Coordination Chemistry

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- Introduction to Coordination Complexes
- Werner's Theory
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➤ Usually, d & f-block elements form complexes

Reason: small size & high charge (large charge/size ratio) favor complexation

Double salts

- > They usually contain two simple salts in equimolar proportions
- Usually contains water of crystallization
- Exist only in solid state, dissociates completely in aqueous solution.
- Ionic compound, no coordinate bond.
- The properties of double salt are same as those of its constituent ions.

Mohr's salt, FeSO₄.(NH₄)₂SO₄.6H₂O

Potash alum, K_2SO_4 . $Al_2(SO_4)_3$.24 H_2O

Chrome alum, K₂SO₄.Cr₂(SO₄)₃.24H₂O

Ferric alum, K₂SO₄.Fe₂(SO₄)₃.24H₂O

Coordination complex

- Coordination complex is defined as compound that results from the combination of two or more stable chemical species and retains its identity in solids as well as in solution phase.
- ➤ A coordination compound contains at least one *complex ion*, which consists of a central metal cation bonded to molecules and/or anions called *ligands*.
- ➤ The complex ion is associated with *counter ions* of opposite charge.
- > The complex ion $[Cr(NH_3)_6]^{3+}$ has a central Cr^{3+} ion bonded to six
 - NH₃ ligands. The complex ion behaves like a polyatomic ion in



In short, complex is a central metal atom or ion surrounded by a set of ligands

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Double salt vs Coordination Compound

- Double salts loose their identity in solution whereas coordination compounds or complex usually retain their identity
- Double salts when dissolved in water gives tests for constituent ions whereas complex salts normally do not.
- > $FeSO_4.(NH_4)_2SO_4.6H_2O$ is a double salt and gives the tests foe Fe^{2+} , NH_4^+ , and SO_4^{-2-} ions in solution
- ≻ $K_3[Cr(ox)_3]$ is a complex and gives the tests for K⁺ and $[Cr(ox)_3]^{3-}$ ions in solution

Components of a coordination compound



 $[Co(NH_3)_6]Cl_3$ dissolves in water. The six

ligands remain bound to the complex ion.

 $[Pt(NH_3)_4]Br_2$ has four NH_3 ligands

and two Br⁻ counter ions

Coordination compounds can be distinguished by measuring their molar conductivities and by qualitative analysis

- The cations to which one or more neutral molecules or ions are coordinated is called the central ion
- The central ion together with molecules or ions coordinated to it constitute the coordination sphere, represented within square bracket []
- ➤ In $[Co(NH_3)_6]Cl_3$ complex, the coordination sphere is $[Co(NH_3)_6]^{3+}$
- The charge carried by a complex ion is the algebraic sum of the charges of central ion and ligands coordinated to it.
- A coordination compound sometimes may not have any charge. For example, the complex $[CoCl_3(NH_3)_3]$ is neutral.
- ➤ In $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]^{3+}$ is a cationic complex
- ➤ In K₃[Fe(CN)₆], [Fe(CN)₆]³⁻ is an anionic complex
- [Co(NH₃)₆][Ni(CN)₅] is a coordination compound with [Co(NH₃)₆]³⁺ as cationic and [Ni(CN)₅]³⁻ as anionic complex

In terms of Lewis acid-base concept, a complex is a combination of Lewis acid with a number of Lewis base

 M^{n+} (Lewis acid) + xL (Lewis base) $\rightarrow [MLx]^{n+}$

Donor atom

- The atom in the ligand that is bound to (coordinated to) the central metal atom or ion is called the donor atom
- ▶ In $[Co(NH_3)_6]Cl_3$ complex bearing NH₃ ligand, the N-atom is the donor atom

Acceptor atom

- \succ It is the central metal atom or ion
- > In the above complex, Co^{3+} is the acceptor ion
- All metals from all blocks of the periodic table have the ability to form coordination compound

Application of coordination compounds

- Coordination compounds find widespread applications in our day to day life
- The principles of coordination chemistry are extensively used in analytical chemistry for detection and estimation of metal ions
- Coordination chemistry is also used in soil treatment, water softening, corrosion control etc.
- ➢ It is widely used in inorganic catalytic reactions
- ➢ It is very important medical sciences
- Such compounds are vital to the functioning of living beings
- Hemoglobin, cytochromes, cis-platin, Vit B₁₂, Chlorophyll etc. are all coordination compounds

Coordination Number (CN)

- > The CN is the *number of ligand atoms* bonded *directly* to the central metal ion.
- CN is *specific* for a given metal ion in a particular oxidation state and compound
- ➤ The most CN in complex ions is 2, 4 and 6, but 3, 5, 7, 9 and 12 may also occur.
- \succ The geometry of a given complex ion depends *both* on the coordination number and the

metal ion

CN	Shape	Examples
2	Linear	$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar	[Ni(CN) ₄] ²⁻ , [PdCl ₄] ²⁻ , [Pt(NH ₃) ₄] ²⁺ , [Cu(NH ₃) ₄] ²⁺
4	Tetrahedral	$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$. $[MnCl_4]^{2-}$
6	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn((H_2O_6]^{2+}, [FeCl_6]^{3-}, [Co(en)_3]^{3+})_{Draft Bapan Saha}$



