

COORDINATION COMPOUNDS

Key Points

A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are bonded to the metal atom or ion by a coordinate bond.

Example: $\text{K}_4[\text{Fe}(\text{CN})_6]$

They do not dissociate into simple ions when dissolved in water.

- **Double salt**

When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called double salts.

Example: $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt)

They dissociate into simple ions when dissolved in water.

- **Coordination entity:**

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.

Example: In $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Fe}(\text{CN})_6]^{4-}$ represents coordination entity.

- **Central atom or 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.

Example: In $\text{K}_4[\text{Fe}(\text{CN})_6]$, Fe^{2+} is the central metal ion.

- **Ligands:**

A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.

It may be neutral, positively or negatively charged.

Examples: H_2O , CN^- , NO^+ etc.

- **Donor atom:**

An atom of the ligand attached directly to the metal is called the donor atom.

Example: In the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$, CN^- is a donor atom.

- **Coordination number:**

The coordination number of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.

Example: In the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$, the coordination number of central metal atom is 6.

- **Counter ions:**

The ions present outside the coordination sphere are called counter ions.

Example: In the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$, K^+ is the counter ion.

- **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.

Examples: $[\text{PtCl}_4]^{2-}$ is square planar, $[\text{Ni}(\text{CO})_4]$ is tetrahedral while $[\text{Co}(\text{NH}_3)_6]^{3+}$ is octahedral.

- **Denticity:**

The number of ligating (linking) atoms present in a ligand is called denticity.

- **Unidentate ligands or Monodentate ligands:**

The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands.

Examples: H_2O , NH_3 , CO , CN^- etc.

- **Didentate ligand or Bidentate ligand:**

The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.

Examples: Ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) has two nitrogen atoms, oxalate ion ($\text{C}_2\text{O}_4^{2-}$) has two oxygen atoms which can bind with the metal atom.

- **Polydentate ligand:**

When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.

Examples: In $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be polydentate and Ethylenediaminetetraacetate ion **EDTA** $^{4-}$ is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

- **Chelate:**

An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points.

An example is the complex ion formed between ethylenediamine and cupric ion, $[\text{Cu}(\text{en})_2]^{2+}$.

- **Ambidentate ligand:**

Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligand.

Example: NO_2^- and SCN^- . Here NO_2^- can link through N as well as O while SCN^- can link through S as well as N atom.

- **Werner's coordination theory:**

Werner was able to explain the nature of bonding in complexes.

The postulates of Werner's theory are:

Metal shows two different kinds of valencies: primary valence and secondary valence.

- **Primary Valence**

1. This valence is normally ionisable.
2. It is equal to positive charge on central metal atom.
3. These valences are satisfied by negatively charged ions.
4. It is equal to oxidation state of central metal ion.

- **Secondary Valence**

1. This valence is non – ionisable.
2. The secondary valence equals the number of ligand atoms coordinated to the metal. It is also called coordination number of the metal.
3. It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

- **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.

- **Homoleptic complexes:** Those complexes in which central metal atom/ion is coordinate bonded to only one kind of donor atoms. For example: $[\text{Co}(\text{NH}_3)_6]^{3+}$
- **Heteroleptic complexes:** Those complexes in which central metal atom/ion is coordinate bonded to more than one kind of donor atoms.

Isomers: Two or more compounds which have same chemical formula but different arrangement are called isomers.

- **Types of isomerism:**

(a) Structural Isomerism -

- **Linkage isomerism:**

1. It arises in a coordination compound containing ambidentate ligand.
2. In the isomerism, a ligand can form linkage with metal through different atoms.
3. Example: $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

- **Ionisation isomerism:**

1. It arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.
2. Example: $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$.

- **Solvate isomerism:**

1. It is isomerism in which solvent is involved as ligand.
2. If solvent is water it is called hydrate isomerism, e.g. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

Coordination isomerism:

1. This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
2. Example: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Co}(\text{CN})_6][\text{Cr}(\text{NH}_3)_6]$.

