Introduction of coordination chemistry :

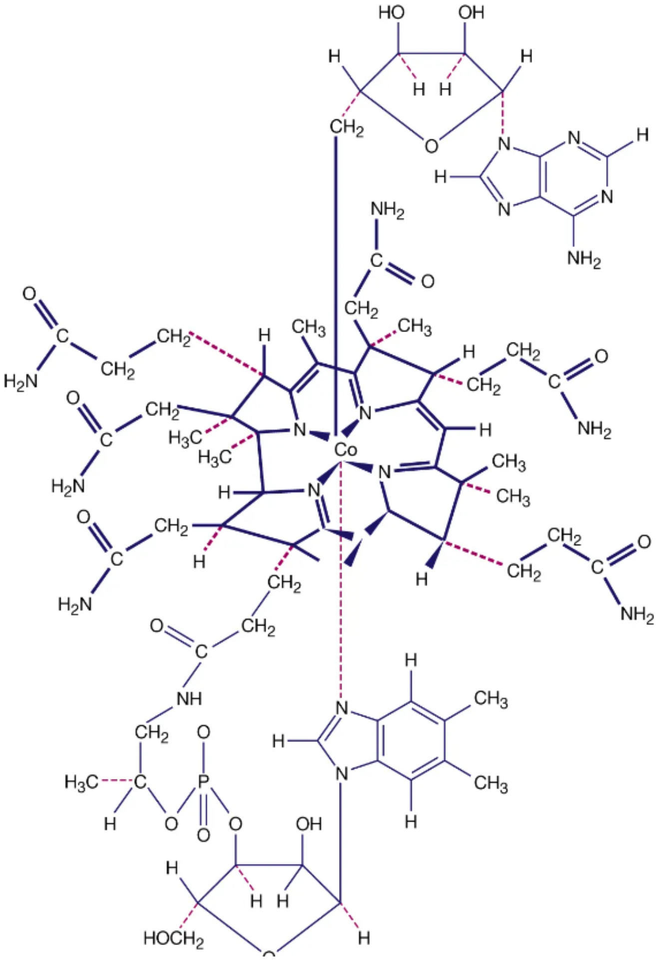
Coordination of complexes compound

Coordination complexes are molecules that possess a metal center that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions. Some methods of verifying the presence of complex ions include studying its chemical behavior. This can be achieved by observing the compounds' color, solubility, absorption spectrum, magnetic properties, etc. The properties of complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both the metal and the ligand are altered.

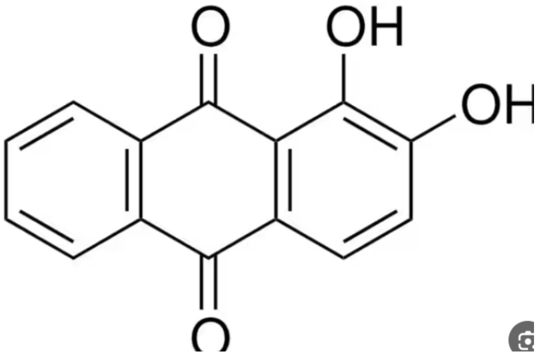
Metal-ligand bonds are typically thought of Lewis acid-base interactions. The metal atom acts as an electron pair acceptor (Lewis acid), while the ligands act as electron pair donors (Lewis base). The nature of the bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and the ligand, but are weaker than covalent bonds and ionic bonds

The branch of inorganic chemistry that deals with the study of coordination compounds is called coordination chemistry.
The name coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. Because these compounds are usually formed by donation of electron pairs of ligands to metals, the name is appropriate.
Although the history of bonding and interpretation of reactions of coordination compounds really begins with Alfred Werner (1866-1919), coordination compounds were known earlier. Many coordination compounds have been used as pigments since antiquity. Examples still use include Prussian blue $KFe[Fe(CN)6]$ and aureolin $K3[Co(NO2)6].6H2O$, yellow.
Coordination compound, any of a class of substances with chemical structures in which a central metal atom is surrounded by nonmetal atoms or groups of atoms, called ligands, joined to it by chemical bonds. Coordination compounds include such substances as vitamin B12 , hemoglobin, and chlorophyll, dyes and pigments, and catalysts used in preparing organic substances.

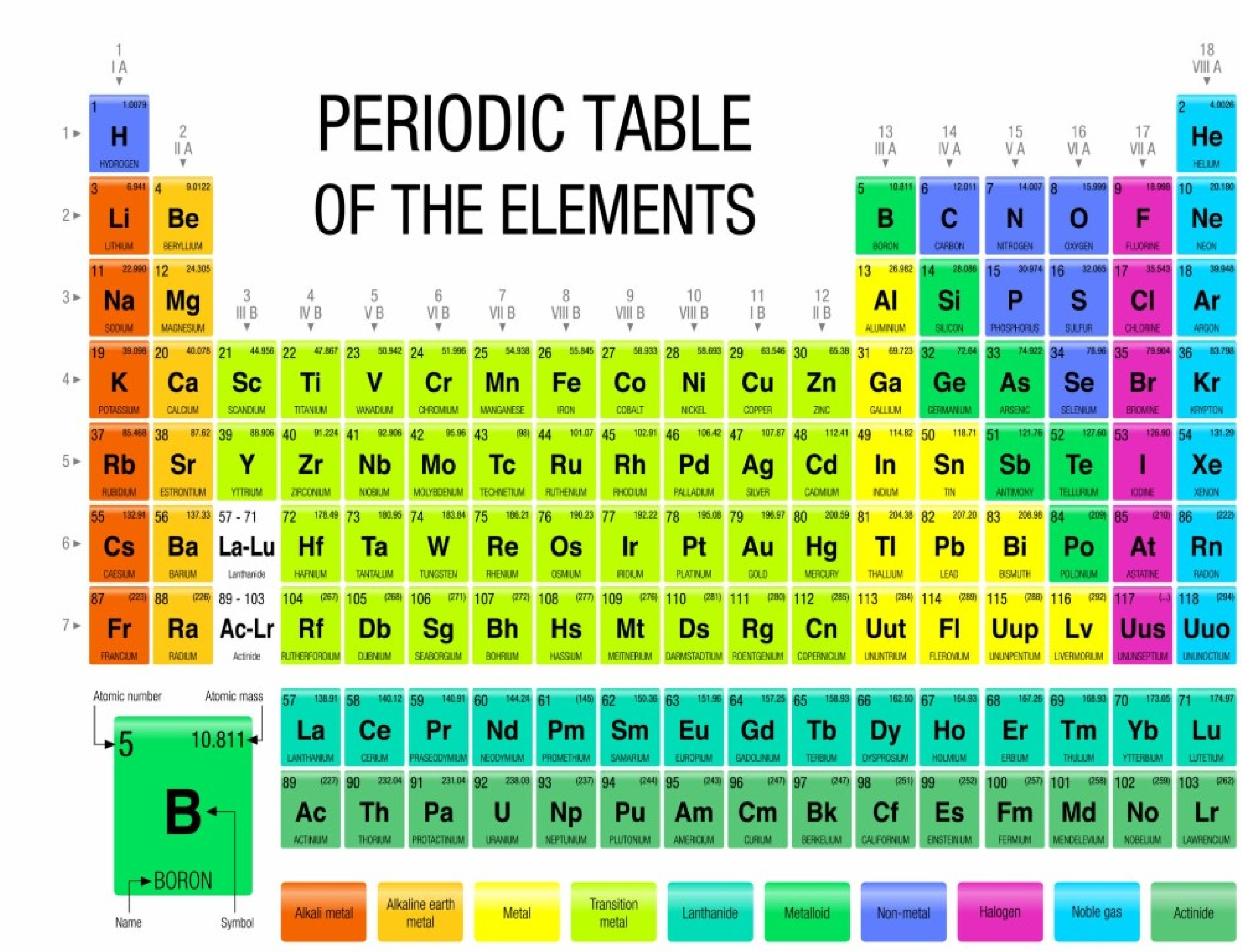
- The earliest known coordination compound is the bright red alizarin dye , it is a calcium aluminum chelate complex of hydroxyanthraquinone.
- Another example of a coordination compound is the substance Prussian blue, with formula $KFe[Fe(CN)6]$
- The branch of chemistry which deals with the study of coordination compounds or metal complexes or complex salts is called coordination chemistry.
- Nearly 75 % research activities in inorganic chemistry are related with synthesis and applications of coordination compounds.
- These are having very vast applications in medicines, separations, Purification of metals and catalysis



فيتامين B غير مطلوب للحفظ



Alizarin dye



PERIODIC TABLE OF THE ELEMENTS

	1 I A	2 II A	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII B	9 VIII B	10 VIII B	11 I B	12 II B	13 III A	14 IV A	15 V A	16 VI A	17 VII A	18 VIII A
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULFUR	17 35.543 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr ESTRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57 - 71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.20 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89 - 103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (284) Uut UNUNTRIUM	114 (289) Fl FLEROVIUM	115 (288) Uup UNUNPENTIUM	116 (292) Lv LIVERMORIUM	117 (...) Uus UNUNSEPTIUM	118 (294) Uuo UNUNOCTIUM

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

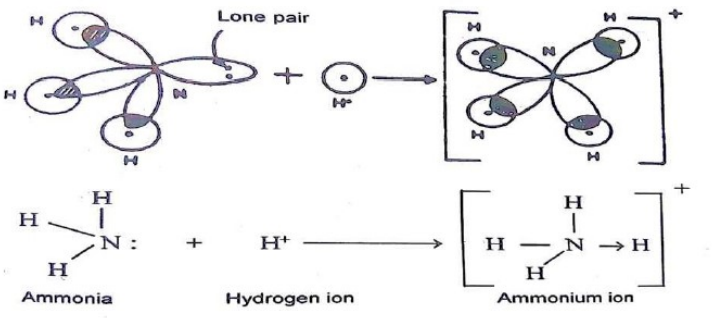
Atomic number
Atomic mass
5 10.811
B
BORON
Name
Symbol

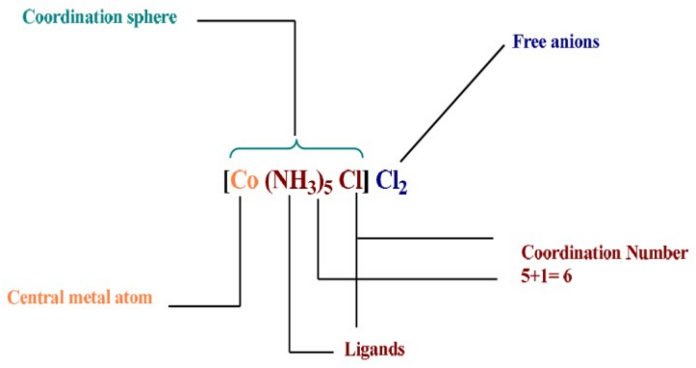
Alkali metal	Alkaline earth metal	Metal	Transition metal	Lanthanide	Metalloid	Non-metal	Halogen	Noble gas	Actinide

Coordinate bond :

A coordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom.