Werner's Coordination Theory, 1893

➢ Warner, studied the behavior of transition metal ions with NH₃ ligands and established some rules leading to the foundation of the subject Coordination theory (Warner's Theory)

Postulates

- Metal atoms possess two types of valency primary (ionizable) & secondary (non ionizable).
- Primary valency is ionizable & non directional and secondary valency is non-ionizable & directional. Primary valency corresponds to oxidation state and secondary valency corresponds to the coordination number
- Every metal atom has a fixed number of secondary valencies/CN



Alfred Warner, Nobel prize 1913

- The metal atom tends to satisfy both its primary and secondary valencies. Primary valencies are satisfied by negative ions while secondary valencies are satisfied either by negative ions or neutral molecules
- Secondary valency leads to definite geometry of the complex



- The complex is shown inside the square bracket
- Ionizable ions are shown outside the square bracket
- Primary valencies are related to ionic interaction
- Secondary valencies are related to coordination bonds



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Illustration

- ≻ Let us consider the $[Co(NH_3)_6]Cl_3$ complex
- ➤ The coordination number of Co is 6, secondary valency is represented by NH₃ molecules
- ➤ The complex is octahedral, Because CN of Co is 6.
- ➤ The primary valency is 3, represented by Cl⁻ ions
- ➢ Primary valency is ionizable, all Cl⁻ can be precipitated using

AgNO₃ solution



Limitations

Werner's theory cannot answer the following basic questions

- ➤ Why only certain elements form coordination compounds and not others?
- ➤ Why the coordination sphere/entity has a definite geometry?
- > Why do these compounds possess definite magnetic and optical properties?

To overcome the above issues, a number of attempts have been made.

- ➢ Valence bond theory (VBT)
- Crystal field theory (CFT)
- ➢ Ligand field theory (LFT)
- ➢ Molecular orbital theory (MOT)

Ligands

- ➤ The molecules or ions attached with the central ion in coordination compounds are termed as ligands (may be neutral, cationic or anionic)
- > The ligands are attached to central ion through coordinate (dative) bonds
- Ligands can have one or more *donor atoms*. Each donor atom donates a *lone pair of electrons* to the metal ion to form a coordinate covalent bond
- ➤ Denticity is defined as the number of donor atoms of a ligand available for coordination to the central metal or metal ions
- Ligands are classified in terms of their number of donor atoms, or "teeth": monodentate, bidentate and polydentate ligands bond through a one, two and more than two donor atoms respectively. Draft Bapan Saha

Some Common Ligands in Coordination Compounds



➤ The monodentate ligands which have two coordinating or donor atoms but during complexation, only one of these two are used as donor at a time are defined as

ambidentate ligands (cyanido, nitro, cyanato, thiocyanato etc.)

Chelates

- ➢ Bidentate and polydentate ligands give rise to *rings* in the complex ion. Such ligands are called chelating ligand (oxalate, en, DMG, acac, DMG etc.)
- ➤ A complex ion containing this type of structure is called a *chelate* because the ligand seems to grab the metal ion like claws.
- \blacktriangleright EDTA has six donor atoms and forms very stable complexes with metal ions.



How to write formulas of Coordination Compounds?

- ≻ The central atom is written first
- \succ The ligand symbols are then listed in alphabetical order, no space in between
- The order of the ligand does not depend on the charge of the ligand
- > The polyatomic ligands are written within the parenthesis
- ➢ Organic ligands may be represented in abbreviation within parenthesis, their places in the formula are decided by the first symbols of their formulae, not by the first letter of their common names
- > The coordination sphere is represented within a square bracket
- \succ The overall charge is written outside the square bracket as superscripts.

Determining the charge of the metal ion

- The charge of the cation(s) is/are balanced by the charge of the anion(s)
- ≻ $K_2[Co(NH_3)_2Cl_4]$ contains a complex *anion*.
- The charge of the anion is balanced by the two K⁺ counter ions, so the anion must be [Co(NH₃)₂Cl₄]²⁻
- There are two neutral NH_3 ligands and four Cl⁻ ligands. To have an overall charge of 2-, the metal ion must have a charge of +2
- Charge of complex ion = charge of metal ion + total charge of ligands

2- = charge of metal ion + $[(2 \times 0) + (4 \times -1)]$

Charge of metal ion = (-2) - (-4) = +2

> The metal ion in this complex anion is Go^{2}

- \succ [Co(NH₃)₄Cl₂]Cl contains a complex *cation*.
- The charge of the cation is balanced by the Cl⁻ counter ion, so the cation must be $[Co(NH_3)_4Cl_2]^+$.
- There are four neutral NH_3 ligands and two Cl⁻ ligands. To have an overall charge of 1+, the metal ion must have a charge of 3+.

Charge of complex ion = charge of metal ion + total charge of ligands

1+ = charge of metal ion + [(4 x 0) + (2 x 1-)]

Charge of metal ion = (+1) - (2-) = +3

> The metal ion in this complex cation is Co^{3+} .

