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CHEMISTRY

Target : JEE (Main)

COORDINATION COMPOUNDS

COORDINATION COMPOUNDS

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JEE (MAIN) SYLLABUS

Introduction to co-ordination compounds, Werner's theory; ligands, coordination number, denticity, chelation ; IUPAC nomenclature of mononuclear co-ordination compounds, isomerism ; Bonding-Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; Importance of co-ordination compounds (in qualitative analysis, extraction of metals and in biological systems).

JEE(ADVANCED) SYLLABUS

Nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

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Coordination Compounds

Addition Compounds :

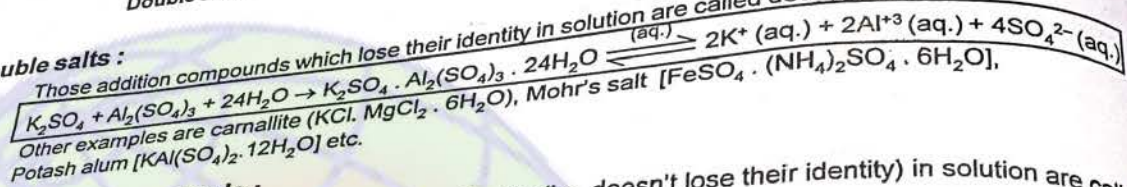
They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Double salts

Coordination compounds (Complexes)

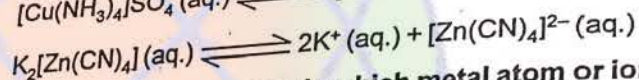
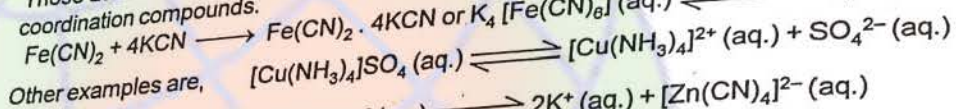
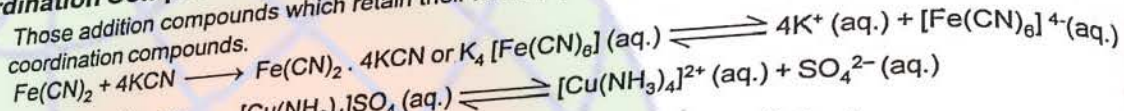
Double salts :

Those addition compounds which lose their identity in solution are called double salts.



Coordination Compounds :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are called coordination compounds.



Coordination compound is defined as a species in which metal atom or ion is attached to group of neutral molecules / ions by coordinate covalent bonds.

Solved Examples

- Ex.1** Explain that $Fe(NH_4)_2(SO_4)_2$ is a double salt but $K_3Fe(CN)_6$ is a complex.
- Sol.** $Fe(NH_4)_2(SO_4)_2$ is a double salt because its solution gives tests of Fe^{2+} , NH_4^+ and SO_4^{2-} . $K_3Fe(CN)_6$ is not a double salt but it is a complex because the solution of this compound renders K^+ and $[Fe(CN)_6]^{3-}$ ions and further $[Fe(CN)_6]^{3-}$ does not give the tests of Fe^{3+} and CN^- .

Werner's Theory :

Werner in 1893 presented a theory known as Werner's coordination theory. More important postulates of this theory are :

Most element exhibit two types of valencies : (a) Primary valency and (b) Secondary valency.

(a) Primary valency :

This corresponds to oxidation state of the metal ion. This is also called principal, ionisable or ionic valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

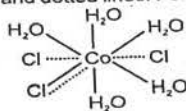
(b) Secondary or auxiliary valency :

It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules having lone pair of electrons (e.g., H_2O , NH_3 etc.) or even sometimes by some positive groups. The ligands which satisfy the coordination number are directly attached to the metal atom or ion and shown by thick lines.

Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e. it may satisfy both primary and secondary valencies since in every case the fulfillment of coordination number of the central metal ion appears essential. This dual

Coordination Compounds

behaviour is represented by both thick and dotted lines. For example, $[\text{CoCl}(\text{H}_2\text{O})_5]\text{Cl}_2$ is represented as



The ions/groups bound by the secondary valencies have characteristic spatial arrangements corresponding to different coordination number. In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

C.N. = 2 linear
C.N. = 3 triangular
C.N. = 4 tetrahedral or square planar
C.N. = 6 octahedral.