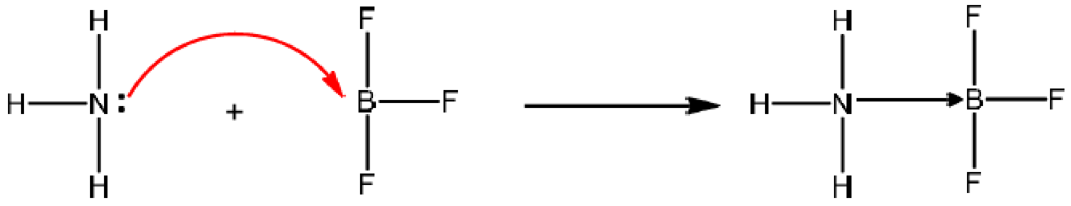
- **It is pointing from by an arrow ( ) pointing from donor to acceptor. NH_4^+ , NH_3-BF_3 .**
- **The atom which donates a pair of electrons is known as donor, while the atom which accept the pair of electrons is called acceptor.**
- **Coordinate bond is also known as coionic or semipolar bond .**
- **To form coordinate bond donor atom must possess at least one lone pair of electrons.**
- **Acceptor atom must have an empty orbital in the valence shell.**
- **There should be appreciable overlap between filled and empty orbitals of donor and acceptor atom. Formation of NH_4^+**
- **In ammonia molecule nitrogen is a center atom with sp^3 hybridization**
- **Three sp^3 hybrid orbitals of nitrogen with unpaired electrons overlap with half filled s orbital of hydrogen. The forth sp^3 orbital with lone pair of electrons overlap with empty orbital of the H^+ to form NH_4^+**

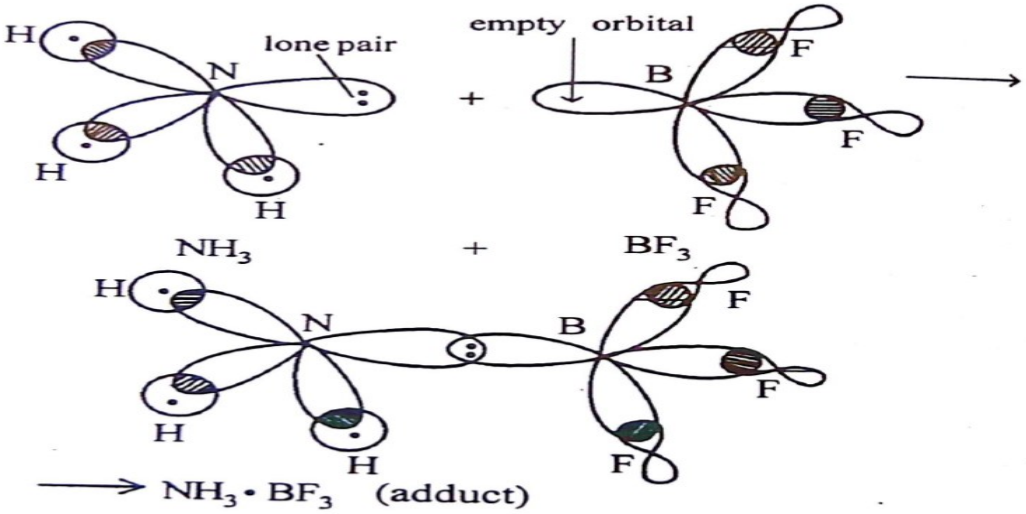




Formation of NH3-BF3

- **When ammonia is treated with boron trifluoride an adduct is formed. In BF3 boron is the central atom .**
- **Boron is sp2 hybridized with one empty 'p' orbital**
- **In ammonia nitrogen is sp3 hybridized with lone pair of electrons in one of the sp3 hybrid orbital.**
- **The filled orbital of ammonia overlap with empty orbital of boron trifluoride to form NH3-BF3 adduct.**





Complex ion

Complex ion is a positively or negatively charged species which contains a central metallic atom and a suitable number of ligands surrounding the central metallic atom. The central metallic atom may be in zero, positive or negative oxidation state. The ligands may be either neutral molecules or anions (generally) or combination of the neutral molecules and anions. Examples of complex ions are $[Co3+(NH3)6]3+$,$[Ni0(CN)4]4-$, $[Fe2+(CN)6]^{4-}$, $[Co-(CO)4]^{-}$, $[Co3+(NH3)5Cl]^{2+}$.

Neutral complex

A complex which has no charge on it is called neutral complex. It is a non electrolyte, dose not undergo ionization and hence dose not give any ions in aqueous solution. Examples of neutral complexes are $[Co^{3+}(NH3)_3Cl_3]0$, $[Ni^{0}(CO)_4]0$, $[Pt^{2+(}NH3)_2Cl_2]0$, $[Ni^{2+(}dmg)_2]0$.

Ligands or coordinating groups and central metallic atom

The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called ligands or co-ordinating groups. For example in the complex ion,$[Fe(CN)6]3-$ the six CN- ions which are attached with the central Fe3+ ion act as ligands. In Lewis sense, in most of the complex compounds the ligands act as Lewis bases (electron pair donors) and the central metal ion acts as a Lewis acid (electron pair acceptor), i.e. in most of the complex compounds the ligands donate one or more electron pairs to the central metal ion.

$$\underset{\substack{\text{Central metal}\\\text{ion(Lewis acid}\\\text{or electron pair}\\\text{acceptor)}}}{M^{n+}} \quad + \quad \underset{\substack{\text{Ligand (Lewis}\\\text{base or electron}\\\text{pair donor)}}}{x\,L} \quad \longrightarrow \quad \underset{\substack{\text{Complex}\\\text{compound}}}{[ML_x]^{n+}}$$

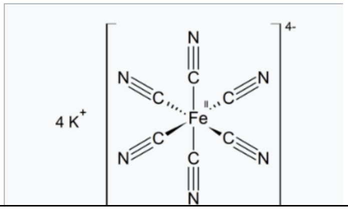
In a ligand the atom which actually donates the electron pair to the central metal ion is called donor or coordinating atom. The ligands are attached with the central metal ion through their donor atom (or atoms).

The metallic atom with which the ligands are attached through coordinating bonds is called central metallic atom. This metallic atom may be in zero, positive or negative oxidation state

Coordination sphere and ionization sphere

While writing the structural formula of a given complex compound the central metal atom and the ligands attached with it are always written in a square bracket, [ ]. This square bracket is called coordination (or inner) sphere. The portion outside the coordination sphere is called ionization (or outer) sphere. Thus in $[Co(NH_3)_5Cl]Cl_2$, the square bracket which contains the central metal ion (Co^{3+} ion) and the ligands (five NH_3 molecules and one Cl^- ion) is coordination sphere and the portion that contains two Cl^- ions is ionization sphere.

The species written in ionization sphere are ionizable and hence can be precipitated by means of a suitable precipitating agent while those given in the coordination sphere (i.e. metallic atom and ligands) are non ionizable and hence cannot be precipitated.

Double salts	**Complex salts**
• These are made up of two or more simple salts	• These are made by the combination of simple salt with electron rich ligands
• They exist in crystalline state, in aqueous state dissociate completely into ions.	• They exist in solid state as well as in aqueous state.
• Nature of bonding is ionic, weak Vander Walls forces	• Usually nature of bonding is ionic, covalent and coordinate
• Complex ion absent	• Complex ion present
The Properties of double salts are same as those of its constituents compounds.	• The properties of coordination compounds are different from its constituent.
• In double salts metals show their normal valence.	• In complex salts metals satisfy two types of valencies, primary and secondary valencies.
• Double salt loses its identity in solution	• Complex salt retains its identity in solution
• E.x. Mohars salt, Potash alum $(NH_4)_2Fe(SO_4)_2 6H_2O$ and is known as ammonium iron (II) sulphate. It consists of two primary cations called ammonium cation and ferrous cation. It is a double salt of ammonium sulfate and ferrous sulphat $KAl(SO_4)_2\cdot 12H_2O$ Potash alum	• E.x. Potassium ferrocyanide $K_4[Fe(CN)_6]\cdot 3H_2O$., Tetra ammine copper(II) sulphate , [Cu(NH3)4(H2O)n]SO4 **Potassium hexacyanidoferrate(II)** 
$K_2SO_4 + Al_2(SO_4)_3 + \mathbf{24}H_2O \rightarrow \mathbf{2}KAl(SO_4)_2\cdot 12H_2O$	

Application of the formation of metal complexes

1- Used as anti-cancer compounds (carboplatin and cisplatin).

2- Formation of chelates in analytical chemistry. Examples are:

a- Gravimetric estimation and identification of Ni2+ ions by dimethyl glyoxime.

b- Separation of Co2+ ion from Ni2+ ion by - nitroso - naphthol solution.

c- Estimation of Mg2+ ion and Ca2+ ion by EDTA.

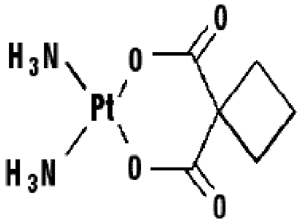
3- Formation of chelates in softening water and estimation of hardness of water.