Naming (IUPAC-2005) Coordination Compounds

- \blacktriangleright In ionic coordination complexes, the cation is named before the anion
- Neutral complexes (non ionic complexes) are given one word name
- ➢ In naming coordination sphere, the ligands are named first followed by central metal ion
- > The ligands are named alphabetically irrespective of their charges
- > The neutral ligands are named as such (pyridine, ethylenediamine) with exception to few such as H_2O (aqua), NO (nitrosyl), NH₃ (ammine), CO (carbonyl) etc.
- The names of negative ligands end in -o and of positive ligands end in -ium after the root name (illustrated in next page).

Names of Some Neutral and Anionic Ligands

Ligands		Ligands	
Formula	Name	Formula	Name
F-	Fluorido	NO ₃ -	Nitrato
Cl-	Chlorido	NH ²⁻	Imido
Br	Bromido	NCS-	Thiocyanato-N
I-	Iodido	SCN-	Thiocyanato-S
OH-	Hydroxido	SO ₄ ²⁻	Sulphato
CN-	Cyanido	NO ₂ -	Nitrito-N
ONO-	Nitrito-O	O ₂ ²⁻	Peroxido
C ₂ O ₄ ²⁻	Oxalato	NO^+	Nitrosonium
NH ₂ -	Amido	NO ₂ ⁺	Nitronium
H-	Hydrido	NH ₂ NH ₃ ⁺	Hydrazinium
CH ₃ COO ⁻	Acetato		
CO ₃ ²⁻	Carbonato Draft Bapan	Saha	24

A numerical prefix is used to indicate the number of ligands of a particular type. Prefixes do not affect the alphabetical order of ligand names. Ligands that include a numerical prefix in the name use the prefixes *bis* (2), *tris* (3), or *tetrakis* (4) to indicate their number.

If the complex is anionic, the names of central metal atom ends in -ate (Latin root name), Fe (ferrate), Cu (cuprate), Pb (plumbate), Ag (argentate), Au (aurate), Sn (stannate), Pt (platinate) etc.

- ➤ A Roman numeral is used to indicate the oxidation state for a metal within parenthesis, without any space
- ➢ For bridging ligands, Greek letter µ is written before their names, repeated before the name of each kind of bridging liganchan Saha
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- ➤ If a ligand can coordinate via more than one donor atoms, the symbol of ligating atom is mentioned within parenthesis after the name of the ligand
- ➢ In naming geometrical isomers, the term *cis* (adjacent) and *trans* (opposite) are used
- ➢ In naming optical isomers, + or d (dextro rotatory) and − or l (laevo rotatory) are used.
- ➢ For complicated molecules, abbreviations are generally used.

Writing Names and Formulas of Coordination Compounds

Problems

- (a) What is the systematic name of $Na_3[AlF_6]$?
- (b) What is the systematic name of $[Co(en)_2Cl_2]NO_3$?
- (c) What is the formula of tetraamminebromidochloridoplatinum(IV) chloride?
- (d) What is the formula of hexaamminecobalt(III) tetrachloridoferrate(III)?

Solutions:

- a) The complex ion is $[AlF_6]^{3-}$. There are six (*hexa-*) F⁻ ions (*fluorido*) as ligands. The complex ion is an anion, so the ending of the metal name must be changed to –ate. Since Al has only one oxidation state, no Roman numerals are used. The IUPAC name is *sodium hexafluoridoaluminate*
- b) There are two ligands, Cl^{-} (*chlorido*) and en (*ethylenediamine*). The ethylenediamine ligand already has a numerical prefix in its name, the two -en ligands are prefixed by *bis* instead of *di*. The complex ion is a cation, so the metal name is unchanged, but we need to specify the oxidation state of Co. The counter ion is $NO_{3^{-}}$, so the complex ion is $[Co(en)_2Cl_2]^+$. 27

Charge of complex ion = charge of metal ion + total charge of ligands

1+ = charge of metal ion +
$$[(2 \times 0) + (2 \times 1)]$$

Charge of metal ion = (+1) - (-2) = +3

The ligands must be named in alphabetical order. The IUPAC name is *dichloridobis(ethylenediamine)cobalt(III) nitrate*

(c) The central metal ion is written first, followed by the neutral ligands and then (in alphabetical order) by the negative ligands.

Charge of complex ion = charge of metal ion + total charge of ligands

 $= (4+) + [(4 \times 0) + (1 \times 1-) + (1 \times 1-)] = +4 + (-2) = +2$

We will therefore need two Cl⁻ counter ions to balance the charge on the complex ion, $[Pt(NH_3)_4BrCl]Cl_2$

(d) This compound consists of two different complex ions. In the cation, there are six NH_3 ligands and the metal ion is Co^{3+} , so the cation is $[Co(NH_3)_6]^{3+}$. The anion has four Cl-ligands and the central metal ion is Fe³⁺, so the ion is $[FeCl_4]^-$.

The charge on the cation must be balanced by the charge on the anion, so we need three anions for every one cation, $[Co(NH_3)_6][FeCl_4]_3^{Draft Bapan Saha}$ ²⁸

Name the compound $[Co(NH_3)_4Cl_2]Cl.$

We start by naming the complex cation. The ligands are named alphabetically with ammine first and then chloro. There are four ammonias and two chlorides, so the prefixes *tetra*- and *di*- are used. The cobalt oxidation state is determined by tracing the charges back as follows: The net charge on the complex cation must be 1+ to balance the one 1- chloride anion. Since there are two 1- chlorides in the coordination sphere, the cobalt must be 3+in order for the net charge on the cation to come out as 1+. With all this in mind, the full name of the compound is

tetraamminedichlorocobalt(III) chloride

EXAMPLE 2.2

Name the compound $(NH_4)_2[Pt(NCS)_6]$.

