ion

Hexadentate ligand


Ethylenediaminetetraacetate ion ($EDTA^{4-}$)

On the basis of nature, addition (or) molecular compounds are divided into two categories. They are double salts and coordination (or) complex compounds.



differences between double salt and co-ordination compound.

Double Salt	*Co-ordination compound*
1. These exist only in solid state and dissociate into constituent species in their solution.	1. They retain their identity in solid as well as in solution state.
2. They lose their identity in dissolved state.	2. They do not lose their identity in dissolved state.
3. Their properties are essentially the same as those of constituent species.	3. Their properties are different from those of their constituents. For example $K_4[Fe(CN)_6]$ does not show the test of Fe^{2+} and CN^- ions.
4. In double salts the metal atom/ion exhibit normal valency.	4. In co-ordination compounds, the number negative ions or molecules surrounding the central metal atom is beyond its normal valency.

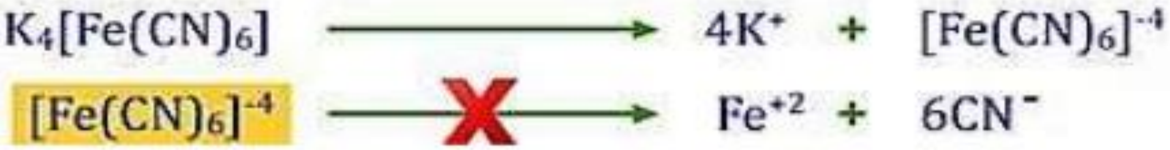
Mohr's salt: $FeSO_4.(NH_4)_2SO_4.6H_2O$ double salt.

Double salt and coordination compound

- Ex: An aqueous solution of potash alum will give the tests for K^+, Al^{+3}, and SO_4^{-2}

$K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow 2K^+ + 2Al^{+3} + 4SO_4^{-2} + 24H_2O$

- On the other hand, coordination compounds are molecular compounds that retain their identity even when dissolved in water.
- Ex: When potassium ferrocyanide is dissolved in water, it does not give the usual tests for Fe^{+2} and CN^{-1}, indicating that, $[Fe(CN)_6]^{-4}$ does not dissociate into Fe^{+2} and CN^{-1}.



$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{-4}$

$[Fe(CN)_6]^{-4} \xrightarrow{\times} Fe^{+2} + 6CN^-$

- If solution containing cobalt (II) chloride and ammonium chloride is treated with ammonium hydroxide then with current of air, then made strongly acidic with hydrochloric acid, several products are obtained:

$CoCl_3.6NH_3$	yellow
$CoCl_3.5NH_3$	purple
$CoCl_3.4NH_3$	green
$CoCl_3.3NH_3$	

- A remarkable properties of these cobaltammines compounds are observed:

1. The ammonia in them is not readily removed by acid or when heated to boiling
2. Treatment with sodium hydroxide does not precipitate the cobalt

this means that all ammine groups and cobalt are inert in the compounds

3. Treatment the compounds described before with silver nitrate, very significant difference is found in the behavior of the chloride atoms:

$CoCl_3.6NH_3 + AgNO_3 \rightarrow 3AgCl$

$CoCl_3.5NH_3 + AgNO_3 \rightarrow 2AgCl$

$CoCl_3.4NH_3 + AgNO_3 \rightarrow 1AgCl$

$CoCl_3.3NH_3 + AgNO_3 \rightarrow$ none of AgCl

$CoCl_3.6NH_3 \rightarrow 3AgCl + Co.6NH_3$

$[Co(NH_3)_6]Cl_3$

$CoCl_3.5NH_3 \rightarrow 2AgCl + CoCl.5NH_3$

$[CoCl(NH_3)_5]Cl_2$

$CoCl_3.4NH_3 \rightarrow 1AgCl + CoCl_2.4NH_3$

$[CoCl_2(NH_3)_4]Cl$

$CoCl_3.3NH_3 \rightarrow$ -ve AgCl + $CoCl_3.3NH_3$

$[CoCl_3(NH_3)_3]$

- Note that:
- In all compounds cobalt atom surrounded by six groups
- Metals , ions or molecules in Inner sphere (coodination sphere) all are inert (inactive)
- Ions in the outer sphere are labile (active)

Summary of Werner's theory

1. Most of the elements exhibit two types of valencies namely primary valence and secondary valence and each element tend to satisfy both the valencies. the primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

2. The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions. For example in the complex $CoCl_3.6NH_3$, The primary valence of Co is +3 and is satisfied by $3Cl^-$ ions.

3. The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these. For example, in $CoCl_3.6NH_3$ the secondary valence of cobalt is 6 and is satisfied by six neutral ammonia molecules, whereas in $CoCl_3.5NH_3$ the secondary valence of cobalt is satisfied by five neutral ammonia molecules and a Cl^- ion.

4. Every complex is characterized by “coordination number” which indicates the number of atoms, ions, or molecules that surround the central atom. The coordination number may be high or low.

5. The coordinated atoms are on the *inner sphere* of the complex compound. They are known as *addends* (or *ligands*).

6. The central atom and the inner sphere constitute the nucleus of the complex, which is enclosed in brackets. The nucleus of a complex may be neutral or charged positively as well as negatively.

7. If the nucleus of a complex is charged, the complex has an outer sphere because a charged complex (or rather its nucleus) may be attract oppositely charged ions.

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.

9. The central atom is usually a cation (Co^{3+}, Fe^{3+}, etc) or less commonly an anion (e.g., O^{2-} in beryllium oxyacetate $[[O^{2-}]Be(CH_3COO)_6]^0$. Sometimes the central atoms are formally uncharged particles for ex. $[Ni(CO)_4]$.

10. The main and secondary valencies according to werner in the nuclei of the complexes do not differ either in strength or in nature.

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.

Limitations of the Werner's theory

Werner could not provide a valid explanation of the nature of secondary valency as well as the factors responsible for coordination of the central ion with a particular number of ligands.

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).