4- Formation of chelates in removing poisonous metals from the body.

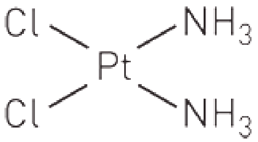
5- Separation of ions by solvent extraction method.

6- Role of metal chelates in living system (hemoglobin, chlorophyll in plants).

Carboplatin



Cis-Platin



General Characteristics of Transition Metals (d- Block Elements)

The position of d- block elements

*d-block elements lie between s-and p- block elements

**d-block elements are present in 4th period (21Sc to 30Zn = 10 elements), 5th period (39Y to 48Cd = 10 elements), 6th period (57La, 72Hf to 80Hg =10 elements) and 7th (incomplete)

period which contains 8 elements 89Ac, 104Ku to 110Uun.

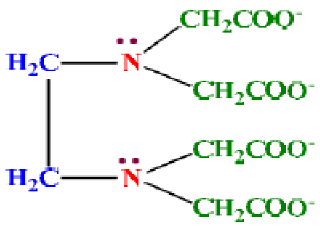
***d-block elements are present in (3 – 12 groups).

Terminology in coordination chemistry

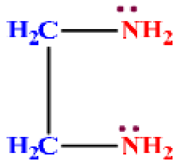
- **When a ligand can bind through two donor atoms as in H2NCH2CH2NH2 (ethane-1,2-diamine) or C2O4 2– (oxalate), the ligand is said to be bidentate. Polydentate ligands are those that can bind to the metal ion through several donor atoms. Examples are N(CH2CH2NH2)3 and Ethylenediaminetetraacetate ion (EDTA4–). EDTA is an important hexadentate ligand that can bind to a central metal ion through two nitrogen and four oxygen atoms.**

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

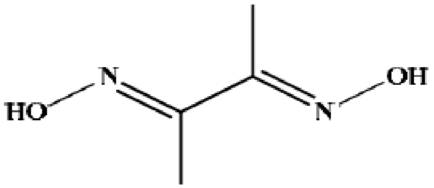
- **Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the NO2 – and SCN – ions. NO2 – ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN– ion can coordinate through the Sulphur or nitrogen atom**



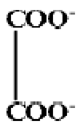
Ethylene diamine tetraacetate



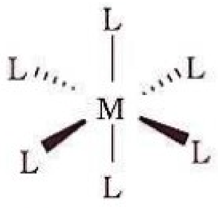
Ethylenediamine



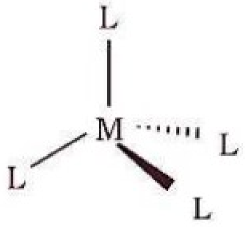
dimethyl glyoxime



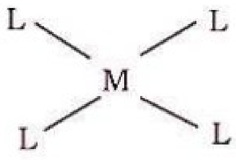
oxalato



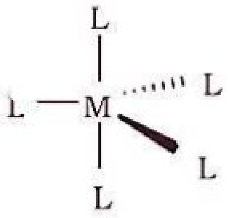
Octahedral



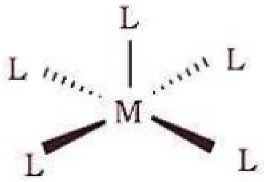
Tetrahedral



Square planar



Trigonal bipyramidal



Square pyramidal

- **Oxidation number of central atom :The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).**

- **Homoleptic and heteroleptic complexes : Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g., $[Co(NH_3)_4Cl_2]^{+}$, are known as heteroleptic.**

Electronic Configuration

d-block elements are defined as those elements whose outer shells are incomplete (partially-filled).

1st or 3d series

(4th period)

Scandium	$_{21}Sc$	$[_{18}Ar]\ 3d^1\ 4s^2$
Titanium	$_{22}Ti$	$[_{18}Ar]\ 3d^2\ 4s^2$
Vanadium	$_{23}V$	$[_{18}Ar]\ 3d^3\ 4s^2$
Chromium	$_{24}Cr$	$[_{18}Ar]\ 3d^5\ 4s^1$ *
Manganese	$_{25}Mn$	$[_{18}Ar]\ 3d^5\ 4s^2$
Iron	$_{26}Fe$	$[_{18}Ar]\ 3d^6\ 4s^2$
Cobalt	$_{27}Co$	$[_{18}Ar]\ 3d^7\ 4s^2$
Nickel	$_{28}Ni$	$[_{18}Ar]\ 3d^8\ 4s^2$
Copper	$_{29}Cu$	$[_{18}Ar]\ 3d^{10}\ 4s^1$ *
Zinc	$_{30}Zn$	$[_{18}Ar]\ 3d^{10}\ 4s^2$

2nd or 4d series

(5th period)

Yttrium	$_{39}Y$	$[_{36}Kr]\ 4d^1\ 5s^2$
Zirconium	$_{40}Zr$	$[_{36}Kr]\ 4d^2\ 5s^2$
Niobium	$_{41}Nb$	$[_{36}Kr]\ 4d^4\ 5s^1$ *
Molybdenum	$_{42}Mo$	$[_{36}Kr]\ 4d^5\ 5s^1$ *
Technetium	$_{43}Tc$	$[_{36}Kr]\ 4d^6\ 5s^1$ *
Ruthenium	$_{44}Ru$	$[_{36}Kr]\ 4d^7\ 5s^1$ *
Rhodium	$_{45}Rh$	$[_{36}Kr]\ 4d^8\ 5s^1$ *
Palladium	$_{46}Pd$	$[_{36}Kr]\ 4d^{10}\ 5s^0$ *
Silver	$_{47}Ag$	$[_{36}Kr]\ 4d^{10}\ 5s^1$ *
Cadmium	$_{48}Cd$	$[_{36}Kr]\ 4d^{10}\ 5s^2$

3rd or 5d series

(6th period)

Lanthanum $_{57}La$ $[_{54}Xe]$ $4f^0$ $5d^1$ $6s^2$

Hafnium $_{72}Hf$ $[_{54}Xe]$ $4f^{14}$ $5d^2$ $6s^2$

Tantalum $_{73}Ta$ $[_{54}Xe]$ $4f^{14}$ $5d^3$ $6s^2$

Tungsten $_{74}W$ $[_{54}Xe]$ $4f^{14}$ $5d^4$ $6s^2$

Rhenium $_{75}Re$ $[_{54}Xe]$ $4f^{14}$ $5d^5$ $6s^2$

Osmium $_{76}Os$ $[_{54}Xe]$ $4f^{14}$ $5d^6$ $6s^2$

Iridium $_{77}Ir$ $[_{54}Xe]$ $4f^{14}$ $5d^7$ $6s^2$

Platinum $_{78}Pb$ $[_{54}Xe]$ $4f^{14}$ $5d^9$ $6s^1$ *

Gold $_{79}Au$ $[_{54}Xe]$ $4f^{14}$ $5d^{10}$ $6s^1$ *

Mercury $_{80}Hg$ $[_{54}Xe]$ $4f^{14}$ $5d^{10}$ $6s^2$

Physico-chemical Properties

The transition elements show several properties. Some of these properties and their trends of variation are discussed below:

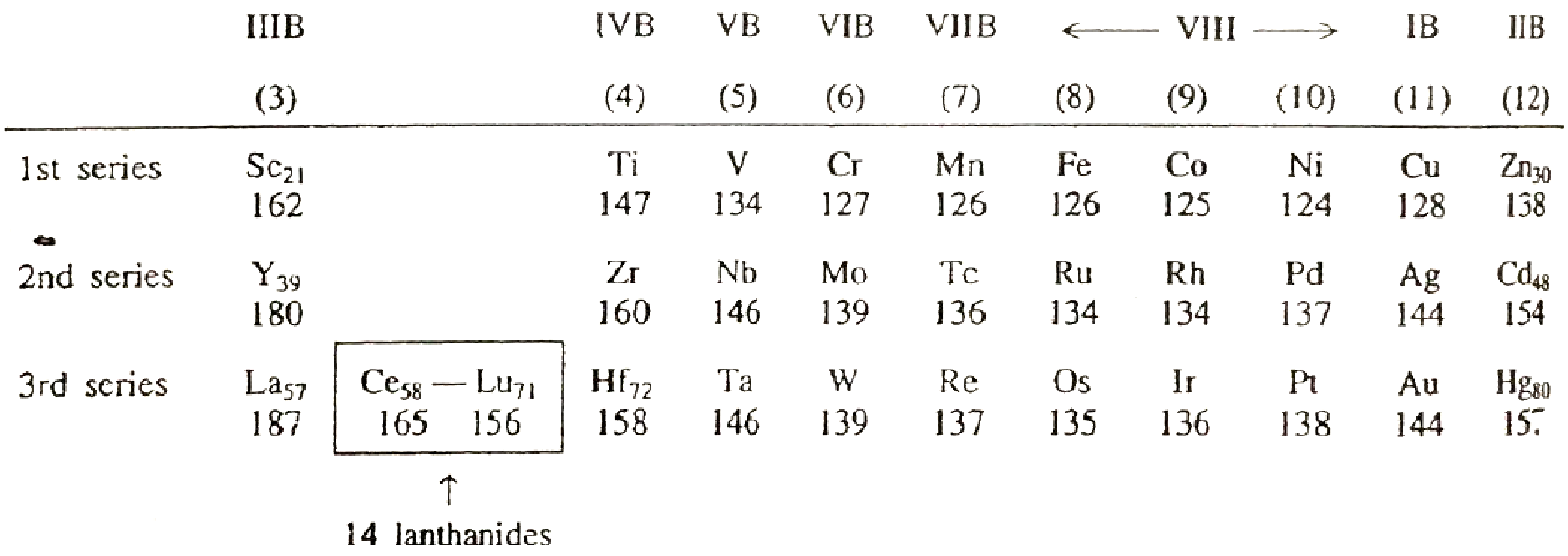
1- Atomic radii

The atomic radii of d-block elements are given in (Table 1). The following trends may be observed:

***Variation of atomic radii in a given series (period)**

For the elements from Sc to Mn the atomic radii decrease. This decrease is because of the gradual increase in nuclear charge with the increase in atomic number. The increased nuclear charge makes the atom to shrink in size and hence the size of the atom decreases. However, since the electrons added to 3d orbitals screen the 4s electron(s), the attraction between the nucleus and the 4s electron(s) decreases, i.e. due to the screening effect

caused by 3d electrons the magnitude of nuclear charge decreases and consequently the atomic radii for the elements from Fe to Cu remain almost unchanged. Towards the end of each series, there is an increase in electron-electron repulsion between the electrons being added to 3d orbitals. This increase in repulsion becomes greater than that of the attraction between the nucleus and the 4s electron(s). Because of the greater magnitude of electron-electron repulsion, the electron cloud of Zn expands and hence its size also becomes greater than of Cu.