Here we have a platinum-containing complex anion and the common ammonium ion, NH_4^+ , as the cation. Given that the ligand is written with the N symbol first, we know that it is the isothiocyanato (or, alternatively, *N*-thiocyanato) form of the ambidentate ligand. There are six of these ligands, so we use the *hexa*- prefix. The anion must have a net charge of 2to balance the two 1+ ammonium cations. Since the thiocyanate ion is also 1-, the platinum oxidation state must be 4+ to give a net 2- charge on the anion. Because the platinum is contained in a complex anion, its *-um* suffix is removed and replaced with *-ate*. Accordingly, the full name of the compound is

> ammonium hexaisothiocyanatoplatinate(IV) Draft Bapan Saha

Name the compound [Cu(NH₂CH₂CH₂NH₂)₂]SO₄.

As in Example 2.1, we again have a complex cation. The ligand is ethylenediamine, which is often abbreviated as "en" so that the formula for this compound is usually shortened to $[Cu(en)_2]SO_4$. There are two ethylenediamine ligands, but since it is a neutral ligand with *di*- within its name, the prefix *bis*is used and, since this is a neutral ligand without a special name, "ethylenediamine" is enclosed in parentheses. The copper oxidation state will be the same as the net charge on the complex cation (since the ligands are neutral). That charge must be 2+ to balance the 2- of the sulfate ion. The full name of this compound is

bis(ethylenediamine)copper(II) sulfate

EXAMPLE 2.4

Name the compound $[Ag(CH_3NH_2)_2][Mn(H_2O)_2(C_2O_4)_2].$

In this case both the cation and the anion are complex. To indicate that there are two methylamine ligands in the cation we will use the *bis*- prefix. [Note that if we used the *di*- prefix we would have "dimethylamine" which could be readily construed as one $(CH_3)_2NH$ ligand instead of two CH_3NH_2 ligands.] In the anion, the two aqua (water) ligands come alphabetically

before the two oxalato ligands. The name manganese is amended to manganate because this metal is in a complex anion. The oxidation states here must be such that a 1:1 ratio of the cation and anion results. This could be Ag(I)/Mn(III), Ag(II)/Mn(II), or similar values in which, in this case, the sum of the oxidation states is 4. Considering the chemistry of silver and manganese, the first case is the most appropriate. (In time, you will become familiar enough with common transition metal oxidation states that you will not need to debate such matters.) The full name of this compound is

bis(methylamine)silver(I) diaquadioxalatomanganate(III)

Name the compound



This is our first example of a bridged compound. The three hydroxides bridge between the two cobalt ions. We name such compounds from left to right and remember to put a μ in front of the bridging ligands. The oxidation states of the metals could be (III) and (III), (II) and (IV), (I) and (V), or any other combination adding up to 6, but even from our brief exposure to cobalt chemistry, you would probably (and correctly) choose the first alternative. The full name of the compound is

 $triamminecobalt (III) - \mu - trihydroxotriamminecobalt (III) nitrate$

EXAMPLE 2.6

Write the formula for the compound (acetylacetonato)tetraaquacobalt (II) chloride.

The formula for the bidentate acetylacetonate ligand is given in Table 2.3, but this 1- anion is usually abbreviated as acac. The acac and four waters constitute the coordination sphere that with the cobalt(II) cation are set apart in brackets. The net charge on the complex cation is 1+ (because the acac is 1-), so one chloride counteranion is needed. The formula of the compound is

[Co(acac)(H₂O)₄]Cl

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Write the formula for the compound triamminechloro(ethylene)nitroplatinum(IV) phosphate.

This compound has four different types of ligands in the coordination sphere: NH_3 , Cl^- , C_2H_4 , and NO_2^- (bonded through the nitrogen). The only real difficulty in constructing this formula is figuring out how many cations and anions there must be. The cation has a net charge of 2+, and the anion is 3-. Therefore, there must be three cations and two anions to ensure electrical neutrality. The formula for this compound is

 $[Pt(NH_3)_3Cl(C_2H_4)NO_2]_3(PO_4)_2$

EXAMPLE 2.8

Write the formula for tetraamminechromium(III)- μ -amido- μ -hydroxobis (ethylenediamine)iron(III) sulfate.

The OH^- and NH_2^- are bridging ligands between the cobalt and iron cations. The overall charge on this huge cation is 4+ (6+ from the two 3+ cations and 2- from the two 1- anions). Therefore, there must be two 2- sulfates in the formula:



Write the formula for cesium trichlorotantalum(III)- μ -trichlorotrichlorotantalate(III).