- 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.

$$NH_3 + BF_3 \rightarrow \quad H_3N \rightarrow BF_3 \ \text{ or } \ H_3N^+ \rightarrow {}^-BF_3$$

- An important distinction of donor-acceptor bonding from the ordinary covalent one is not only ***its origin*** but also, and mainly, its ***ionic nature***.
- 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.

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

A. 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.

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.

B. Complexes resulting from the formation of coordinate bonds:

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.

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

1. The central ion tends to accept electrons to fill incomplete stable orbitals, and each completed orbital contains a pair of electrons of opposite spins.
2. 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:

“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 $24 + (6 x 2) = 36$.

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	

Nomenclature of Coordination Compounds

$[Co(NH_3)_5Cl]Cl_2$

$$\overbrace{\underbrace{\text{Chloro}}_{\downarrow\ \text{(Cl}^-\text{ ligand)}}\underbrace{\text{pentaammine}}_{\downarrow\ \text{(5 NH}_3\text{ ligands)}}\underbrace{\text{cobalt(III)}}_{\downarrow\ \text{(Cobalt in +3 oxidation state)}}}^{\text{Cation}}\quad\overbrace{\text{Chloride}}^{\text{Anion}}$$

$K_4[Fe(CN)_6]$

$$\overbrace{\text{Potassium}}^{\text{Cation}}\quad\overbrace{\underbrace{\text{Hexacyano}}_{\downarrow\ \text{(6 CN}^-\text{ ligands)}}\underbrace{\text{ferrate(II)}}_{\downarrow\ \text{(Iron in +2 oxidation state)}}}^{\text{Anion}}$$

1. $[Ni(H_2O)_6]SO_4$

Hexaaquonickel(II) sulfate

2. $[Cr(en)_2(CN)_2]Cl$

Dicyanobis(ethylenediamine)chromium(III) chloride

3. $K[Pt(NH_3)Cl_3]$

Potassium trichloroammineplatinate(II)

4. $[Co(NH_3)_6]Cl_3$

Hexaamminecobalt(III) chloride

5. $[Co(NH_3)_5Cl]^{2+}$

Chloropentamminecobalt(III) ion

6. $[Co(NH_3)_4SO_4]NO_3$

Sulphatotetramminecobalt(III) nitrate

7. $[Co(NH_3)_3(NO_2)_3]$

Trinitrotriamminecobalt(III)

8. $[Cr(en)_3]Cl_3$

Tris(ethylenediamine)chromium(III) chloride

9. $K_4[Fe(CN)_6]$

Potassium hexacyanoferrate(II)

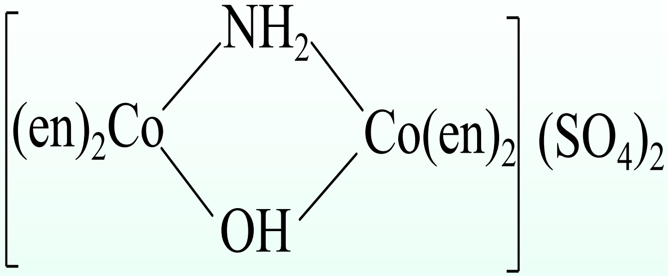
10. $[Pt(py)_4][PtCl_4]$

Tetrapyridineplatinum(II)tetrachloroplatinate(II)

11. $[(NH_3)_5Co.NH.Co(NH_3)_5](NO_3)_5$

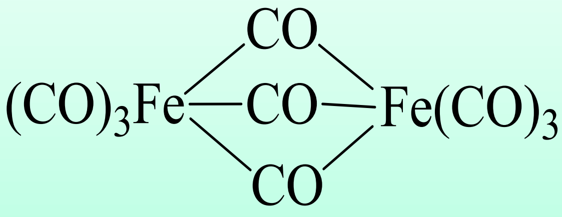
Decammine-μ-amidodicobalt(III) nitrate

12.



Tetrakis(ethylenediamine)-*μ*-amido-*μ*-hydroxo-dicobalt(III) sulphate

13.



Tri-μ-carbonylbis(tricarbonyliron(III))

OR

Hexacarbonyltri-m-carbonyl-diiron(III)

14. $[Cr(H_2O)_4Cl_2]Cl$

Dichlorotetraaquochromium(III) chloride

15. $[Co(NH_3)_4(H_2O)Cl]Br_2$

Chloroaquotetraamminecobalt(III) bromide

16. $[Pt(en)_2Cl_2]Cl_2$

Dichlorobis(ethylenediamine)platinium(IV)

Chloride

17. $[Co(NH_3)_5Br]SO_4$

Bromopentaamminecobalt(III) Sulfate

Practice writing the complex compound formulas:

hexaaquochromium(III) chloride

potassium hexacyanoferrate(II)

potassium hexacyanoferrate (III)

Practice naming some complex compounds:

$[Pt(NH_3)_4]Cl_2$

$[Pt(NH_3)_3Cl]Cl$

$Na[CoCl_4(NH_3)_2]$

$[Pt(Cl_2)(NH_3)_2]$

$K_2[PtCl_4]$

(a) Write the names of the following compounds.

(i) $[Fe(H_2O)_6]Cl_2$

(ii) $[Cu(NH_3)_4]Cl_2$

(iii) $[PtCl_4(NH_3)_2]$

(iv) $K_2[CoCl_4]$

(v) $[Cr(NH_3)_4SO_4]NO_3$

(vi) $[Co(H_2O)_2(NH_3)_3Cl]Cl$

(vii) $K_3[AlF_6]$

Nomenclature of Coordination Compounds

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.

Naming Coordination Compounds

LIGAND	Name of Ligand in Coord. Cpd.
Bromide, Br^-	Bromo
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Hydorxide, OH^-	Hydroxo
Oixde, O^{2-}	Oxo
Carbonate, CO_3^{2-}	Carbanato
Nitrite, NO_3^-	Nitro
Oxolate, $C_2O_4^{2-}$	Oxolato
Ammonia, NH_3	Ammine
Carbon monoxide, CO	Carbonyl
Water, H_2O	Aquo
Ethylenediamine(en)	Ethylenediamine

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 *phen**yl*** and *meth**yl***. 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.