	IIIB		IVB	VB	VIB	VIIB	←	VIII	→	IB	IIB
	(3)		(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1st series	Sc_{21} 162		Ti 147	V 134	Cr 127	Mn 126	Fe 126	Co 125	Ni 124	Cu 128	Zn_{30} 138
2nd series	Y_{39} 180		Zr 160	Nb 146	Mo 139	Tc 136	Ru 134	Rh 134	Pd 137	Ag 144	Cd_{48} 154
3rd series	La_{57} 187	Ce_{58} — Lu_{71} 165 156	Hf_{72} 158	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg_{80} 157

↑
14 lanthanides

Common oxidation states:

Sc= +3 ,,Ti=+2, +3, +4, V=+2, +3, +4, 5

Cr: +2, +3, +6,

Mn: +2, +3, +4, +6, +7,

Fe: +2, +3, +4,+5, +6, Co: +2, +3,

Ni: +2, +4 Pd= +2, Pt +2,+4

Zn: +2, , Cd: +2, Pb: +2, +4.

Cu: +1, +2, Ag: +1, Au =+1, +3

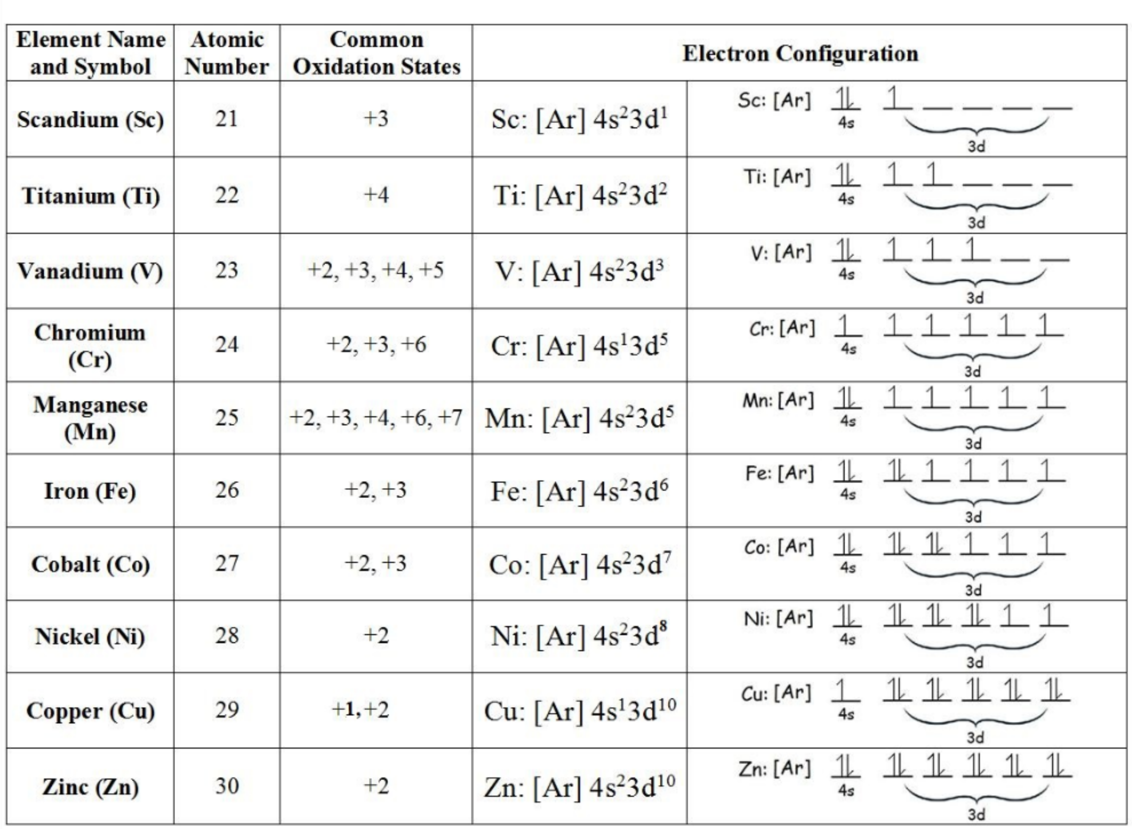
The common oxidation states for the given transition metals and other elements are as follows:

21	سكانديوم	Sc						0	1+	2+	**3+**						
22	التيتانيوم	Ti				2−	1−	0	1+	2+	3+	**4+**					
23	الفاناديوم	V			3−		1−	0	1+	2+	3+	4+	**5+**				
24	الكروم	Cr		4−		2−	1−	0	1+	2+	**3+**	4+	5+	**6+**			
25	المنغنيز	Mn			3−	2−	1−	0	1+	**2+**	3+	**4+**	5+	6+	**7+**		
26	حديد	Fe		4−		2−	1−	0	1+	**2+**	**3+**	4+	5+	**6+**	7+		
27	كوبالت	Co			3−		1−	0	1+	**2+**	**3+**	4+	5+				
28	نيكل	Ni				2−	1−	0	1+	**2+**	3+	4+					
29	النحاس	Cu				2−		0	**1+**	**2+**	3+	4+					
30	زنك	Zn				2−		0	1+	**2+**							

These oxidation states are the most stable and commonly observed in various compounds and chemical reactions.

The transition metals, in particular, exhibit a wide range of oxidation states due to the involvement of their d orbitals in bonding.

The specific oxidation states listed are a result of the electronic configurations of these elements and their chemical properties.



Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	Sc: [Ar] ⇅ 4s ↑ _ _ _ _ 3d
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	Ti: [Ar] ⇅ 4s ↑ ↑ _ _ _ 3d
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	V: [Ar] ⇅ 4s ↑ ↑ ↑ _ _ 3d
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	Cr: [Ar] ↑ 4s ↑ ↑ ↑ ↑ ↑ 3d
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	Mn: [Ar] ⇅ 4s ↑ ↑ ↑ ↑ ↑ 3d
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	Fe: [Ar] ⇅ 4s ⇅ ↑ ↑ ↑ ↑ 3d
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^7$	Co: [Ar] ⇅ 4s ⇅ ⇅ ↑ ↑ ↑ 3d
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^8$	Ni: [Ar] ⇅ 4s ⇅ ⇅ ⇅ ↑ ↑ 3d
Copper (Cu)	29	+1,+2	Cu: [Ar] $4s^1 3d^{10}$	Cu: [Ar] ↑ 4s ⇅ ⇅ ⇅ ⇅ ⇅ 3d
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	Zn: [Ar] ⇅ 4s ⇅ ⇅ ⇅ ⇅ ⇅ 3d

In connection with the oxidation states exhibited by the d-block elements of 1st transition series the following points may be noted:

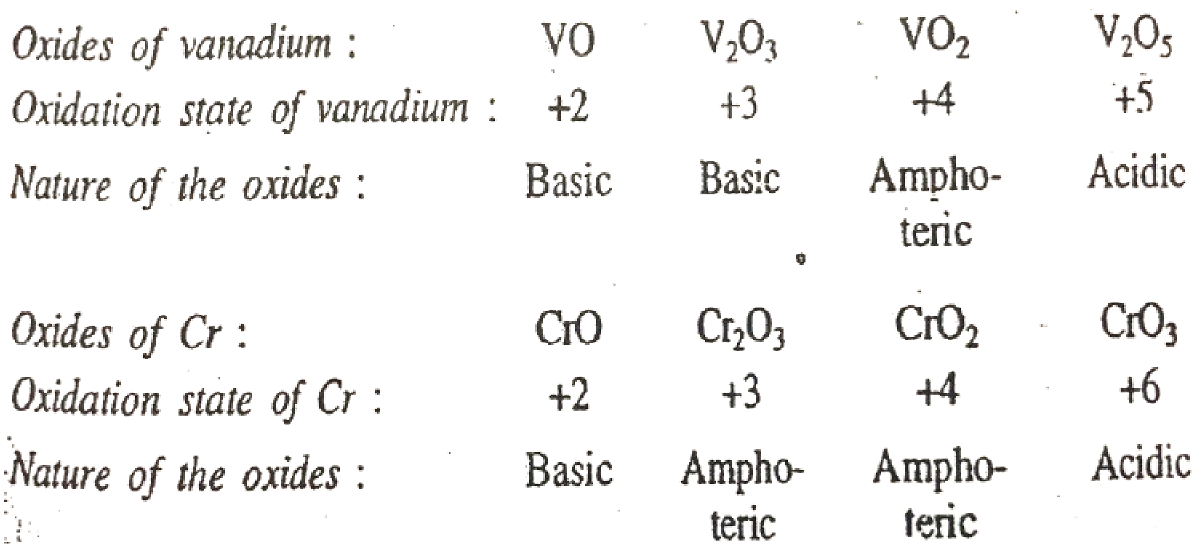
1- +1 and +2 oxidation states. The oxidation states shown in bracket are unstable oxidation states. These are low oxidation states. The remaining oxidation states are stable. Out of these stable oxidation states, +1 is the lowest oxidation states for Cu while for other elements the lowest oxidation state is +2. Cr and Cu both show +2 oxidation state when one 4s and one 3d electrons are lost while the remaining elements exhibit this oxidation state (+2) when both ns electrons are involved in bonding.