- **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.

- **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.

- **Optical isomerism:** Optical isomers are mirror images that cannot be superimposed on one another.

- **Magnetic properties of Coordination Compounds:**

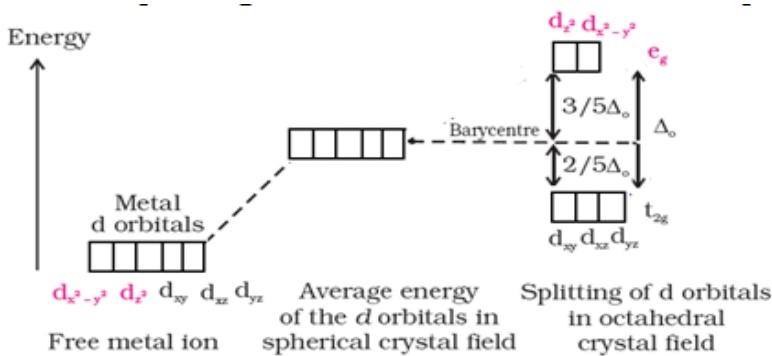
A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic moment : $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

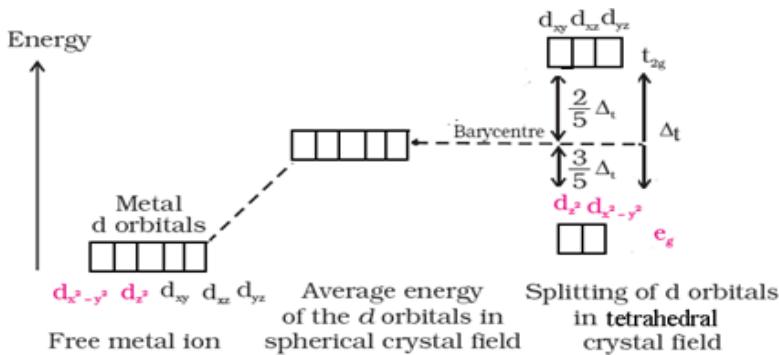
- **Crystal Field Theory:**

1. It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion.
2. It is theoretical assumption.

- **Crystal field splitting in Octahedral coordination complexes:**



- **Crystal field splitting in Tetrahedral coordination complexes:**

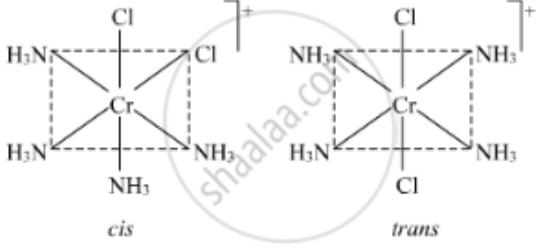


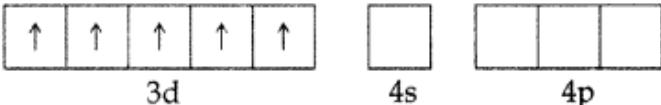
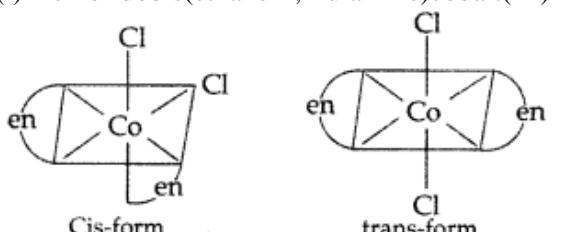
- For the same metal, the same ligands and metal-ligand distances,