In this case the anion is complex. It contains two tantalum(III) cations bridged by three chloride ions. Each tantalum also has three monodentate chlorides attached to it. The overall charge on the anion is 3-(6+ from the two 3+ tantalum cations and 9- from the nine 1- chlorides. There must be three Cs⁺ cations to balance the one 3- anion. The formula for this compound is



Formula	Name
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt (III) chloride
$[Cr(H_2O)_4Cl_2]NO_3$	Tetraaquadichloridochromium (III) nitrate
$[Co(NH_3)_4Cl(NO_2)]NO_3$	Tetraamminechloridonitrocobalt (III) nitrate
$[Cr(en)_3]Cl_3$	Tris(ethylelenediamine)chromium (III) chloride Tris(ethane-1,2-diamine)chromium (III) chloride
$[CoCl_2(en)_2]SO_4$	Dichloridobis(ethane-1,2-diamine)cobalt (IV) sulphate
$[Co(NH_3)_4(H_2O)Br](NO_3)_2$	Tetraammineaquabromidocobalt (III) nitrate
$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium (III) chloride
$[CoCl(en)_2(ONO)]^+$	Chloridobis(ethane-1,2-diamine)nitritocobalt (III) ion
$[Cr(H_2O)_4Cl_2]Cl$	Tetraquadichloridochromium (III) chloride
[Co(NH ₃) ₅ CO ₃]Cl	Pentaamminecarbonatocbalt (III) chloride
$[CoCl_2(en)_2]SO_4$	Dichloridobis(ethane-1,2-diamine)cobalt (IV) sulphate
[Co(NH ₃) ₆]ClSO ₄	Hexaamminecobalt (III) chloride sulphate
[(NH3) ₅ Cr-OH-Cr-(NH ₃) ₅]Cl ₅	Pentaamminechromium(III)-µ- hydroxopentamminechromium (III) chloride

Formula	Name
$K_3[Fe(C_2O_4)_3]$	Potassium trioxalatoferrate (III)
$K_3[Co(CN)_5(NO)]$	Potassium pentacyanonitrosylcobaltate (II)
K[Pt(NH ₃)Cl ₃]	Potassium amminetrichloridoplatinate (II)
$Na_2[CrF_4O]$	Sodium tetrafluridooxochromate (IV)
$Na_2[SiF_6]$	Sodium hexafluridosilicate (IV)
Dextro $K_3[Ir(C_2O_4)_3]$	Potassium (+) or d-trioxalatoiridate (III)
$Na_3[Fe(C_2O_4)_3]$	Sodium trioxalatoferrate (III)
Hg[Co(NCS) ₄]	Mercury tetraisothiocyanatocobaltate (II) Mercury tetrathiocyanato –N-cobaltate (II)
$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate (0)
$Fe_4[Fe(CN)_6]_3$	Ferric hexacyanoferrate (II)
Li[AlH ₄]	Lithium tetrahydridoaluminate (III)
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III)
$K_3[Ag(S_2O_3)_2]$	Potassium dithiosulphatoargentate (I)
$[(en)_2Co(NH_2)(OH)Co(en)_2]$	Bis(ethane-1,2-diamine) cobalt(III)-µ-amido-µ- hydroxobis(ethane-1,2-diamine)cobalt (III)
$[(\mathrm{NH}_3)_4\mathrm{Co}(\mathrm{NH}_2)(\mathrm{NO}_2)\mathrm{Co}(\mathrm{NH}_3)_4$	Tetraamminecobalt(III)-µ-amido-µ-nitrotetraammine cobalt

Formula	Name
[Pt(NH ₃) ₄ Cl ₂][PtCl ₄]	Tetraamminedichloridoplatinum (IV) tetrachloridoplatinate (II)
$[Co(NH_3)_4Cl_2]_3[Cr(CN)_6]$	Tetraamminedichloridocobalt (III) hexacyanochromate (III)
$[Ag(NH_3)_2][Ag(CN)_2]$	Diammine silver (I) dicyanido argentate (I)
$[Pt(py)_4][PtCl_4]$	Tetrapyridine platinum (II) tetrachloride platinate (II)
[Cr(NH ₃) ₅ (NCS)][ZnCl ₄]	Pentaammine isothiocyanato chromium (III) tetrachloridozincate
$[\mathrm{Co}(\mathrm{NH}_3)_3(\mathrm{NO}_2)_3]$	Triamminetrinitrocobalt (III)
$[Pt(NH_3)_2Cl_2]$	Diamminedichloridoplanitum (II)
$[Cr(PPh_3)(CO)_5]$	Pentacarbonyltriphenylphosphinechromium (0)
$[Fe(C_5H_5)_2]$	Bis(cyclopentadienyl)iron (II)
[Ni(CO) ₄]	Tetracarbonylnickel (0)
$[Mn_3(CO)_{12}]$	Dodecarbonyltrimanganese (0)
$[Ni(dmg)_2]$	Bis(dimethylglyoximato)nickel (II)
$[(CO)_3 Fe(CO)_3 Fe(CO)_3]$	Tri-µ-carbonyl-bis(tricarbonyl iron (0))
$Na_3[Co(ONO)_6]$	Sodium hexanitritocobaltate (III)
$Na_2[Fe(CN)_5NO]$	Sodium nitrosoniumpentacyanoferrate (II)
$Hg[Co(CNS)_4]$	Mercury tetrathiocyanatocobaltate (III)
$[Cl(Ph_3P)_3-Pd-(Cl)(Cl)-$	Chloridotriphenylphosphine palladium (II)-µ-dichloride-
Name	Formula
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Tetrammineaquachloridocobalt (III) Chloride	[Co(NH ₃) ₄ (H ₂ O)Cl]Cl ₂
Sodiumpentacyanonitrosylsulphidoferrate (III)	$Na_4[Fe(CN)_5(NO)S]$
Potassium tetrahydroxozincate (II)	$K_2[Zn(OH)_4]$
Potassium pentacyanonitrosylcobaltate (III)	$K_2[Co(CN)_5NO]$
Bis(acetylacetonato)oxovanadium (IV)	[V(acac) ₂ O]
Sodium ethylenediaminetetraacetato chromate (II)	$Na_2[Cr(CH_3COO)_4(en)]$
Chlorido-bis(ethylenediamine) nitrocobalt (III) ion	$[\text{CoCl(en)}_2(\text{NO}_2)]^+$
Pentaaminenitrito-O-cobalt (III)	$[Co(NH_3)_5(ONO)]^{2+}$
Sodium dicyanidourate (I)	$Na[U(CN)_2]$
Tetraammine chloridonitrito-N-platinum (IV) sulphate	[Pt(NH ₃) ₄ Cl(NO ₂)]SO ₄
Potassium trioxalatoaluminate (III)	$K_3[Al(C_2O_4)_3]$
Dichlorido(ethane-1,2-diamine)cobalt (III)	$[\text{CoCl}_2(\text{en})_2]^+$
Potassium tetracyanonickelate (III)	K[Ni(CN) ₄]
Tris (ethane-1,2-diamine)chromium (III) chloride	$[Cr(en)_3Cl_3]$
Chloridodiammine platinum (II) ion	$[Pt(NH_3)_2Cl]^+$
Hexaaquairon (II) sulphate	$[Fe(H_2O)_6]SO_4$