2- Stabilization of unstable (low) oxidation states. It may be seen that the low oxidation states like -1, 0, +1 are unstable. These states are stabilized by forming complexes with π-acid ligands like CO, CNR (isocyanide), CN^- and C_6H_6. Examples $[Cr^{+1}(C_6H_6)_2]^+$, $Na^+[Co^{-1}(CO)_4]$, $[Ni^0(CNR)_4]^0$.

3- High oxidation state. The highest (maximum) oxidation state for the first five elements (Sc to Mn) is equal to the sum of the electrons in 4s and 3d orbitals, On the other hand, the highest oxidation state for the remaining five elements (Fe to Zn) is not equal to the sum of the electrons in 4s and 3d orbitals.

The high oxidation states of many transition metals like V(V), Cr(VI), Mn(IV),
Mn(VII), Fe(III), Fe(VI), Co(III), Cu(III), Ag(II), Ag(III) etc. are oxidizing (unstable).
These unstable oxidation states which are high oxidation states get stabilized by forming complexes with small highly electronegative ligands like O^{2-}, F^- , Cl^- , per iodate $(IO_6)^{5-}$,
tellurate $(TeO_6)^{6-}$.
4-
4- Ionic/ covalent character of compounds of a given transition metal in various oxidation states. With the increase in the oxidation state of a given transition metal, the covalent character of its compounds increases. Thus the compounds of a given transition metal in lower oxidation states are ionic while those of the same metal in high oxidation states are covalent. Example VCl_2 is ionic,VCl_3 is less ionic while VCl_4 is covalent.
As the oxidation state of the transition metal increases, the charge density on the metal also increases. This results in the increase of the polarization of the anion charge cloud by the metal and hence covalent character increases (Fajan's Rules).
5- **Acidic/basic character of the compounds of a given transition metal in various oxidation states.** The increase in the covalent character also increases the acidic character of the compound. Thus the compounds of a given transition metal becomes more and more acidic as the oxidation state of the transition metal increases.

The variation of acidic, basic and amphoteric character of the oxides as shown below indicates that the oxides of a given transition metal in lower oxidation states are basic, those of the same in intermediate oxidation states are amphoteric while those of the metal in higher oxidation states are acidic.



Oxides of vanadium :	VO	V_2O_3	VO_2	V_2O_5
Oxidation state of vanadium :	+2	+3	+4	+5
Nature of the oxides :	Basic	Basic	Amphoteric	Acidic

Oxides of Cr :	CrO	Cr_2O_3	CrO_2	CrO_3
Oxidation state of Cr :	+2	+3	+4	+6
Nature of the oxides :	Basic	Amphoteric	Amphoteric	Acidic

4- Color of transition metal complex

The transition metal complex ions and complex compounds whose central atom contains partially-filled d-orbitals are usually colored in the solid form or in solution form.

When white light which is composed of many different colors falls on a colored complex ion or complex compound of a transition metal, the ion or the compound absorbs some portion of the white light and the remaining portion of the incident light is transmitted or reflected by the complex compound or ion.

* The transition metal complex ions whose central atom contains empty (d0 configuration) or completely-filled d-orbitals (d10 configuration) are colorless. This is because of the fact that since the d-orbitals of the central metal ion donot contain any electron (empty d-orbitals) or are completely-filled (contain all the electrons in the paired state), d-d electron transition is not possible and hence no light of any color or wavelength is absorbed by such ions in the visible region. Thus the transition metal ions containing empty d-orbitals (Sc3+ and Ti4+ ions) or completely-filled d-orbital (Cu+ , Ag+, Zn2+, Cd2+ , Hg2+ etc.) are colorless.

5- Magnetic properties of transition metal ions and their complexes

When the transition metal ions or their complexes are placed in a magnetic field, they show different behavior. On the basis of this behavior these substances have been
classified as paramagnetic substances, diamagnetic substances, ferromagnetic substances, antimagnetic substances and ferrimagnetic substances.

The transition metal complexes whose central atom/ion contains one or more unpaired electrons are paramagnetic while those whose central atom/ion has no unpaired electrons (all electrons are paired) behave as diamagnetic substances. The paramagnetic character increases with the increase in the number of unpaired electrons.

6- Tendency of transition metals to form complex compounds

The transition metal atoms or the cations derived from them have an ability to form complex compounds with certain molecules (CO, NO, NH_3 etc.) or ions (F^- , Cl^-, CN^- etc.) these molecules or ions are called ligands. These ligands contain one or more lone pair of electrons which they can easily donate to the transition metal or cation and thus complete the vacant orbitals of those atoms or cations through the formation of L M coordinate bonds. The tendency of transition metal atom or cation to form the complex compounds is
due to its following properties:
1- Due to the small size of the transition metal atoms or their cations and high effective nuclear charge, they have a high positive charge density on them. This high positive charge density makes the atoms or cations to attract (accept) the lone pairs from the ligands.

2- The transition metal cations or atoms have vacant d-orbitals [(n-1) d orbitals] in which they can accommodate the lone pairs of electrons donated by the ligands and thus can form L M coordinate bonds.

Terminology in coordination chemistry

- **Coordination entity : A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.**

- **Central atom/ion : In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a**

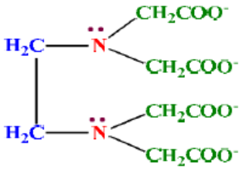
definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+} , respectively. These central atoms/ions are also referred to as Lewis acids.
- **Ligands : The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $H_2NCH_2CH_2NH_2$ or even macromolecules, such as proteins. These are classified as**

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

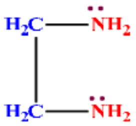
When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be bidentate. Polydentate ligands are those that can bind to the metal ion through several donor atoms. Examples are $N(CH_2CH_2NH_2)_3$ and Ethylenediaminetetraacetate ion ($EDTA^{4-}$). EDTA is an important hexadentate ligand that can bind to a central metal ion through two nitrogen and four oxygen atoms.

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

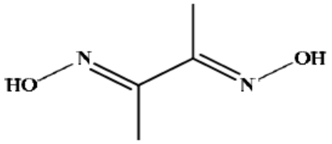
• Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the Sulphur or nitrogen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



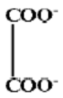
Ethylene diamine tetraacetate



Ethylenediamine



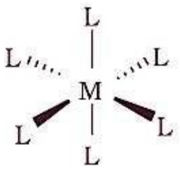
dimethyl glyoxime



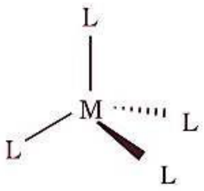
oxalato

Coordination number : The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane- 1,2-diamine) are bidentate ligands.
It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.
Coordination sphere : The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. The ionizable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+ .
Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral.

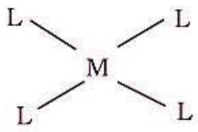
For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar. Fig. below shows the shapes of different coordination polyhedra.



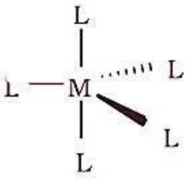
Octahedral



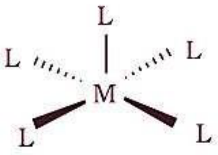
Tetrahedral



Square planar



Trigonal bipyramidal



Square pyramidal

Oxidation number of central atom :The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

- **Homoleptic and heteroleptic complexes : Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g., $[Co(NH_3)_4Cl_2]^{+}$, are known as heteroleptic.**

Classification of ligands

Depending on the number of sites at which one molecule of a ligand is coordinated to the central metallic atom, the ligands have been classified as mono dentate (or uni dentate) and poly dentate (or multi dentate) ligands.

1- Mono dentate ligands

The ligands which have only one donor atom or are co-ordinated through one electron pair are called mono dentate ligands.
Such ligands are coordinated to the central metal ion at one site or by one metal-ligand bond only.
These ligands may be neutral molecules or in anionic form.

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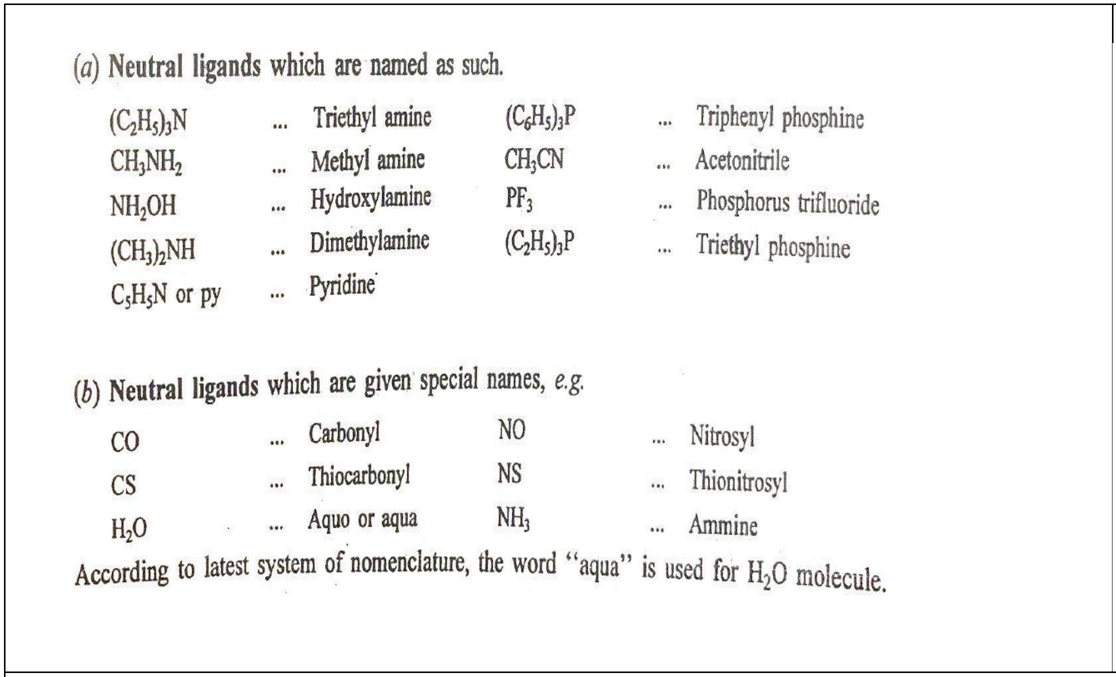