Di	**(2)**
tri	**(3)**
tetra	**(4)**
Penta	**(5)**
Hexa	**(6)**

$[Co(NH_3)_4Cl_2]^+$ are

tetraamminedichloro

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*-.

e.g. $[Cu(en)_2]^{2+}$ bis(ethylenediamine)

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.

$[Cr(NH_3)_4Cl_2]^+$, which is called

tetraamminedichlorochromium(III) ion.

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.

$K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called

hexacyanoferrate(II) ion.

Metal	in anion complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate

Metal	in anion complex
Manganese	Manganate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

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.

Org.Met.Chemistry Of T.E,s.By Robert H.Crabtree.

T.M.org.met.= interaction between inorg.metal and org.molecules.

T.M.ions can bind ligands(L) to give a coord.compounds or complex ML_nas in $M(OH_2)_6^{+2}$ where (M= V,Cr,Mn,Fe,Co,…..).

Organometallic is complex contain an M-C or M-H bond (e.g. $Mo(CO)_6$)

Typical ligands that bind to metals in their lower ox.states are CO,alkenes,arenes e.g.$Mo(CO)_6$, $(C_6H_6)Cr(CO)_3$or $Pt(C_2H_4)_3$.

In this lecturer ,we will review some fundamental ideas of coord.chemistry which also apply to organomet.complexes.

1. Werner complexes.
2. E.A.N.rule and V.B.theory.
3. Soft versus hard ligands.
4. Crystal V.theory.
5. Ligand F.theory.
6. Back bonding.
7. Types of ligands

Werner complexes:

Complexes in which M binds to noncarbon ligands are called classical or Werner complexes e.g. L_nM-$NH_3$where the bond consists of the lone pair of electrons present in free NH_3that are donated to M to form complex.

The metal is a polyvalent Lewis acid accepting the lone pairs of sevseal L,s which act as Lewis bases.

The most common types of complex is ML_6, ML_4 , ML_5.

Finally,the types of complexes as reported by Werner:{ PtCl4} $^{2-,}$ {,Co(NH3)6} $^{3+}$, K2{ PtCl4 }

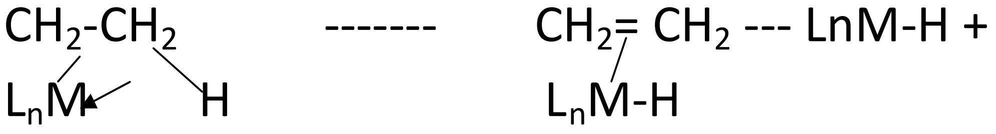
Fourth Year,Chemistry Group.

Metal alkyls,aryls and hydrides.

Attemps to make d-block alkyls failed.This led to the view that transition metal-carbon bonds were unusually weak.In fact ,we now know that such M-C bonds are reasonably strong.Existence of several decomposition pathways that makes many M-alkyls unstable.

1- Beta-elimination. 2- reductive elimination. 3- stability from bulky substituents.

Beta-elim.= the beta-carbon of the alkyl bears a hydrogen,the M-C-C-H unit can take up a roughly coplanar conformation which brings the beta-H close to the metal,and there is a



CH_2= CH_2 i.e. metal alkyl converted into a hydridometal alkene complex.

To have a stable alkyl,we must block the beta-elim.pathway for decomposition. This can happen for: 1-alkyls that have no beta- H e.g. WMe_6 ,$Ti(CH_2ph)_4$,$W(CH_2SiMe_3)_6$, $C_2F_5Mn(CO)_5$,$LAuCF_2CF_2Me$,and $TaCl_2(CH_2CMe_3)_3$.

2- Alkyls for which the beta-H is unable to approach the metal as a result of the geometry of the ligand or because the system is very bulky.e.g. $PtH(C\equiv CH)L_2$ also,$Cr(CMe_3)_4$,,$Pdph_2L_2$,$Cr(CHMe_2)_4$

3- Alkyls in which the M-C-C-H unit cannot become syn-coplanar e.g.cyclic alkyls.

4- A species with firmly bound ligands,which will not dissociate to generate a vacant site:ex,$Cp(CO)_2FeCH_2CH_3$ (no vacant site),$Cp(CO)_3MoCH_2CH_3$,Cp(CO)IrprH.

5-some d^0 alkyls: d(zero) has no.electrons to back donate to sigma * orbital of the C-H bond of Ti(+4) complex.i.e. back donation breaks the C-H bond in the beta elim.This is called agnostic alkyls.

<u>2-Reductive elimination</u>:This is very common decomposition pathway for metal alkyls. This leads to a decrease by two units in both the electron count and the formal ox.s.

$L_nM(Me)X$-------------- LnM' (16 e) + MeX.

<u>3-stability from bulky substituents:</u>

Associative decomposition pathways,such as by reaction with the solvent or with another molecule of the complex is very important especially with bulky coligands.Ex: square planar Ni(II) alkyls are vulnerable to attack along the Z direction perpendicular to the plane.The o-tolyl complex in which this approach is blocked is more stable than the analogous diphenyl(see the Figure in ref.).This steric factor has made the use of bulky alkyl gps.as neopentyl (CH_2CMe_3) or trimethylsilylmethyl(CH_2SiMe_3) common in org.met.chemistry.

Alpha elimination sometimes takes over.This leads to formation of species called carbenes,which have M=C double bonds.

Ex: $L_nM(CH_3)_2$ ------ $L_nM=CH_2$ +CH_4

2 $L_nM=CH_2$ ------ $CH_2=CH_2$

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2- E.A.N.rule and V.B.theory.Ex: prove that the following apply or not E.A.N.rule: $[Fe(CN)_6]^{-4}$,Fe(+2)=26-2=24,6CN=12,total=36=Kr gas.Also $[Ni(CO)4]^0$,Ni=28,4CO=8,total=36=Kr.

$[Fe(CN)6]^{3-}$,Fe(+3)=26-3=23,6CN=12,total=35 (not apply).

Ex: predicat no.of L,s in complex $[Co^{3+} (NH3)n]^3$, Co=27,Co^3+=24,therefore, [24+(2n)]=36,n= 36-24 =12,n =6.