Isomerism in coordination compounds

- The compounds having the same molecular formula but different structures and hence different physical and chemical properties are called isomers
- > The phenomenon of the existence of such compounds is known as isomerism
- Coordination compounds give rise to a wide variety of isomers due to different types of linkage and structural arrangements.
- Isomerism in coordination compounds may be classified in two types viz. structural (constitutional) isomerism and stereo (space) isomerism



Structural Isomerism

Ionization isomerism:

- Ionization isomerism occurs when ligand and counterion in one compound exchange places
- Ionization isomers result from the interchange of an anionic ligand within the first coordination sphere with an anion outside the coordination sphere
- Example, [PtCl₂(NH₃)₄]Br₂ and [PtBr₂(NH₃)₄]Cl₂. In solution, the two isomers exist as different ionic species in solution (with free Br and Cl⁻ ions respectively)
- Similarly, violet [Co(NH₃)₅Br]SO₄ and red [Co(NH₃)₅SO₄]Br giving ionic SO₄²⁻ or Br, respectively.

Hydrate/solvate isomerism:

- Hydrate isomerism, which arises when one of the ligands is water (replacement of a coordinated group by water of hydration)
- Hydration isomers result from the interchange of H₂O and another ligand between the first coordination sphere and the ligands outside it.
- > They differ largely from one another in their physical and chemical properties.
- Example, there are three differently colored hydration isomers of a compound with molecular formula $CrCl_3 \cdot 6H_2O$: the violet $[Cr(OH_2)_6]Cl_3$, the pale green $[CrCl(OH_2)_5]Cl_2 \cdot H_2O$, and the dark green $[CrCl_2(OH_2)_4]Cl.2H_2O$

Coordination isomerism:

- Coordination isomerism arises when there are different complex ions that can form from the same molecular formula
- Arises when both positive and negative ions of salt are complex ions and the two isomers differ in the distribution of ligands in the cation and the anion.
- Coordination isomers are possible only for salts in which both cation and anion are complex ions; the isomers arise from interchange of ligands between the two metal centres.
- > This can occur by the exchange of a ligand and a counter ion or by the exchange of ligands.
- $\succ \text{ Example, } [Co(NH_3)_6][Cr(CN)_6] \text{ and } [Cr(NH_3)_6][Co(CN)_6].$
- \blacktriangleright [Co(NH₃)₆][Co(NO₂)₆] and [Co(NH₃)₄(NO₂)₂[Co(NH₃)₂(NO₂)₄]
- $\succ [Pt^{II}(NH_3)_4][Pt^{IV}Cl_6] \text{ and } [Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4].$

Linkage isomerism:

- Arises in compounds containing ambidentate ligands, when more than one atom in a unidentate ligand may function as a donor.
- Linkage isomers occur when the composition of the complex ion is the same but the ligand donor atom is different (same ligand may link through different atoms)
- The complex [Co(NH₃)₅(NCS)]²⁺ has two isomers with formulae [Co(NH₃)₅(NCS-N)]²⁺, N-donor thiocyanate and [Co(NH₃)₅(NCS-S)]²⁺ with S-donor thiocyanate
- ➤ This type of isomerism accounts for the red and yellow isomers of the formula [Co(NH₃)₅(NO₂)]²⁺. The red compound has a nitrito-O Co-O link; the yellow isomer has a nitrito-N Co-N link.



Coordination position isomerism:

This type of isomerism is exhibited by bridged complexes and results from different placement of ligands. Q. What types of isomerism are possible for complexes with the following molecular formulas: (a) $[Pt(PEt_3)_3SCN]^+$, (b) $CoBr(NH_3)_5SO_4$, (c) $FeCl_2(H_2O)_6$?