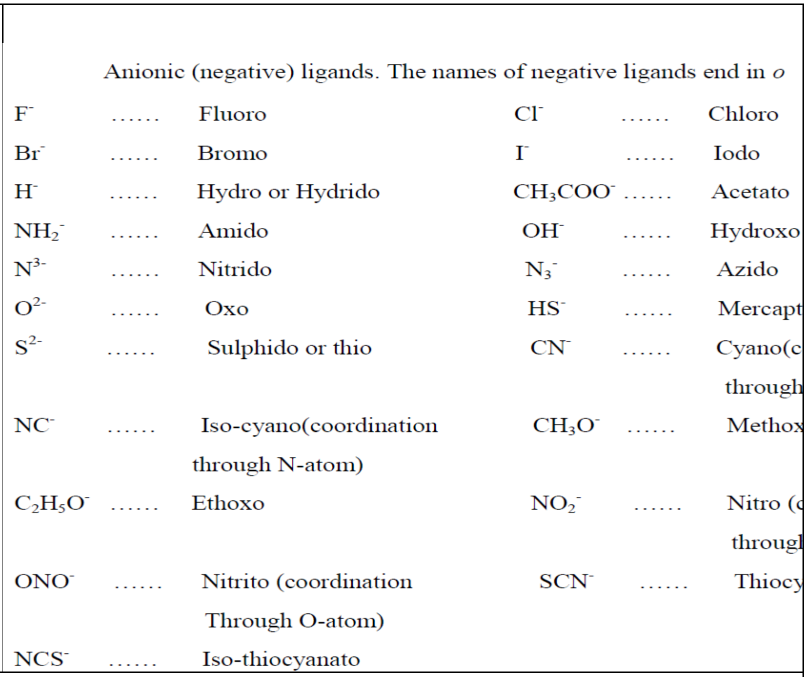
(*a*) **Neutral ligands which are named as such.**

$(C_2H_5)_3N$	...	Triethyl amine	$(C_6H_5)_3P$	...	Triphenyl phosphine
CH_3NH_2	...	Methyl amine	CH_3CN	...	Acetonitrile
NH_2OH	...	Hydroxylamine	PF_3	...	Phosphorus trifluoride
$(CH_3)_2NH$	...	Dimethylamine	$(C_2H_5)_3P$	...	Triethyl phosphine
C_5H_5N or py	...	Pyridine			

(*b*) **Neutral ligands which are given special names,** *e.g.*

CO	...	Carbonyl	NO	...	Nitrosyl
CS	...	Thiocarbonyl	NS	...	Thionitrosyl
H_2O	...	Aquo or aqua	NH_3	...	Ammine

According to latest system of nomenclature, the word "aqua" is used for H_2O molecule.



Anionic (negative) ligands. The names of negative ligands end in *o*

F^-	......	Fluoro	Cl^-	......	Chloro
Br^-	......	Bromo	I^-	......	Iodo
H^-	......	Hydro or Hydrido	CH_3COO^-	......	Acetato
NH_2^-	......	Amido	OH^-	......	Hydroxo
N^{3-}	......	Nitrido	N_3^-	......	Azido
O^{2-}	......	Oxo	HS^-	......	Mercapt
S^{2-}	......	Sulphido or thio	CN^-	......	Cyano(c through
NC^-	......	Iso-cyano(coordination through N-atom)	CH_3O^-	......	Methox
$C_2H_5O^-$	......	Ethoxo	NO_2^-	......	Nitro (c throug
ONO^-	......	Nitrito (coordination Through O-atom)	SCN^-	......	Thiocy
NCS^-	......	Iso-thiocyanato			

2- Poly-dentate ligands

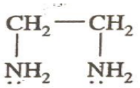
These may be bi-dentate, tri-dentate, tetra-dentate, penta-dentate and hexa-dentate, if the number of donor atoms present in one molecule of the ligand attached with the central metallic atom is 2, 3, 4, 5 and 6 respectively.

(one molecule of these ligands makes 2, 3, 4, 5 and 6 metal-ligand coordinated bonds respectively.

Bi-dentate ligands may be neutral molecules or anions.

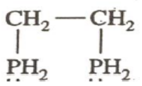
Examples of bi-dentate ligands

Ethylene diamine (*en*)



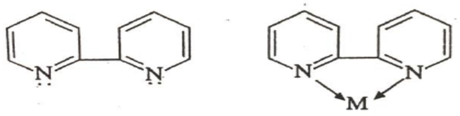
$\underset{\ddot{N}H_2}{CH_2}-\underset{\ddot{N}H_2}{CH_2}$

Ethylene diphosphine (*diphos*)

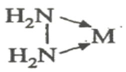


$\underset{\ddot{P}H_2}{CH_2}-\underset{\ddot{P}H_2}{CH_2}$

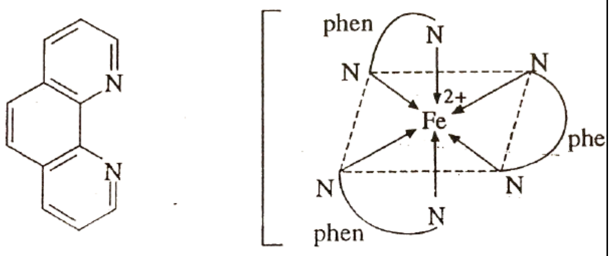
*2,2-bipyridine (bipy)



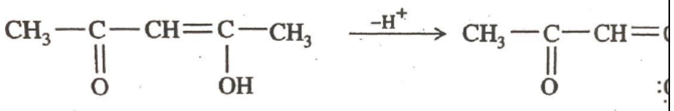
*Hydrazine



*o-phenanthroline or 1,10-phenanthroline (0-phen or phen or phenan)

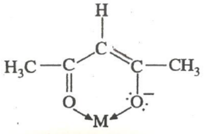


*Acetylacetonato ion (acac)

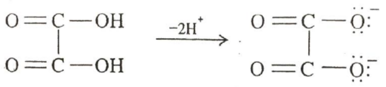


$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{-H^+} CH_3-\underset{\underset{O}{\|}}{C}-CH=$

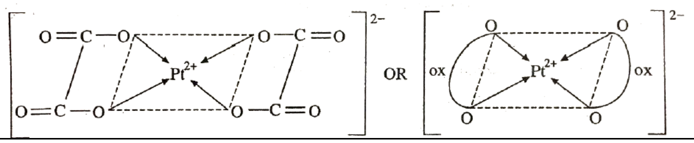
Mode of attachment of acetylacetanato ion to the metal atom, M.

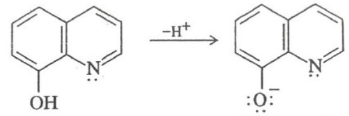


*Oxalato ion $C_2O_4^{2-}$ (ox^{2-})



$[Pt^{2+}(ox)_2]^{2-}$

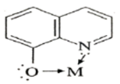




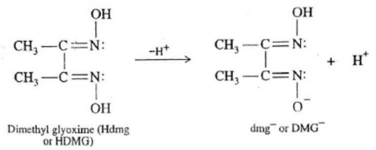
8-hydroxy quinoline molecule, Hoxine

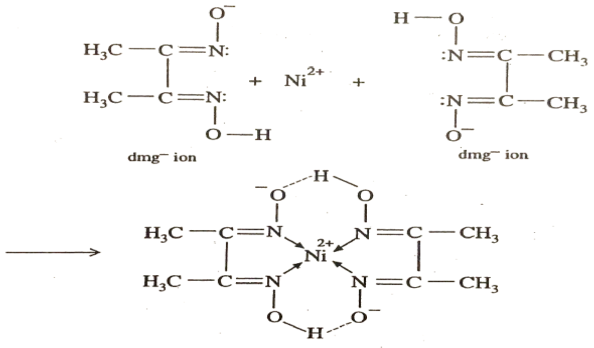
8-hydroxy quinolinato ion, oxine⁻

Attachment of oxine ion to a metal atom (M) in complex compounds



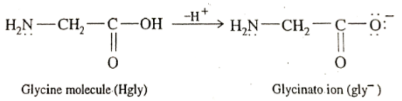
*Dimethyl glyoximato ion (dmg⁻ or DMG⁻)

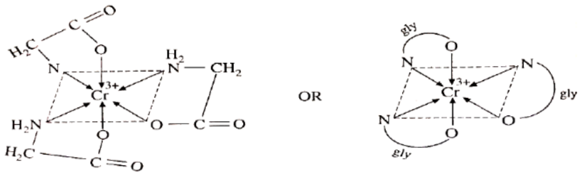




Bis-(dimethylglyoximato) nickel (II) chelated complex, $[Ni(dmg)_2]^0$ (red ppt.)