$$\Delta_t = 4/9 \Delta_o$$

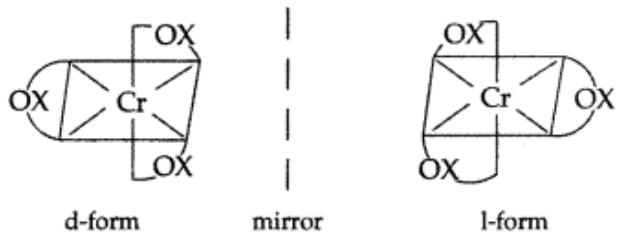
	MCQ Type Questions:
1.	IUPAC name of $[\text{Pt}(\text{NH}_3)_3\text{Br}(\text{NO}_2)\text{Cl}] \text{ Cl}$ is (a) triamminechlorodibromidoplatinum (IV) chloride (b) triamminechloridobromidonitrochloride- platinum (IV) chloride (c) triamminebromidochloridonitroplatinum (IV) chloride (d) triaminenitrochlorobromoplatinum (IV) chloride
2	Primary and secondary valence of Pt in $[\text{Pt}(\text{en})_2\text{Cl}_2]$ are (a) 4, 4 (b) 4, 6 (c) 6, 4 (d) 2, 6
3	The complex ions $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ are called (a) Ionization isomers (b) Linkage isomers (c) Co-ordination isomers (d) Geometrical isomers
4	The oxidation state of nickel in $[\text{Ni}(\text{CO}_4)]$ is (a) 0 (b) 1 (c) 2 (d) 3
5	According to Werner's theory of coordination compounds (a) Primary valence is ionisable (b) Secondary valence is ionisable (c) Primary and secondary valencies are ionisable (d) Neither primary nor secondary valence is ionisable
6	Which of the following has square planar structure? (a) $[\text{NiCl}_4]^{2-}$ (b) $[\text{Ni}(\text{CO})_4]$ (c) $[\text{Ni}(\text{CN})_4]^{2-}$ (d) None of these
7	The ligand $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ is (a) bidentate (b) tridentate (c) tetridentate (d) pentadentate
8	Which of the following is a hexadentate ligand? (a) EDTA^{4-} (b) $(\text{COO})_2^{2-}$ (c) en (d) NH_3
9	Mohr's salt is (a) $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (b) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (c) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (d) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
10	Which of the following is not a neutral ligand? (a) H_2O (b) NH_3 (c) ONO^{2-} (d) en
	<u>Assertion Reason Type questions</u> Directions: These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

	<p>(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion</p> <p>(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.</p> <p>(c) If the Assertion is correct but Reason is incorrect.</p> <p>(d) If both the Assertion and Reason are incorrect</p>
11.	<p>Assertion : NF_3 is a weaker ligand than $\text{N}(\text{CH}_3)_3$.</p> <p>Reason : NF_3 ionizes to give F^- ions in aqueous solution</p>
12.	<p>Assertion : $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.</p> <p>Reason : $[\text{Fe}(\text{CN})_6]^{3-}$ has +3 oxidation state while $[\text{Fe}(\text{CN})_6]^{4-}$ has +2 oxidation state.</p>
13.	<p>Assertion : $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.</p> <p>Reason : d-d transition is not possible in $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$.</p>
14.	<p>Assertion: Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.</p> <p>Reason: Geometrical isomerism is not shown by complexes of coordination number 6.</p>
15.	<p>Assertion: $[\text{Fe}(\text{CN})_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.</p> <p>Reason: Because it has d^2sp^3 type hybridization.</p>
	<p><u>2 Marks type questions:</u></p>
16.	<p>Write IUPAC name of the complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$. Draw structures of geometrical isomers for this complex.</p>
17.	<p>Using IUPAC norms write the formulae for the following :</p> <p>(a)Pentaamminenitrito-O-cobalt(III) ion</p> <p>(b)Potassium tetracyanidonickelate(II)</p>
18.	<p>Write the hybridization and geometry of $[\text{Ni}(\text{CN})_4]^{2-}$ [Atomic number , Ni = 28].</p>
19.	<p>Give the formulae of the following compounds :</p> <p>(a) Potassium tetrahydroxidozincate(II)</p> <p>(b) Hexaammineplatinum(IV) chloride</p>
20.	<p>Which complex ion is formed when undecomposed AgBr is washed with hypo solution in photography?</p>
	<p><u>3 Mark questions:</u></p>
21.	<p>Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory:</p> <p>$[\text{CoF}_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Cu}(\text{NH}_3)_6]^{2+}$</p>
22.	<p>$\text{CoSO}_4\text{Cl.5NH}_3$ exists in two isomeric forms ‘A’ and ‘B’. Isomer ‘A’ reacts with AgNO_3 to give white precipitate, but does not react with BaCl_2. Isomer ‘B’ gives white precipitate with BaCl_2 but does not react with AgNO_3. Answer the following questions.</p> <p>(i) Identify ‘A’ and ‘B’ and write their structural formulas.</p> <p>(ii) Name the type of isomerism involved.</p> <p>(iii) Give the IUPAC name of ‘A’ and ‘B’.</p>