V.B.theory:

[Fe(+2)(CN)6],Fe=----$4S^2 3d^6$, Fe(+2)= $3d^6$

I I I I I I   _   _ _ _

$3d^6$ ------- 4s ----- 4p

II II II - -   -   - - - i.e. d2sp3 or sp3d2 and magnetic moment can be cal.

Also: [Ni(CO)4],Ni =28,i.e $3d^8 4s^2 4p^0$ and after rearrangemet $3d^{10}$ $4s^0 4p^0$(sp3) .

For Ni(+2) complexes ,sp3 is possible and also dsp^2.

3 -Soft versus hard ligands: Metal ions in their usual ox.state tend to bindsaturated L,s. e.g. NH3,H2O or F-,which called hard ligands (low polarizability).

Ag+,Hg+2 and a few others form stronger complexes with unsaturated or polarizable ligands as Br^-,I^-,pph_3 or C_2H_4 (called soft).Also soft ligands with double or triple bondse.g. en, acetylene,benzene.All T.M. can become soft if they are reduced to alow valence and tend to bind soft ligands,the reason:metals have excess electron density and therefore avoid stroge donor L,s but prefer L,s which can form covalencies and that have available empty orbitals. High ox.state metal,are short of electron and require good donor ligands.

4- Crystal field theory: An important advance in understanding the spectra,structure and magnetism of T.M.complexex.The theory explain how the d- orbitals are affected by the presence of L,s.The ligands act as negative charges.As the L approach the M from the six octahedral directions (-+x, -+y ,-+z).The d orbitals take the form:

_ _ eg (point toward L gp.

_ _ _ _ _

_ _ _ t2g(away from L)

The energy difference between the d sigma and d pi set called crystal field splitting .

Ex: Co(+3),Co=$4s^2 3d^7$,Co(+3)=$3d^6$, diamagnetic and spin paired complex .On the other hand if L splitting is smallenough,the electrons may rearrange to give high spin formand paramagnetic.Magnetic moment can be measured.

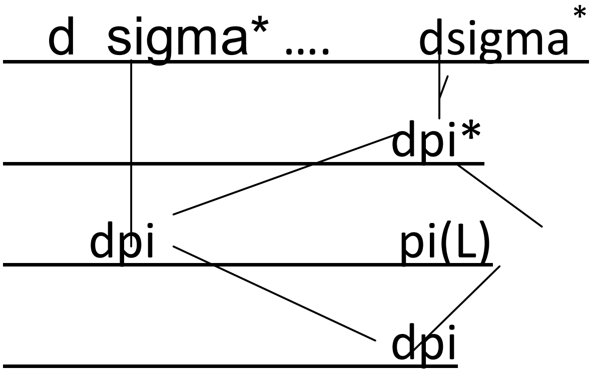
Another ex: octahedral d^7 ions:t_{2g} level will contain 6 electrons and eg will contain one electron.i.e. $t_{2g}{}^6$ eg^1 .The results:d^7 more reactive than d^6 .

Finally, Co(3+) and other d6 ions are referred as coordinatively inert.d3 ions (Cr3+) are also inert(t2g is half filled).On the other hand, Co(2+) and other non d6 or d3 ions can be coordinatively labile.

π (pi) donor ligands:

Ligands such as OR$^-$,F$^-$ and Cl$^-$ are pi donors as a result of the lone pairs that are left one lone pair has formed the M-L sigma bond.

Instead of stabilizing the d –pi electrons of a d^6 ion as does a pi acceptor, these electrons are now destabilized by what is effectively a repulsion between two filled orbitals.This lowers Δ,as shown in next Fig. and leads to a weaker M-L bond than in the pi acceptor case.



The occupied,and relatively stable,lone pair (pi) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled d-pi orbitals of the complex and so decreace Δ. This is effectively a repulsion between two lone pairs, one on the metal and the other on the ligand. If the metal has empty d –pi orbitals as in the d^0 ion Ti^{4+}, pi donation from the ligand to the metal d-pi orbitals now leads to stronger M-L bonding, d^0 metals therefore form particularly strong bonds with pi donor ligands.

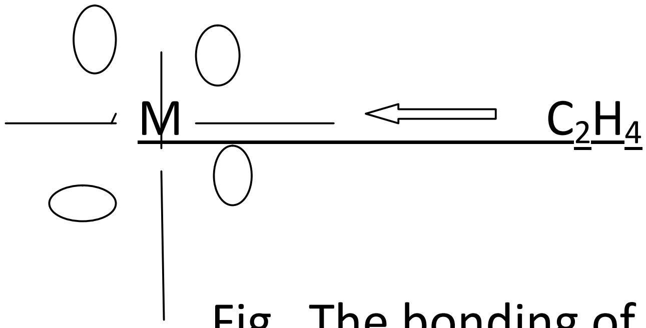
7- Types of ligands:

Most ligands form the M-L sigma bond by using a lone pair (nonbonding electrons in the free ligand) = classical Werner coord. Complexes.

There are two other types of L found in org.met.compounds:ex: C_2H_4 and H_2 are typical

Ethylene, $CH_2 = CH_2$

C_2H_4 is a molecule that has no lone pairs ,yet it binds strogly to low valent metals. The homo is the C=C pi bond, and it is these electrons that form the



Fig…The bonding of a pi bond donor(ethylene) to a metal.It is clear that the electron donation takes place from the filled C=C pi bond to the empty d sigma orbital on the metal.On the other hand, the back donation takes place from the filled M(dpi) orbital to the empty C=C pi *.This type of bonding is sometimes represented as eta-two ethylene, where eta represents the hapticity of the ligand,defined as the number of atoms in the ligand bonded to the metal.

Molecular hydrogen (H_2): Hydrogen has neither a lone pair nor a Pi-bond,yet it also binds as an intact molecule to metals as [$W(eta\text{-}H_2)(CO)_3L_2$]. The only available electron pair is the H-H sigma bond and this becomes the donor.

Metal orbitals H-H

Back donation is accepted by the H_2 sigma* orbital. Electron donation from the filled H-H sigma bond to the empty dsigm orbital on the metal. The back donation takes place from the filled M(d pi) orbital to the empty H-H sigma*.