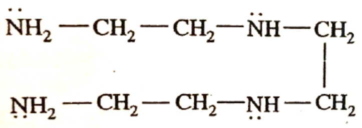
*Glycinato ion (gly⁻)

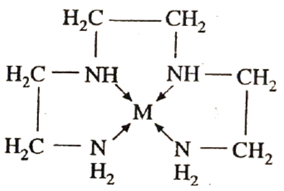




Example of tetra-dentate ligand

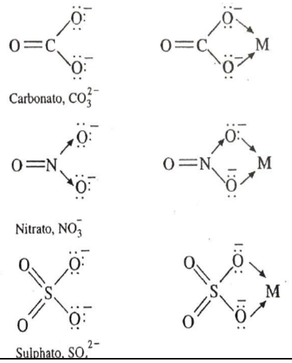
Triethylene tetraamine (trien)



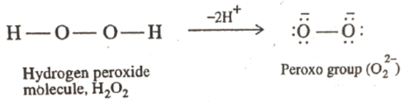


*Carbonato CO_3^{2-}, nitrato NO_3^- and sulphato SO_4^{2-}

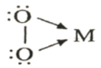
The structure of these ions and the way in which they are coordinated to the metal atom are shown blow:



* Peroxo, O_2^{2-}

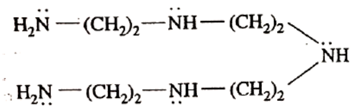


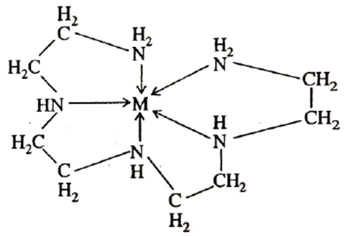
O_2^{2-} group gets coordinated to the central metal ion as:



Example of penta-dentate ligand

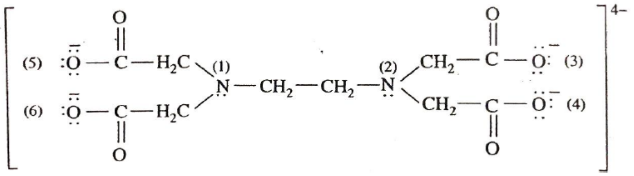
Tetraethylene pentaamine (tetraen)





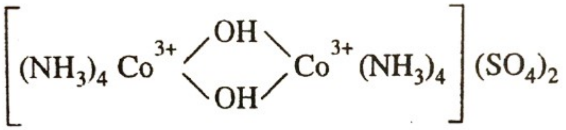
Example of hexa-dentate ligand

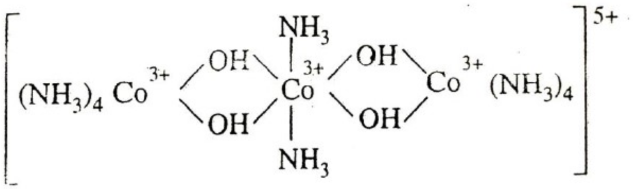
Ethylene diamine tetraacetate ion ($edta^{4-}$ or $EDTA^{4-}$ or Y^{4-})

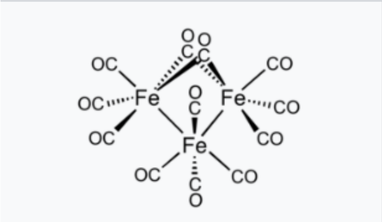


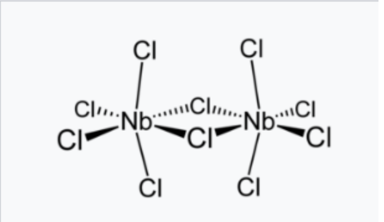
3.Bridging Ligand and Bridged Complexes

Although the ligands like OH^- (hydroxo), NH_2^- (amido or amino), NH^{2-} (imido), Cl^-, F^-, SO_4^{2-}, NO_2^-, CO etc. are mono-dentate ligands, they also act as bi-dentate ligands when they attached with two separate metals atoms, making a bridge between them. Such ligands are called bridging ligands and the complexes thus formed are called bridged (or polynuclear ligands or multinuclear) complexes. Each ligand makes two -bonds with two metal atoms. A bridging ligand must have at least two lone pairs of electrons which the ligand uses to get coordinated to two metal atoms. The polynuclear complex may be dinuclear, trinuclear, teranuclear etc.









IUPAC Nomenclature of Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature.

- **The cation is named first in both positively and negatively charged coordination entities.**

$K_4[Fe(CN)_6]$- Potassium hexacyano ferrate (II), $[Ni(NH_3)_6]Cl_2$ – Hexammine nickel (II) chloride

- **While naming complex ion always named ligands first followed by name of the metal. $[Fe(CN)_6]^{3-}$ - Hexacyano ferrate (III), $[Co(en)_3]^{3+}$- Trisethylenediammine cobalt (III)**

- **Ligands are always named according to their alphabetical order, Names of the anionic ligands end in - o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3 , carbonyl for CO and nitrosyl for NO. $[NiCl_2(H_2O)_4]$ – Tetraqua dichloro nickel (II)**

- **Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses.**

For example, $[NiCl_2(PPh_3)_2]$ is named as dichloro bis(triphenylphosphine) nickel (II).

IUPAC Nomenclature of Coordination Compounds

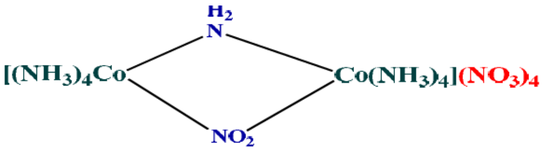
The names of coordination compounds are derived by following the principles of additive nomenclature.

☐ Naming the bridging ligands: Ligands that bridge between the two coordination centers designated by Greek word μ, which is repeated before the each kind of bridging ligand.

Octammine μ-amido μ-nitrito N dicobalt (III) nitrate

☐ Ambidentate ligands are named by placing the symbol of an element attached with metal followed by its name. e.g. NO2- - when linked through 'N' it is named as nitrito (N) while through 'O' it is named nitrito (O).

(NH4)2 [Co(NO2)(C2O4)2] – Ammonium nitrito-N bis oxalato cobaltate



Octammine μ-amido μ-nitrito N dicobalt (III) nitrate

IUPAC Nomenclature of Coordination Compounds

☐ If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, [Co (SCN)4]2- is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.

☐ The neutral complex molecule is named similar to that of the complex cation.

☐ Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

☐ Geometrical isomers are named using the prefixes cis or trans or by a numbering system if the structure is complicated.

1,6 dichloro 4,5 (ethylene diamine) 2,3 dinitrito N platinum (IV)

☐ The solvent of crystallization is named after the name of the complex, number of solvent molecules are designated by Arabic numeral.

[Cu(NH3)4]SO4. H2O – Tetrammine copper (II) sulphate-1-hydrate.

nomenclature of complexes

A. Name the following complex compounds or ions.

1. [Al (H2O)6] Br3 **Hexaaquaaluminum (III) bromide**

2. $[Cr(NH_3)_6]Cl_3$ **Hexaamminechromium (III) chloride**

3. $K_3[FeF_6]$ **Potassium hexafluoroferrate (III)**

4. $[Pt(NH_3)_4Br_2]^{+2}$ **Tetrammine dibromo palatinate(IV) ion**

5. $K_3[MnF_6]$ **Potasium hexafloro manganite(III)**

6. $[Cu(PH_3)_4][Cu(CN)_4]$ **Tetra phosphine copper(II)-tetracyano cuprate(II)**

7. $[Pt(NH_3)_4Cl_2][PtCl_6]$ **Tetraamminedichloroplatinum (IV) hexachloroplatinate (IV)**

8. $[Os(en)_2(C_2O_4)]Br$ **Bis(ethylenediamine) oxalate osmium(III) bromide**

9. $[Co_2Cl_2(en)_4]Cl_4$ **Tetrakis(ethylenediamine-diμ-chloro dicobalt(III) chloride**

B. Write the formula for each of the following complex compounds or ions.

1. Hexaamminecobalt (III) chloride **$[Co(NH_3)_6]Cl_3$**

2. Diamminetetrabromoplatinum (VI) bromide **$[Pt(NH_3)_2Br_4]Br_2$**

3. Tetraaquacadmium (II) nitrate **$[Cd(H_2O)_4](NO_3)_2$**

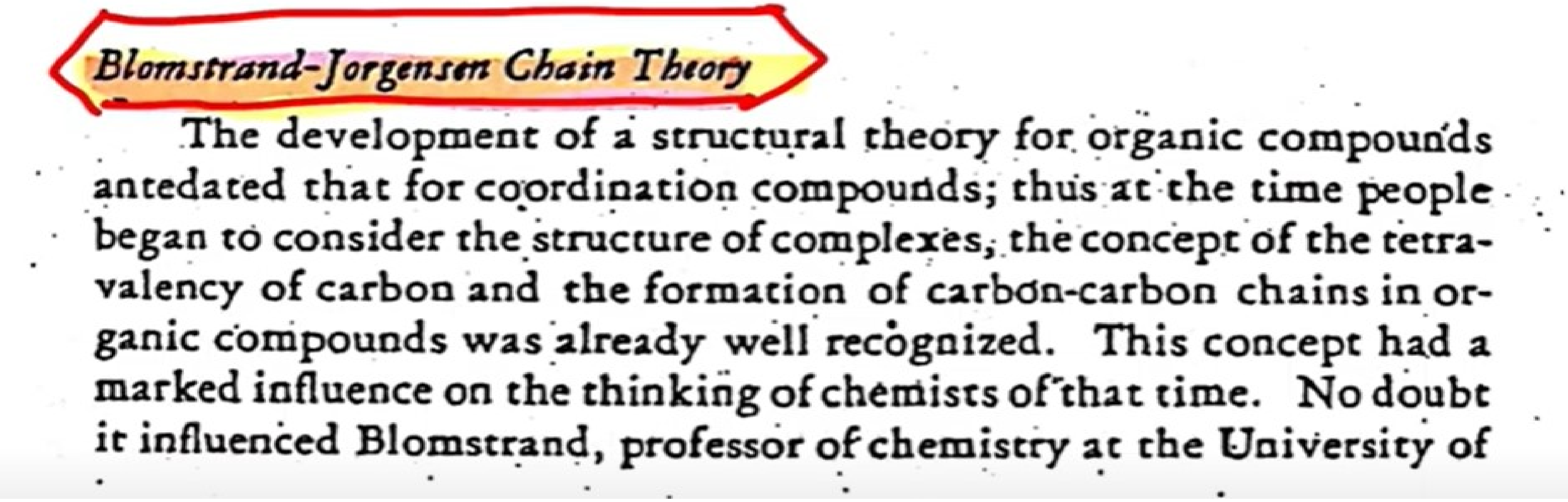
4. Diamminesilver (I) ion **$[Ag(NH_3)_2]^+$**