	(b) Giving a suitable example for each, explain the following : (i) Crystal field splitting (ii) Ambidentate ligand
	<u>ANSWER KEY:</u>
	MCQ type questions
1.	(c)
2.	(d)
3.	(b)
4.	(a)
5.	(a)
6.	(c)
7.	(a)
8.	(a)
9.	(b)
10.	(c)
	<u>Assertion Reason type questions:</u>
11.	(c)
12.	(b)
13.	(a)
14.	(c)
15.	(d)
	<u>ANSWERS OF 2 Mark type questions:</u>
16.	The IUPAC name of the complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is Tetraamminedichlorochromium(III) ion . This complex exhibits geometrical isomerism. 
17.	(i) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ (ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$
18.	The atomic number of Ni is 28 and its valence shell electronic configuration is $3d^8 4s^2$. Ni is in +2 oxidation state in the complex $[\text{Ni}(\text{CN})_4]^{2-}$. Hence, $[\text{Ni}(\text{CN})_4]^{2-}$ is dsp² hybridised and it is square planar in shape.
19.	(i) $\text{K}_2[\text{Zn}(\text{OH})_4]$ (ii) $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$

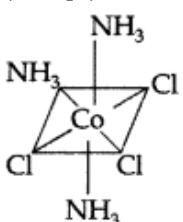
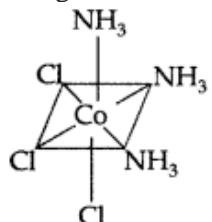
20.	Sodium dithiosulphatoargentate (I) complex is formed. $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$ <p style="text-align: center;">Complex</p>
	<u>ANSWERS OF 3 marks questions</u>
21.	$[\text{CoF}_6]^{3-}, \text{Co}^{3+} \rightarrow (3d^6) \rightarrow t_{2g}^4 e_g^2$ $[\text{Fe}(\text{CN})_6]^{4-}, \text{Fe}^{2+} \rightarrow (3d^6) \rightarrow t_{2g}^6 e_g^0$ $[\text{Cu}(\text{NH}_3)_6]^{2+}, \text{Cu}^{2+} \rightarrow (3d^9) \rightarrow t_{2g}^6 e_g^3$
22.	(i) As isomer A reacts with AgNO_3 to give a white precipitate, Cl^- must be present in the ionisation sphere. As it does not react with BaCl_2 , SO_4^{2-} must be present in the coordination sphere. Therefore the formula of A = $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ (coordination no. of Co = 6) As reactions are reversed for isomer B, formula B = $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ (ii) The type of isomerism involved is Ionisation isomerism (iii) The IUPAC name of A = Pentaamminesulphatocobalt(III) chloride , B = Pentaamminechloridocobalt(III) sulphate
23.	(i) Tetrachloridonickelate(II) ion (ii) sp^3 (iii) Tetrahedral
24.	In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe^{3+} is :  In the presence of CN^- , the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is d^2sp^3 forming inner orbital complex which is weakly paramagnetic. In the presence of H_2O (a weak ligand), 3d electrons do not pair up. The hybridisation involved is sp^3d^2 forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic.
25.	(i) Dichloridobis(ethane-1,2-diamine)cobalt(III) ion  The geometrical isomers of $[\text{CoCl}_2(\text{en})_2]^+$ (2 isomers)