Related sigma-bond complexes are formed with C-H, Si-H ,B-H and M-H bonds.

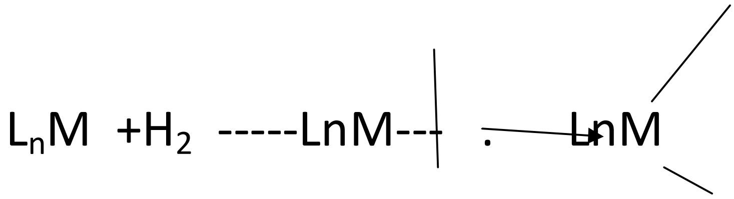
In general, the basicity of electron pairs decreases in the order: lone pairs>pi-bonding pairs>sigma-bonding pairs because being part of a bond stabilizes electrons.Therefore,the usual order of binding ability is as follows:

Lone pair donor>pi-bond donor>sigma-bond donor.In the pi bond a M(d-pi) electron pair is donated to an empty antibonding orbital of the ligand,usually a pi-* for pi-bond donors and a sigma* for sigma-bond donors.

Back bonding into C_2H_4 weakens the C=C pi bond but not break it because C_2H_4 is still held together by strong C-C and C-H sigma bonds that are not involved in M-L bond formation.

For sigma-bond donors such as H_2,forming the M-L sigma bond partially depletes the H-H sigm bond because electrons that were fully engaged in keeping the two H atoms together in free H2 are now also delocalized over the metal.

Back bonding into the H-H sigma* causes additional weakening of the H-H sigma bond because the sigma*is antibonding with respect to H-H.Eventually the H-H bond breaks and a dihydride is formed.



$L_nM + H_2$ -----LnM--- . $\rightarrow$ LnM

This is called the oxidative addition reaction.

Some ligands have several types of electron pair available for bonding e.g. aldehydes H-C -R have the C=O pi bond and lone pairs on the oxygen.When they act as pi-bond donors,aldehydes bind side-on like ethylene and when they act as lone pair donors,they bind end-on.

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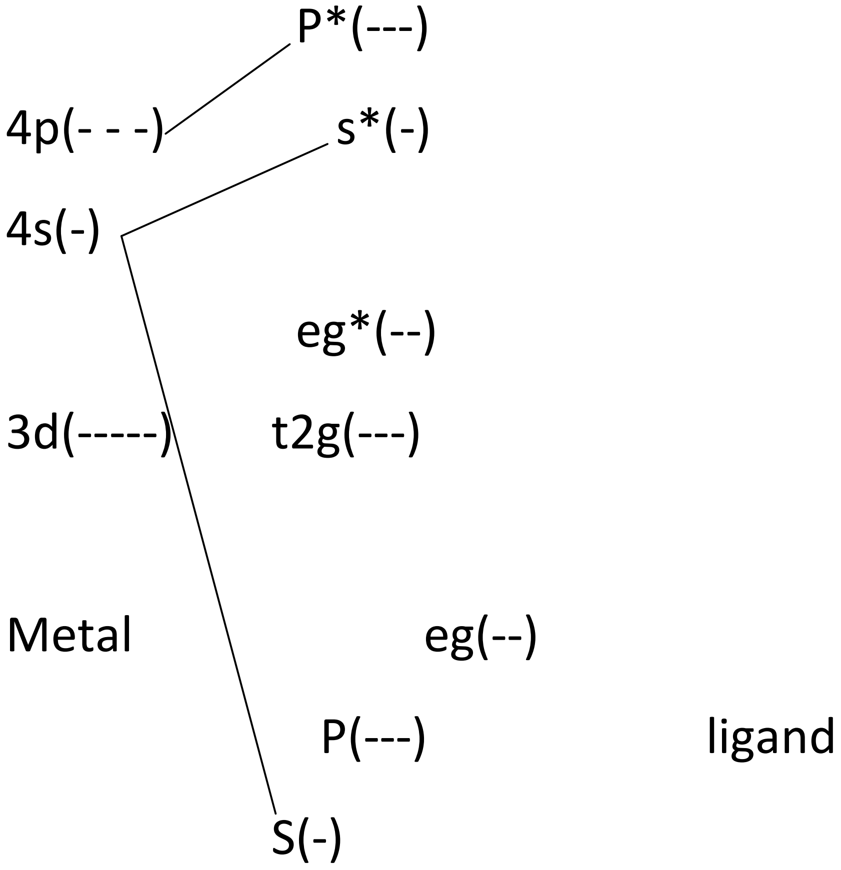
Spectrochemical Series: The following ligands refer to their effect on splitting d- orbitals (high or low,i.e. weak or strong ligand fields).The order is from left to right :CO> CN^- >NO^{2-}> 1,10 phenanthroline > dipy >en > NH_3 >py >EDTA > NCS^- >H_2O > $C_2O_4^{2-}$> OH^- >F^- > S^{2-} >Cl^- >SCN^- >Br^- >I^-

5-Ligand Field Theory: (M.O.theory)

We consider S, three p and five d orbitals of metal as well as the six lone pair orbitals of pure sigma donor ligands in octahedral around the metal.

Six of metal orbitals (s ,three p and two d-sigma)find symmetry matches in the six L lone pair orbitals.

In combining the six M orbitals wiyh six L orbitals, we make a bonding set of six that are stabilized, and an antibonding set of six (the M-L antibonding sigma levels) that are destabilized when the six L gp.approach bonding distance.The remaining d –pi set do not find a match among the L orbitals and remain nonbonding.



In a d^6 ion,we have 6e from Co(+3) and 12e from the L,giving 18e in all.i.e. all the levels up to and including the d-pi set are filled and the M-L sigma* levels remain unfilled. An orbital that is higher in energy will appear higher in m.o.diagram and any electrons in it will tend to be less stable and more available for chemical interactions.

6- Back bonding: Ligands like NH3 are good sigma donors but are not significant pi acceptors.

In contrast, CO is an ex.of a good pi acceptor,(called a pi acid ligand), and tend to be very high-field ligands and form strong M-L bonds.