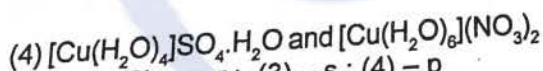
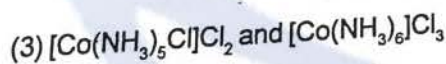
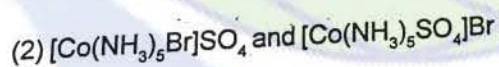
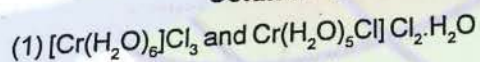
To distinguish between the two types of valencies, Werner introduced the square brackets [] to enclose those atoms making up the coordination complex and which are, therefore, not ionized. On the basis of the above postulates Werner formulated the coordination compounds, $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ as : $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ respectively; the species within the square brackets being the coordination entities (complexes) and the ions outside the square brackets the counter ions. He further postulated that octahedral, square, planar and tetrahedral geometrical shapes are more common in coordination compounds of transition metals. Thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, $[\text{CoCl}_2(\text{NH}_3)_4]^+$ are octahedral entities, while $[\text{Ni}(\text{CO})_4]$ and $[\text{PtCl}_4]^{2-}$ are tetrahedral and square-planar, respectively.

S.No.	Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
1	$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$	six (NH_3)	three (Cl^-)
2	$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
3	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
4	$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

Solved Examples

Ex.2 Match the pairs of complexes listed in column-I with the method(s) used for their differentiation listed in column-II.

Column - I



Column-II

(p) Only neutral molecule(s) satisfy(es) all secondary valences in both complexes.

(q) Negative ion(s) satisfy(es) both primary as well as secondary valences in both complexes.

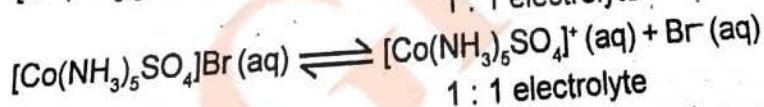
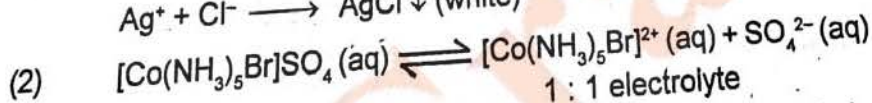
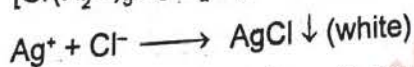
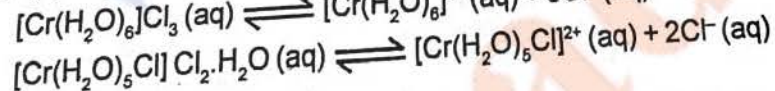
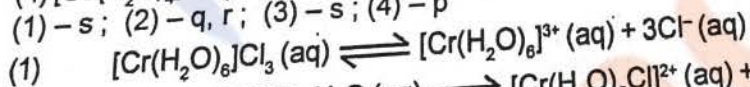
(r) Both complexes give same number of ions in aqueous solution.

(s) Both complexes give white precipitate with AgNO_3 .

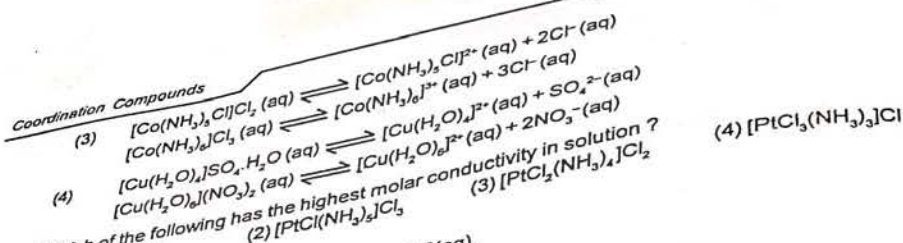
Ans.

Sol.

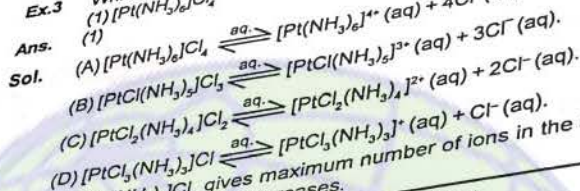
(1) - s ; (2) - q, r ; (3) - s ; (4) - p



Br^- and SO_4^{2-} satisfy both primary as well as secondary valences.