(ii) Trioxalatochromate(III) ion



(iii) Triamminetrichloridocobalt(III) ion

The geometrical isomers of $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (2 isomers) :



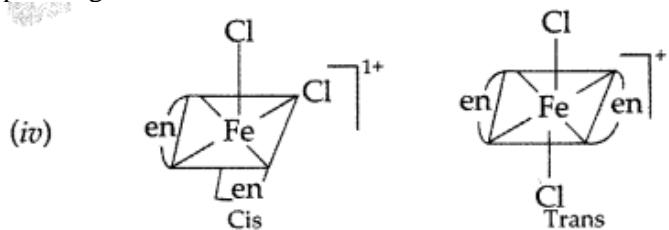
Case Study type

26. (i) (c)
(ii) $\Delta_t = 4/9 \Delta_0$
(iii) (a) $t_{2g}^4 e_g^0$ (b) $t_{2g}^3 e_g^1$
(iv) For $[\text{FeF}_6]^{4-}$, $n = 4$, Magnetic moment = 4. 89BM.

27. (i) (d) It involves d^2sp^3 hybridization.
(ii) It is an octahedral, diamagnetic, and inner orbital complex.
(iii) Due to presence of 4 unpaired electrons.
(iv) $[\text{Co}(\text{CN})_6]^{3-}$

ANSWERS OF 5 marks questions

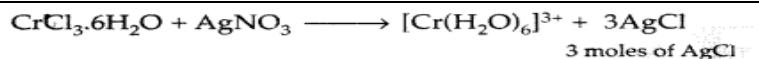
28. (i) $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$ or $x + 0 + 2 (-1) = 1$
 $x + (-2) = 1$ or $x = +3$
 \therefore Oxidation number of iron, $x = +3$
(ii) The complex has two bidentate ligands and two monodentate ligands. Therefore, the coordination number is 6 and hybridization will be d^2sp^3 and shape will be octahedral.
(iii) Due to presence of one unpaired electrons in 3d orbitals the complex is paramagnetic.



The number of geometrical isomers are two.

(v) Name of complex: Dichloridobis(ethane-1,2-diamine)iron(III) chloride.

29.

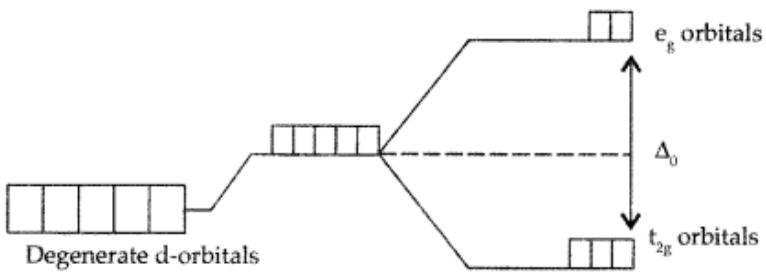


(a)(i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

(ii) Hexaaquaechromium(III) chloride

(iii) Paramagnetic, unpaired electrons = 3

(b)(i) Crystal field splitting: It is the splitting of the degenerate energy levels due to the presence of ligands. When ligand approaches a transition metal ion, the degenerate d-orbitals split into two sets, one with lower energy and the other with higher energy. This is known as crystal field splitting and the difference between the lower energy set and higher energy set is known as crystal field splitting energy (CFSE)



Splitting of d-orbitals in an octahedral complex

(ii) Ambidentate ligand: The unidentate ligands with more than one donor atoms but only one donor atom binds to central metal atom/ion at a time is known as ambidentate ligand. For example, NO_2^- can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.