All have empty orbitals of the right symmetry to overlap with a filled d pi orbital of the metal.In CO, the orbital is CO pi*.

………M…….   …..C=O

The filled metal d pi orbital overlapped with empty CO pi* orbital and give M-CO bond.The M-CO sigma bond is formed by the donation of a lone pair on C into an empty d sigma orbital on the metal.

Ex: ligand field diagram for the case of W(CO)$_6$by including the pi* levels of CO,Figure below:

dpi*   pi*

dsigma*   dsigma*

dpi

dpi

The dpi set of levels still find no match with the six CO sigma orbitals,which are lone pairs on C.They do interact strongly with the empty CO pi* levels. With d6 complex,the result is that d pi that were metal centered now spend some of their time on the ligands.This is called back bonding.This can also happen in d^2 or higher(d^0 ion like Ti^{+4} cannot back bond i.e. cannot form stable carbonyl complexes.

As antibonding orbitals ,the CO pi* level are highin energy,but they are able to stabilize the dpi set.The results are : 1- The L.F.splitting parameter rises.2- Allows low valent or zero valent metals to form complexesTherefor,in $W(CO)_6$ back bonding is so effective that compound is air stable and relatively unreactive. In $W(pMe_3)$ back bonding is inefficient and the compound is very air sensitive and reactive.

Frontier Orbitals: Each L has a filled orbital that act as a sigma donor and an empty orbital that acts as a pi acceptor.The highest filled (homo) and lowest unoccupied molecular orbitals(lumo) of L,respectively.The homo of L is a donor to the lumo of the metal which is normally d_{sigma}. The lumo of the ligand accepts back donation from a filled d pi orbital of the metal.

General properties of organometallic complexes.

1- The metals are more electron-rich, in the sense that the metal bears a greater negative charge in the org.met.complex.
2- The M-L bonds are much mote covalent and often have a substantial pi-component.
3- The metal d-orbitals are higher in energy and by back donation perturb the electronic structure of the ligands much more than is the case for coord.compounds.
4- The org.met,ligands can be polarized and therefore activated towards chemical reactions,sigma and pi bonds in the ligands can be weakened or broken and chemical bonds can be made or broken within and between different ligands.

The 18-electrons rule

This rule is a way to help us decide whether a given d- block org.met.complex is likely to be stable.Ex:CH_5 requires a 5-valent carbon and is therefore not stable. Stable compounds as CH_4have the noble gas octet and so carbon can be thought of as following an 8- electron rule.Carbon using its S and three p orbitals to form four filled bonding otbitals and four unfilled antibonding orbitals.Using covalent model, the eight electrons required to fill the bonding orbitals,,four come from C and one each comes from the four H.Each H atom is being a 1e ligand to carbon.

Using an ionic model on the compound CH_4:each electron pair in any bond is assigned to the most electronegative of the two atoms or gps that constitute the bond,i.e. C^{-4}+ $4H^{+}$(C more electronegative) i.e. CH_4 is 8e compound with an oxidation state of -4 (written C(-IV))

The 18e rule which applies to many low –valent T.M. complexes follows a similar line as CH_4.The M has one S, three P and five d orbitals.So we need 18e to fill all 9 orbitals,some will come from the M, the rest from the ligands.

<u>Counting number of electrons</u> :

For carbonyl complexes: each M contributes the same no. of electrons as its gp.no. and each CO contributes 2e for its lone pair.If we start with an odd no.of electrons on the M,we can never reach an even no.18, by adding 2e ligands like CO.

Ex:In $V(CO)_6$ the complex is 17e, but is easily reduced to the 18e anion $V(CO)_6^-$. The $Mn(CO)_5$ also 17e,does dimerize, probably because as a 5 coord.species,there is more space available to make M-M bond.This completes the noble gas conf.for each M because the unpaired electron in each fragment is shared with the other in forming the bond { $(CO)_5$ Mn-M-n $(CO)_5$}.

In the 17e fragment $Co(CO)_4$,dimerization also takes place via a M-M bond, but a pair of CO also move into bridging positions.This makes no. diff.in the electron count,because the bridging CO is a 1e ligand to each M,so an M-M bond is still required to attain 18e.

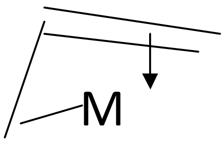
Unfortunately, there are two conventions for counting electrons: ionic and covalent models.Both lead to the same net results, they differ only in the way that the electrons are considered as coming from the metal or from the ligands. Ex: $HMn(CO)_5$,covalent argue that the H atom (one e) is coord. To a 17e $Mn(CO)_5$

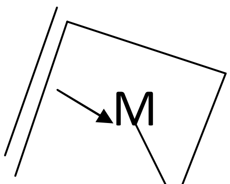
fragment.Ionic model say an anionic $2eH^-$ ligand,coord.to a cationic 16e $Mn(CO)_5^+$.The reason is that H is more electronegative than Mn.

Generally,the symbol L = a neutral ligand which can be : a lone pair donor e.g. CO,NH_3, a pi- bond donor e.g. C_2H_4 and a sigma bond donor e.g.H_2which are all 2e ligands on both models.

The symbol X= ligands such as H,Cl,or Me whichare 1e X ligands on covalent model and $2eX^-$ ligands on ionic model.For benzene ,it is considered as a mcombination of three C=C ligands,i.e. L_3.

Another ex: the allyl gp can be considered as a combination of an alkyl and a C=C gp.





The no. of L atoms bound to M is 3 (Fig.1) ,the no.of electrons is 3e on covalent and 4e on ionic model.Also allyl gp.can bind via one carbon only.

i.e. 1e ligand by covalent and 2e ligand via ionic model.

N.P.: A bridging carbonyl is like a keton,it is a one e donor to each metal(both models regard Co as a neutral ligand even when bridging).Other ligands are bridging methylene, M-CH2-M and bridging oxo M-O-M which are 1e ligands to each M on covalent model and 2e ligands on the ionic model.

For complex ions,we have to adjust for the net ionic charge in making the electron count.