Ex.3 Which of the following has the highest molar conductivity in solution ?
 (1) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$



Sol. Since $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ gives maximum number of ions in the solution and as number of ions increases molar conductivity in solution increases.

Coordination Entity/Coordination Sphere :

A coordination entity constitutes a central atom/ion, usually of a metal, to which are attached a fixed number of other atoms or groups each of which is called a ligand. It may be neutral or charged. Examples being : $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{PtCl}_4]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{NiCl}_2(\text{OH}_2)_4]$ and (NH_3) , (Cl^-) , (CN^-) , (H_2O) are the ligands. The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively called as coordination sphere.

Note : The remaining ions apart from complex ions i.e. outside the coordination sphere are called counter ions, free ions or ionisable ions. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, the potassium (K^+) ion is counter ion of coordination entity $[\text{Fe}(\text{CN})_6]^{4-}$.

Central Atom/ion :

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

Ligands :

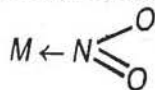
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

These may be simple ions such as Br^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or even macromolecules such as proteins.

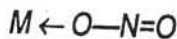
When a ligand is attached to a metal atom/ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be unidentate. Similarly when a ligand is bound through two donor atoms, as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1, 2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be bidentate and when several donor atoms are present in a single ligand as in $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ or ethylenediaminetetraacetic acid (EDTA), the ligand is said to be polydentate.

Ambidentate Ligand :

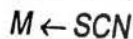
Ligands which can ligate through two different atoms present in it are called ambidentate ligands. Examples of such ligands are the CN^- , NO_2^- and SCN^- ions. NO_2^- ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds. For example,



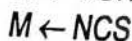
nitrito-N



nitrito-O



thiocyanato or thiocyanato-S



isothiocyanato or thiocyanato-N

Chelate ligand :

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring. The complex formed is referred to as a chelate complex and the process of chelate formation is called chelation. The number of such ligating groups is called the denticity of the ligand.

Denticity and Chelation :

Table : 1
Common Monodentate Ligands

Common Name	IUPAC Name	Formula
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	$\text{C}_5\text{H}_5\text{N}$ (py)
ammonia	ammine	NH_3
water	aqua or aquo	H_2O
carbonyl	carbonyl	CO
nitrosyl	nitrosyl	NO
fluoro	fluoro or fluorido*	F^-
chloro	chloro or chlorido*	Cl^-
bromo	bromo or bromido*	Br^-
iodo	iodo or iodido*	I^-
cyano	cyanido or cyanido-C* (C-bonded)	CN^-
isocyano	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyano	thiocyanato-S(S-bonded)	SCN^-
isothiocyano	thiocyanato-N(N-bonded)	NCS^-
hydroxo	hydroxo or hydroxido*	OH^-
nitro	nitrito-N (N-bonded)	NO_2^-
nitrito	nitrito-O (O-bonded)	ONO^-
nitrate	nitrate	NO_3^-
amido	amido	NH_2^-
nitride	nitrido	N^{3-}
azido	azido	N_3^-
hydride	hydrido	H^-
oxide	oxido	O^{2-}
peroxide	peroxido	O_2^{2-}
superoxide	superoxido	O_2^-
sulphate	sulphato	SO_4^{2-}
sulphide	sulphido or thio	S^{2-}
nitrosylium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	NO_2^+

* The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

Coordination Compounds		Table : 2 Common Chelating Amines		Formula
Chelating Points	Common Name	IUPAC Name	Abbreviation	
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
bidentate	propanediamine	1,2-propanediamine	pn	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$
bidentate	acetylacetonate	2,4-pentanedione or acetylacetonato	acac	
bidentate	2,2'-bipyridine	2,2'-bipyridyl	bipy	
bidentate	1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen, o-phen	
bidentate	oxalate	oxalato	ox	
bidentate	glycinate	glycinato	gly	$\text{NH}_2\text{CH}_2\text{COO}^-$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyl (dinitrilo) tetraacetato or ethylenediaminetetraacetato	EDTA	

Coordination Number :

The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached. Pi-bonds, if any, between the ligating atom and the central atom/ion are not considered for the determination of coordination number. The sigma bonding electrons may be indicated by a pair of dots, preceding the donor atom in the ligand formula as in : $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ni}(\text{CO})_4]$, $[\text{Co}(\text{Cl}_4)]^{2-}$.