Answer (a) The complex contains the ambidentate thiocyanate ligand, SCN-, which can bind through either the S or the N atom to give rise to two linkage isomers: $[Pt(SCN)(PEt_3)_3]^+$ and $[Pt(NCS)(PEt_3)_3]^+$

(b) With an octahedral geometry and five coordinated ammonia ligands, it is possible to have two ionization isomers: $[Co(NH_3)_5SO_4]Br$ and $[CoBr(NH_3)_5]SO_4$.

(c) Hydrate isomerism occurs as complexes of formula $[Fe(OH_2)_6]Cl_2$, $[FeCl(OH_2)_5]Cl H_2O$, and $[FeCl_2(OH_2)_4] \cdot 2H_2O$ are possible.

Q. Two types of isomerism are possible for the six-coordinate complex with the molecular formula $Cr(NO_2)_2(H_2O)_6$. Identify all isomers.

Stereo Isomerism

- Stereoisomers are compounds that have the same atomic connections but different spatial arrangements of their atoms.
- ➤ Geometrical isomerism: Geometric or cis-trans isomers occur when atoms or groups can either be arranged on the same side or on opposite sides of the compound relative to the central metal ion
- Optical isomerism: Optical isomers (enantiomers) are non-superimposable mirror images of each other. They are optically active and rotate (left/right) the plane polarized equally in opposite directions.
- Optical active isomers do not have plane of symmetry and have identical physical and chemical properties.

Geometrical isomers

Geometrical isomerism in complexes with CN 4

- Complexes with CN 4 adopts either tetrahedral or square planar geometry.
- ➢ Only square planar complexes ([MA₂B₂], [MA₂BC], [MABCD] and [M(AB)₂]) show geometrical isomerism.

[MA₂B₂] type complex

With two sets of two different monodentate ligands there is only the case of *cis/trans* isomerism to consider



- > Examples, $[PtCl_2(NH_3)_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[PtCl_2(py)_2]$ etc.
- \triangleright cis-trans isomers can be distinguished by X_{a} ciffraction technique.

[MA₂BC] type complex

With three different ligands, the locations of the two A ligands also allow us to distinguish the geometric isomers as *cis* (two A ligands are adjacent) and *trans* (two A ligands are opposite)



► Examples, [PtClNH₃(py)₂]

[MABCD] type complex

When there are four different ligands, there are three different isomers and we have to specify the geometry more explicitly (drawn by fixing position of one ligand and placing the other ligands trans to it)



> Examples, $[Pt(NO_2)(py)(NH_3)(NH_2OH)]^+$

[M(AB)₂] type complex

Bidentate ligands with different end groups, can also give rise to geometrical isomers that can be classified as *cis* and *trans*.



 \blacktriangleright Examples, [Pt(gly)₂] where gly = NH₂CH₂COO⁻

Geometrical isomerism cannot occur in complexes of the type [MA₄], [MA₃B] or [MAB₃] because all possible spatial arrangements are equivalent

Isomerism (optical) in Tetrahedral complexes (CN-4)

- > The only simple isomers of tetrahedral complexes are optical isomers.
- Tetrahedral complexes should bear four different ligands or have two unsymmetrical bidentate chelating ligands.
- In both cases, the molecules are chiral, not superimposable on their mirror image (gives enantiomeric pair)
- Optical isomers are so called because they are optically active, one enantiomer rotates the plane of polarized light in one direction and the other rotates it through an equal angle in the opposite direction.



Geometrical isomerism in complexes with CN 6

- \triangleright Complexes with coordination no 6, [ML₆] adopt octahedral geometry
- Octahedral complexes also exhibit geometrical isomerism
- There is only one way of arranging the ligands in octahedral complexes of general formula [MA₆] or [MA₅B], so geometrical isomers for these two

[MA₄B₂] type complex

The two B ligands of an [MA₄B₂] complex may be placed on adjacent octahedral positions to give a *cis* isomer or on diametrically opposite positions to give a *trans* isomer.



- > Similarly complex of the type $[MA_4BC]$ also shows geometrical isomerism.
- Example, the structures of cis (violet) and trans (green) forms of tetramminedichloridochromium (III) ion

[MA₃B₃] type complex

- > There are two ways of arranging the ligands in $[MA_3B_3]$ complexes.
- In one isomer, three A ligands lie in one plane and three B ligands lie in a perpendicular plane.
- This complex is designated the *mer* isomer (for meridional) because each set of ligands can be regarded as lying on a meridian of a sphere.
- In the second isomer, all three A (and B) ligands are adjacent and occupy the corners of one triangular face of the octahedron
- This complex is designated the *fac* isomer (for facial) because the ligands sit on the corners of one face of an octahedron (Example, [RhCl₃(py)₃])



[Mabcdef] type complex

- ➢ With six different ligand, 15 different geometrical forms may exist.
- \blacktriangleright Example, [PtBrCl(NO₂)(py)(NH₃)] with three different arrangements are synthesized

[M(AA)₂B₂] or [M(AA)₂BC] type complex

- ➤ With two bidentate ligands (AA)₂, whether the other two ligands are same r different shows geometrical isomerism.
- Example, [M(en)₂bc] where M = Co(III), Cr(III), Ir(III), Rh(III) and Pt (IV), and b and c are NO₂⁻, I⁻, Br⁻, Cl⁻, NH₃, py etc.
- ▶ For example, the complex $[CoCl_2(en)_2]^+$ exists in cis and trans forms