Ex: $CoCp_2^+$(Cp= cyclo petenyl) .using covalent model,Co= 9(gp.no.),two Cp gps.add 10 e ,the net charge is 1+,so one electron has been removed to make the cation.i.e. electron count= 9+10+1=18e.

For complex $[MX_aL_b]^{c+}$,the electron count equation is :

e.count= N+a+2b-c (N= gp.no.)

________ ____________ _________

Limitations of the 18-e electron rule:

There are many cases in which the electron count for a stable complex is not 18.

Ex: $MeTiCl_3$(8e),Me_2NbCl_3 (10e),WMe_6 (12e),$Pt(PCy_3)_2$ (14e).,where Cy =cyclohexyl.

$[M(H_2O)_6]^{2+}$, M= V (15e),Cr(16e),Mn(17e),Fe(18e),$CoCp_2$ (19e) and $NiCp_2$ (20e).

The rule works best for hydrides and carbonyls because : these are sterically small,i.e.they will generally bind as are required to achieve 18e.Also,they have high-field ligands,i.e. Δ for the complex will be large.This mean that the d-sigma* that would be filled if the M had more than 18e are high in energy and therefore poor acceptors. On the other hand ,the d-pi orbitals, which have to give up electrons if the molecule had less than 18e are low in energy because of pi-bonding by CO.The d- pi level is therefore a good acceptor and to be stable,a complex must have this level filled.

Conversely,the rule works least well for high-valent metals with weak field ligands.Ex: $[M(H2O)_6]^{2+}$ where(M= V,Cr,Mn,Fe,Co,Ni),H_2O has two lone pairs,one of which it uses to form a sigma bond.This leaves one remaining on the ligand, which acts as a pi-donor to the metal and so lowers $\triangle$,i.e. H2O is therefore a weak field ligand.If energy is small, then the tendency to adopt the 18e is also small because it is easy to add electrons to the low-lying d –sigma* or remove them from the high lying d-pi.

<u>Oxidation State</u>: The ox.state of M in a complex is the charge that the M would have on the ionic model.For neutral complex we count the no.of X ligands.Ex: Cp_2Fe has two L2X ligands and represented as ML_2X_4 ,this means that the ox.s. is 2+,so Cp_2Fe is said to be Fe(II).For a complex ion,we must take accound of the net charge as shown for $[MX_aL_b]^{c+}$ in equation:

OX.S.= c+a ,ex: Cp_2Fe^+ is Fe(III) and $[W(CO)_5]^{2-}$ is W(-II).In addition, no.of d electrons that would be present in the free M ion can be obtained easily.Ex: for Cp_2Fe^+,the ox.s. is Fe(III) which corresponds to Fe^{3+}ion .Fe atom is in gp.8 has 8e and so the ion has 8-3=5e.i.e. $Cp_2Fe^+$is said to be a d^5 complex.The equation is :

n= N – (c+a) = N –c –a .The odd no.for the given comlex implies paramagnetism where 5 e cannot pair whatever the d-orbital splitting.

High ox. s.org.complexs still rather rare.why,the answer is the back donation is severely reduced in higher ox. complexs,the reason is there are fewer nonbonding d electrons available and the increased partial positive charge on the M in high ox.s.complex strongly stabilizes the d level so that any electrons they contain become less available.

Coordination no. and geometry:

Coord.no.= no.of monodentate ligands present in complex e.g. $[PtCl_4]^{2-}$,C.N.=4, $W(CO)_6$,C.N.=6

Unfortunately,the definition of C.N. and geometry is less clear for org,met species as Cp_2Fe. The best suggest solution is to add no. of L and X from all the ligands.

The following summarize the different counting rules:

C.N.= $a+b$, electron counds= $N+a+2b-c$,ox.s.=$a+c$ and $n=N-$ ox.s. $= N-a-c$ where N=gp.no.of metal.

________ __________ __________

Preparation and properties of metal alkyls and metal hydrides complexes. The synthesis of M-alkyls involve:

1- An R^- reaent 2- an R^+ reagent 3- oxidative addition and 4- insertion. (Typical ex.are shown in following equations).

   1-WCl_6 + LiMe -------- WMe_6 + LiCl

   $NbCl_5$ + $ZnMe_2$------ $NbMe_2Cl_3$ + $ZnCl_2$

2- $Mn(CO)_5^-$ + MeI ---- $MeMn(CO)_5$ +I^-

   $Mn(CO)_5^-$ + CF_3COCl ----- $CF_3COMn(CO)_5$ –CO $\longrightarrow$ $CF_3Mn(CO)_5$.

3- Oxidative addition :

   $IrCl(CO)L_2$ +MeI ---- $MeIrICl(CO)L_2$

   PtL_4 + MeI --- $MePtIL_2$.

   $Cr(+2)_{aq}$ + MeI --- $CrMe(H_2O)_5^{2+}$ + $CrI(H_2O)_5^{+2}$

4- By insertion :

   $PtHCl(PEt_3)_2$ + C_2H_4 ----$PtEtCl(PEt_3)_2$

   $Cp(CO)_3MoH$ + CH_2N_2 --- $Cp(CO)_3MoCH_3$

   The important of insertion method it allows us to make an alkyl from an alkene and a metal hydride. Olefin inseration is the reverse of the beta –elim.reaction.The reversibility of M-alkyl can be trapped using fluoroalkyl CF_2=CF_2

,also is to fill the vacant site that opens up on the metal in the insertion with another ligand.

Properties of M-alkyls:

1- Beta-elim.and reductive elim.

$Cr(t\text{-}Bu)_3(L)_3 + (-CMe_2{=}CH_2)$-----$[Cr(t\text{-}Bu)_2H(L)_3]$ - $CHMe_3$ ----- $Cr(t\text{-}Bu)(L)_3$

2- Migratory insertion :

2- $MeMn(CO)_5$ + CO---- ($MeCO)Mn(CO)_5$

3- Electrophilic attack on an alkyl:

$L_nM\text{-}Me + X^+$ ---- LnM^+--(vacant site) + Me-X

where $X^+ = H^+, Br^+$, or $HgCl^+$.