Some common co-ordination number of important metals are as given below.

Metal	C.N.	Metal	C.N.
Cu^+	2, 4	Ni^{2+}	4, 6
Ag^+	2	Fe^{2+}	6
Au^+	2, 4	Fe^{3+}	6
Cu^{2+}	4, 6	Co^{2+}	6
Ag^{2+}	4	Co^{3+}	6
Pt^{2+}	4	Pt^{4+}	6
Pd^{2+}	4	Pd^{4+}	6

Coordination Compounds

Oxidation number of Central Atom :

The oxidation number of the central atom 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. Metal oxidation number is represented by a Roman numeral in parentheses following the name of the coordination entity. For example oxidation number of iron in $[\text{Fe}(\text{CN})_6]^{3-}$ is +3 and it is written as Fe(III).

Homoleptic and heteroleptic complexes

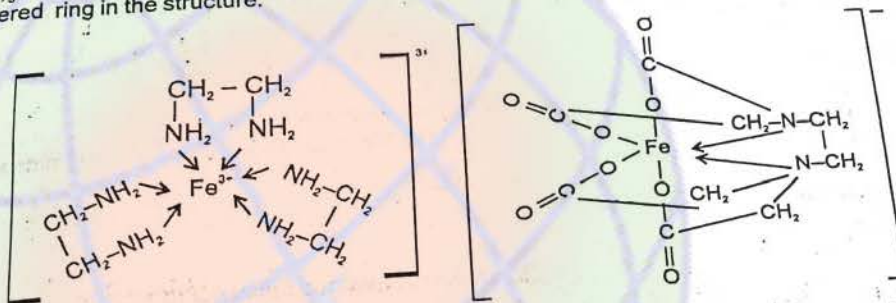
Complexes in which a metal is bound to only one type of donor groups, e.g., $[\text{Cr}(\text{NH}_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$, are known as heteroleptic.

Solved Examples

Ex.4 Give the coordination entities and counter ions in the coordination compounds :
 $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$; $\text{K}_4[\text{Fe}(\text{CN})_6]$; $\text{K}_2[\text{PtCl}_4]$; $[\text{Ni}(\text{CO})_4]$; $\text{K}_2[\text{Ni}(\text{CN})_4]$.

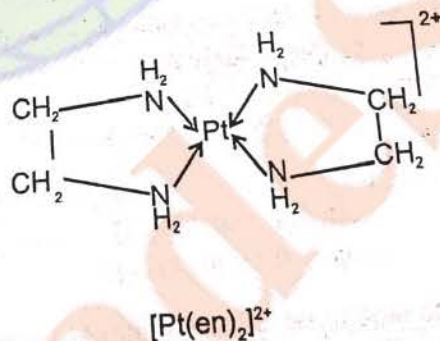
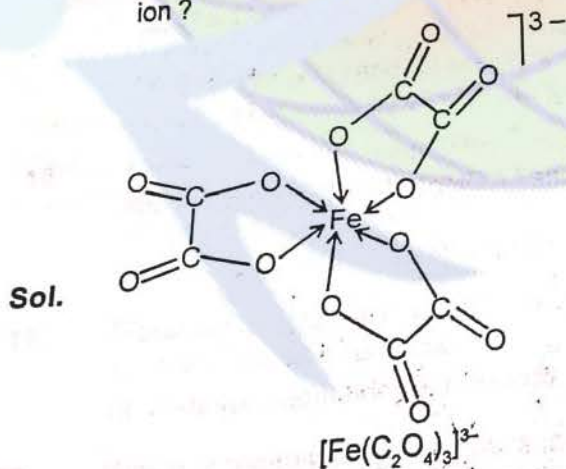
Sol. The respective coordination entities are : $[\text{Cr}(\text{NH}_3)_6]^{3+}$; $[\text{Fe}(\text{CN})_6]^{4-}$; $[\text{PtCl}_4]^{2-}$; $[\text{Ni}(\text{CO})_4]$; and the counter ions are Cl^- , K^+ , K^+ , (no counter ion) and K^+ , respectively in the given coordination compounds.