5. Sodium tetracyanocuprate (I) **$Na_3[Cu(CN)_4]$**

6. Silver hexacyanoferrate (II) **$Ag_4[Fe(CN)_6]$**

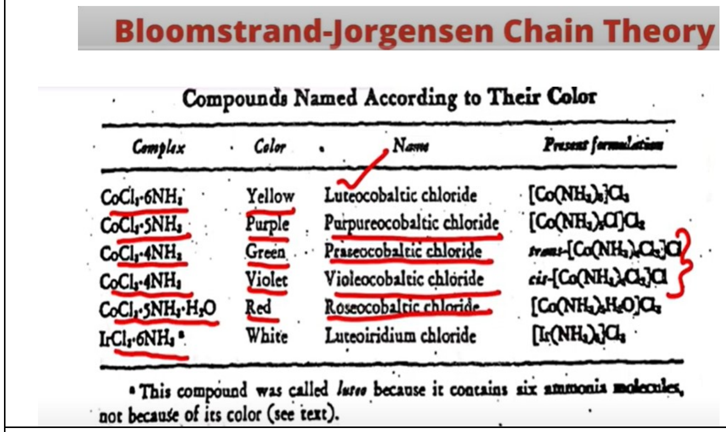
7. Tetraammineoxalatonickel (II) **$[Ni(NH_3)_4C_2O_4]$**

8. Tris(ethylenediamine)chromium(III) chloride **$[Cr(en)_3]Cl_3$**



Blomstrand-Jorgensen Chain Theory

The development of a structural theory for organic compounds antedated that for coordination compounds; thus at the time people began to consider the structure of complexes, the concept of the tetravalency of carbon and the formation of carbon-carbon chains in organic compounds was already well recognized. This concept had a marked influence on the thinking of chemists of that time. No doubt it influenced Blomstrand, professor of chemistry at the University of

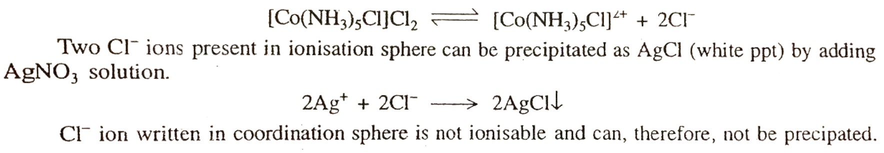


Bloomstrand-Jorgensen Chain Theory

Compounds Named According to Their Color

Complex	*Color*	*Name*	*Present formulation*
$CoCl_3 \cdot 6NH_3$	Yellow	Luteocobaltic chloride	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	Purple	Purpureocobaltic chloride	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	Green	Praseocobaltic chloride	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	Violet	Violeocobaltic chloride	*cis*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 5NH_3 \cdot H_2O$	Red	Roseocobaltic chloride	$[Co(NH_3)_5H_2O]Cl_3$
$IrCl_3 \cdot 6NH_3$ *	White	Luteoiridium chloride	$[Ir(NH_3)_6]Cl_3$

* This compound was called *luteo* because it contains six ammonia molecules, not because of its color (see text).

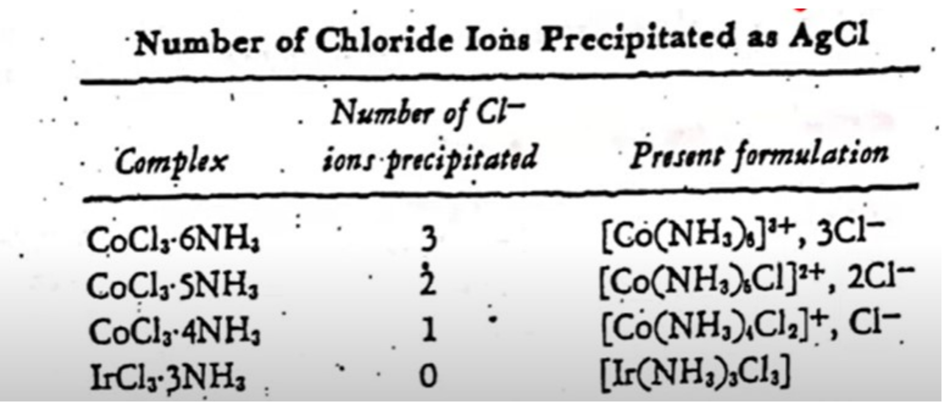


$$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

Two Cl^- ions present in ionisation sphere can be precipitated as AgCl (white ppt) by adding $AgNO_3$ solution.

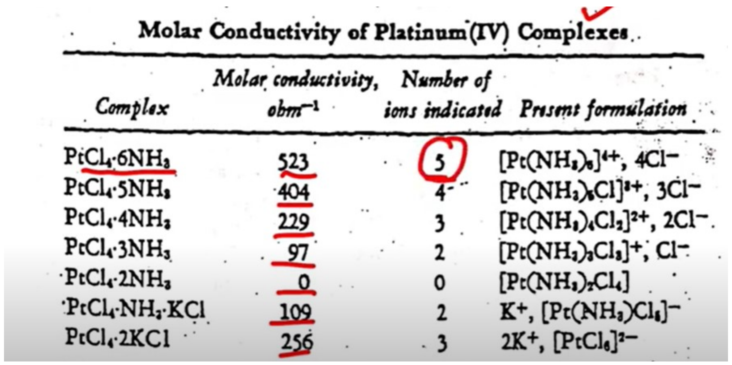
$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl\downarrow$$

Cl^- ion written in coordination sphere is not ionisable and can, therefore, not be precipated.



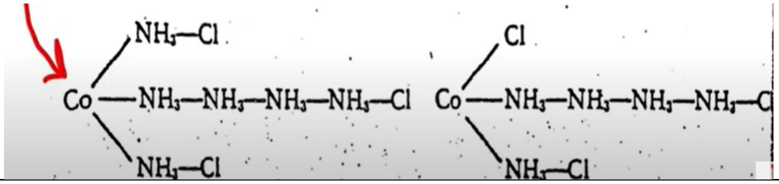
Number of Chloride Ions Precipitated as AgCl

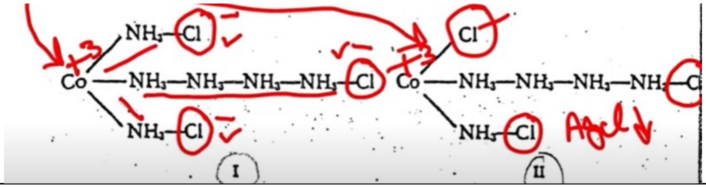
Complex	*Number of Cl⁻ ions precipitated*	*Present formulation*
$CoCl_3 \cdot 6NH_3$	3	$[Co(NH_3)_6]^{3+}, 3Cl^-$
$CoCl_3 \cdot 5NH_3$	2	$[Co(NH_3)_5Cl]^{2+}, 2Cl^-$
$CoCl_3 \cdot 4NH_3$	1	$[Co(NH_3)_4Cl_2]^+, Cl^-$
$IrCl_3 \cdot 3NH_3$	0	$[Ir(NH_3)_3Cl_3]$

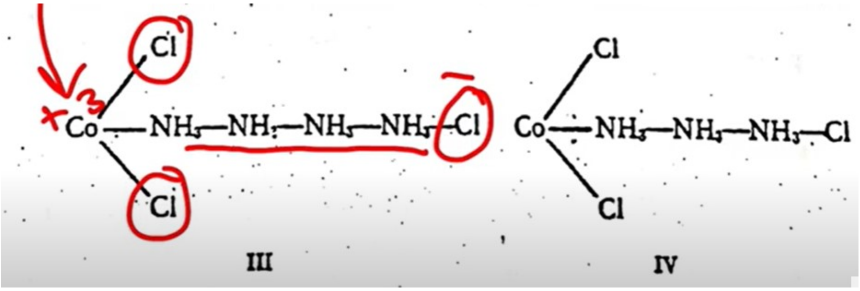


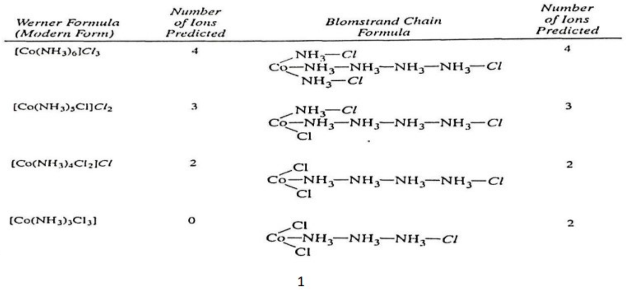
Molar Conductivity of Platinum(IV) Complexes

Complex	*Molar conductivity, ohm⁻¹*	*Number of ions indicated*	*Present formulation*
$PtCl_4 \cdot 6NH_3$	523	5	$[Pt(NH_3)_6]^{4+}, 4Cl^-$
$PtCl_4 \cdot 5NH_3$	404	4	$[Pt(NH_3)_5Cl]^{3+}, 3Cl^-$
$PtCl_4 \cdot 4NH_3$	229	3	$[Pt(NH_3)_4Cl_2]^{2+}, 2Cl^-$
$PtCl_4 \cdot 3NH_3$	97	2	$[Pt(NH_3)_3Cl_3]^+, Cl^-$
$PtCl_4 \cdot 2NH_3$	0	0	$[Pt(NH_3)_2Cl_4]$
$PtCl_4 \cdot NH_3 \cdot KCl$	109	2	$K^+, [Pt(NH_3)Cl_5]^-$
$PtCl_4 \cdot 2KCl$	256	3	$2K^+, [PtCl_6]^{2-}$









Werner Formula (Modern Form)	*Number of Ions Predicted*	*Blomstrand Chain Formula*	*Number of Ions Predicted*
$[Co(NH_3)_6]Cl_3$	4	NH₃—Cl Co—NH₃—NH₃—NH₃—NH₃—Cl NH₃—Cl	4
$[Co(NH_3)_5Cl]Cl_2$	3	NH₃—Cl Co—NH₃—NH₃—NH₃—NH₃—Cl Cl	3
$[Co(NH_3)_4Cl_2]Cl$	2	Cl Co—NH₃—NH₃—NH₃—NH₃—Cl Cl	2
$[Co(NH_3)_3Cl_3]$	0	Cl Co—NH₃—NH₃—NH₃—Cl Cl	2

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