Metal hydride complexes:

Synthesis: 1- By protonation:

$[Fe(CO)_4]^{2-}$ + H+ --- $[HFe(CO)_4]^- + H^+$ --- $H_2Fe(CO)_4$

$Cp_2WH_2 + H^+$ ---- $[Cp_2WH_3]^+$

2- From hydride donors:

WCl_6(acidic) + $LiBEt_3H + PR_3$ ---$WH_6(PR_3)_3$.

3-From H_2: $IrCl(CO)(pph_3)_2$ + H_2--- $IrH_2Cl(CO)(pR_3)_2$

$WMe_6 + PMe_2ph + H_2$ --- $WH_6(pMe_2ph)_3$.

4- From a ligand :

$RuCl_2(pph_3)_3$ +KOCHMe$_2$ +pph$_3$ --- $RuH_2(pph_3)_4$ +Me$_2$CO + KCL.

$Cr(CO)_6$ +OH$^-$ --- [Cr(CO)$_5$(COOH)- - CO$_2$ --- [CrH(CO)$_5$]$^-$ +Cr(CO)$_6$ –CO --- [(CO)$_5$Cr-H-Cr(CO)$_5$]$^-$.

5- Beta- elim.of M-alkyl also used for prep.metal hydride as given before.

Reactions of M-H complexes:

1- Deprotonation:

$WH_6(pMe_3)_3$ + NaH ---- Na[WH$_5$(pMe$_3$)$_3$]+H$_2$.

2- Hydride transfer and insertion:

Cp$_2$*ZrH$_2$ +CH$_2$O ---Cp$_2$*Zr(OMe)$_2$

Cp$_2$ZrHCl +RCH=CH$_2$ ---Cp$_2$ZrCl(CH$_2$-CHR)

3- H atom transfer:

[Co(CN)$_5$H]$^{3-}$ + phCH=CHCOOH –[Co(CN)$_5$]$^{3-}$ +phC.H-CH$_2$COOH .

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Metal carbonyls,carbonyl halides and triphenylphosphine carbonyl halides.

_Preparation neutral metal carbonyls:

1. From metal compounds+ CO+reducing agents.
2. From mono or bi-nuclear carbonyls.
3. From complex cyanides.

Ex: OsO_4+ CO (250c+350p) --- $Os(CO)_5$ + $Os_3(CO)_{12}$ +CO_2.

RuI_3 +CO+Ag (175c+250p) --- $Ru(CO)_5$+ AgI

CoS +CO+ Cu (200c+200p) --- $Co_2(CO)_8$ +Cu_2S.

$Cr(acac)_3$ +CO +Mg (160c+300p) --- $Cr(CO)_6$

$CoCO_3$ +CO +H2 (150c+300p)---- $Co_2(CO)_8$

From mono or binuclear carbonyls:

$Fe(CO)_5$ (ACH+uv+room temp.) ---- $Fe_2(CO)_9$

$Fe_2(CO)_9$ +(50c+heat) --- $Fe(CO)_5$ + ($Fe(CO)_4$

$Fe(CO)_4$ trimerization to give $Fe_3(CO)_{12}$ inlow yield.The best method for prep.with good yield is: $Na[HFe(CO)_4]$ +MnO_2 (methanol)---- $[HFe_3(CO)_{11}]^-$ + H^+ -----$[Fe_3(CO)_{12}]$ +H_2 +Fe^{3+}(salt).

3-From complex cyanides:

$K_2[Ni(CN)_4]$ $+K_{Hg}$ --- $[Ni_2(CN)_6]^{4-}$ +CO ---- $2[Ni_2(CN)_6(CO)_2]^{4-}$ $+2H^+$ ---$[Ni(CO)_4]$ $+3[Ni(CN)_4]$ $+H_2$.

$K_3[Co(CN)_5]$ + CO ---$K[CO(CO)_4]$ $+H^+$ --- $2[HCo(CO)_4]$ ----- $Co_2(CO)_8$ $+2H^{+.}$

Carbonyl halides:

1- From neutral carbonyl

$2Mo(CO)_6 + 2Cl_2$ --- $[Mo(CO)_4Cl_2]_2 + 4CO$

$Fe(CO)_5 + I_2$ – $[Fe(CO)_4I_2]$ +CO

$4Ru(CO)_5 + 4F_2$ --- $[[Ru(CO)_3F_2]_4 + 8CO$

2- From metal halide and CO

$RuCl_3$ +CO in CH_3OH --- $[Ru(CO)_3Cl_2]_2$

$RhCl_3.3H_2O$ +CO (100c) --- $[Rh(CO)_2Cl]$

Properties of carbonyl halides.

1-they undergo substitution of CO by Lewis bases e.g. py,and pph_3.

$Fe(CO)_4I_2 + 2pph_3$ --- $[Fe(CO)_2(pph_3)_2I_2]$ +2CO

$[W(CO)_4Cl_2]_2$ + 4 pph_3 ---- $2[W(CO)_2(pph_3)_2Cl_2]$ + 4CO.

2-Carbonyl halides often dimerize by means of halogen bridges e.g.

$[Mn(CO)_4Br]_2$where the bridge throught two Br.The terminals are 4CO from each side.Also, for $[Ru(CO)_3Br_2]_2$,the bridge via two Br only,the terminals are 3Co with one Br for each side.

Triphenylphosphine carbonyl halides:

$IrCl_3.3H_2O$ + pph_3(reflux in DMF) ----- $[(pph_3)_2Ir(CO)Cl]$.

Also: $(NH_4)IrCl_6$ + pph_3 ----- $[(pph_3)_2Ir(CO)Cl]$ i.e. Vaskas compound.

Some reaction of Vaskas compound : with HCl,CH_3I,$HgCl_2$,$HSiCl_3$,the following products are obtained respectively: $[(pph_3)_2Ir(CO)(Cl)_2(H)$ with HCl, $[(pph_3)_2Ir(CO)(CH_3)(Cl)(I)]$ with CH_3I ,$[(pph_3)_2Ir(CO)(Cl)_2(HgCl)]$ with $HgCl_2$ and finally $[(pph_3)_2Ir(CO)(Cl)(SiCl_3)(H)]$ with $HSiCl_3$.

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