Ex.5 Explain why $[\text{Fe}(\text{en})_3]^{3+}$ is less stable than $[\text{Fe}(\text{EDTA})]^-$?
Sol. $[\text{Fe}(\text{en})_3]^{3+}$ has three, five membered rings in the structure. On the other hand $[\text{Fe}(\text{EDTA})]^-$ has five, six membered ring in the structure.



The five membered rings are less stable than six membered rings; so $[\text{Fe}(\text{en})_3]^{3+}$ is less stable than $[\text{Fe}(\text{EDTA})]^-$.

Ex.6 Draw the structure of the complexes $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Pt}(\text{en})_2]^{2+}$. Determine the denticity of the ligands and identify any chelate rings. What are the coordination number and the oxidation number of the central metal ion?



Coordination Compounds

The ligands, oxalate and ethylenediamine are bidentate as each ligand has to donor atoms. So in 1st case the number of chelate rings (five membered) are three where as in 2nd case the number of chelate rings (five membered) are two.
The coordination number and oxidation state of iron are six and +3 respectively and the coordination number and oxidation state of platinum are four and +2 respectively.

Nomenclature of Coordination Compounds

Writing the formulas of Mononuclear Coordination Entities :
The following rules are followed while writing the formulas :

- The central atom is placed first.
- The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligands abbreviations are also enclosed in parentheses.
- There should be no space between the ligands and the metal within a coordination sphere.
- When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ etc.
- The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

The following rules are followed when naming coordination compounds :

- Like simple salts the cation is named first in both positively and negatively charged coordination entities. Examples : $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, diamminesilver(I)chloride. $\text{K}_3[\text{Fe}(\text{CN})_6]$, potassium hexacyanidoferrate(III).
- The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.

Examples :

- $[\text{Pt}(\text{NH}_3)_2\text{BrCl}(\text{CH}_3\text{NH}_2)]$, amminebromidochloridomethylamineplatinum(II).
 $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})_2]^-$, diaquabis(oxalato)cobaltate(III).
- Names of the anionic ligands end in -o and those of neutral ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO, thiocarbonyl for CS and nitrosyl for NO. But names of cationic ligands end in -ium. The neutral an cationic are placed within enclosing marks () .

Some more important examples of neutral and cationic ligands are :

tetraphosphorus	—	P_4
dioxygen	—	O_2
octasulphur	—	S_8

- Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis

Examples ; $[\text{CoCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]^+$, dichloridobis(ethane-1,2-diamine)cobalt(III).
 $[\text{NiCl}_2(\text{PPh}_3)_2]$, dichloridobis(triphenylphosphine)nickel(II).

- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numerals in the parentheses after the name of metal.

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e-mail: lko@resonance.ac.in

KOLKATA
Tel.: 033-3192222, 6060660/ 01/ 02
e-mail: kolkata@resonance.ac.in

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Tel.: 02462-250220, 606066
e-mail: nanded@resonance.ac.in

MUMBAI
Tel.: 022-31922222, 60606600
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Tel.: 0294-6060660, 5107510, 3192222
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Tel.: 0674-3192222, 3274919, 6060660/ 61
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AGRA
Tel.: 0562-3192222, 6060660
e-mail: agra@resonance.ac.in

RANCHI
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e-mail: ranchi@resonance.ac.in

ALLAHABAD
Tel.: 0532-6060660
e-mail: allahabad@resonance.ac.in

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RAIPUR
Tel.: 0771- 6060660
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Tel.: 0240-6060660
e-mail: aurangabad@resonance.ac.in

JABALPUR
Tel.: 0761- 6060660
e-mail: jabalpur@resonance.ac.in

GWALIOR
Tel.: 0751-6060660
e-mail: gwalior@resonance.ac.in

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e-mail: chandrapur@resonance.ac.in

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VIJAYANAGAR
Tel.: 23111333/ 23111334

YELAHANKA
Tel.: 08028463922/ 42289643

CHIKKAMAGALURU
Mobile: 7411329369, 9448396890

HASSAN
Mobile: 9481392014, 9972038283

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Tel.: 26595151/ 26595153.

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To Know more: sms RESO at 56677 | **E-mail:** contact@resonance.ac.in | **Website:** www.resonance.ac.in

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