[MA₂B₂C₂] type complex

For a complex of composition $[MA_2B_2C_2]$, there are five different geometrical isomers: an all-*trans* isomer; three different isomers where one pair of ligands is *trans* with the other two are *cis*; and an enantiomeric pair of all-*cis* isomers



[MA₂B₂CD] or [MA₃B₂C] type complex

- More complicated compositions, such as [MA₂B₂CD] or [MA₃B₂C], result in more extensive geometrical isomerism.
- ➢ For instance the rhodium compound [RhH(C≡CR)₂(PMe₃)₃] exists as three different isomers: *fac*, *mer-trans*, and *mer-cis*.



Optical isomerism in complexes with CN 6

- ✤ A very simple example is [Mn(acac)₃], where three bidentate acetylacetonato (acac) ligands result in the existence of enantiomers.
- One way of looking at the optical isomers that arise in complexes of this nature is to imagine looking down one of the three-fold axes and seeing the ligand arrangement as a propeller or screw thread.
- Chirality can also exist for complexes of formula [MA₂B₂C₂] when the ligands of each pair are *cis* to each other.
- Many examples of optical isomerism are known for octahedral complexes with both monodentate and polydentate ligands.





- The products of the reaction of cobalt(III) chloride and 1,2-diaminoethane in a 1:2 mole ratio includes a pair of dichlorido complexes, one of which is violet and the other green; they are, respectively, the *cis* and *trans* isomers of dichloridobis(1,2-diaminoethane)cobalt(III), [CoCl₂(en)₂]⁺.
- The *cis* isomer cannot be superimposed on its mirror image. It is therefore chiral and hence optically active.
- The *trans* isomer has a mirror plane and can be superimposed on its mirror image; it is achiral and optically inactive.





Π

trans - [Co(en)2Cl2]+

same as

Structure I and its mirror image, structure II, are optical isomers of *cis* $[Co(en)_2Cl_2]^+$

The *trans* isomer of $[Co(en)_2Cl_2]^+$ does not have optical isomers. Structure I *can* be superimposed on its mirror image, structure II.

Ш

- The absolute configuration of a chiral octahedral complex is described by imagining a view along a three-fold rotation axis of the regular octahedron and noting the handedness of the helix formed by the ligands.
- * Clockwise rotation of the helix is then designated Δ (delta) whereas the anticlockwise rotation is designated Λ (lambda).
- The designation of the absolute configuration must be distinguished from the experimentally determined direction in which an isomer rotates polarized light: some Λ compounds rotate in one direction, others rotate in the opposite direction, and the direction may change with wavelength.
- The isomer that rotates the plane of polarization clockwise (when viewed into the oncoming beam) at a specified wavelength is designated the *d* - isomer, or the (+)-isomer; the one rotating the plane anticlockwise is designated the *l* isomer, or the (-)-isomer.



Figure 7.7* Absolute configurations of $M(L-L)_3$ complexes. Δ is used to indicate clockwise rotation of the helix and Λ to indicate anticlockwise rotation.

Optical isomers

- Optical isomerism is concerned with chirality
- The simplest case of optical isomerism among d-block complexes involves a metal ion surrounded by three bidentate ligands
- \blacktriangleright Example, tris-chelate complexes such as $[Cr(acac)_3]$ or $[Co(en)_3]$
- > Pairs of enantiomers differ only in their action on polarized light.

Sample Problem 23.4 Determining the Type of Stereoisomerism

PROBLEM: Draw stereoisomers for each of the following and state the type of isomerism:

(a) $[Pt(NH_3)_2Br_2]$ (square planar) (b) $[Cr(en)_3]^{3+}$ (en = $H_2NCH_2CH_2NH_2$)

PLAN: We determine the geometry around each metal ion and the nature of the ligands. If there are different ligands that can be placed in different positions relative to each other, geometric (*cis-trans*) isomerism occurs. Then we see whether the mirror image of an isomer is superimposable on the original. If it is *not*, optical isomerism also occurs.

Sample Problem 23.4

SOLUTION:

(a) The square planar Pt(II) complex has two different types of monodentate ligands. Each pair of ligands can be next to each other or across from each other. Thus *geometric isomerism* occurs.



These are geometric isomers; they do not have optical isomers since each compound *is* superimposable on its mirror image.

Sample Problem 23.4

(b) Ethylenediamine (en) is a bidentate ligand. The Cr³⁺ ion has a coordination number of 6 and an octahedral geometry, like Co³⁺. The three bidentate ligands are identical, so there is no geometric isomerism. However, the complex ion has a nonsuperimposable mirror image. Thus *optical isomerism* occurs.



Sample Problem 23.4 Determining the Type of Stereoisomerism

PROBLEM: Draw stereoisomers for each of the following and state the type of isomerism:

(a) $[Pt(NH_3)_2Br_2]$ (square planar) (b) $[Cr(en)_3]^{3+}$ (en = $H_2NCH_2CH_2NH_2$)

PLAN: We determine the geometry around each metal ion and the nature of the ligands. If there are different ligands that can be placed in different positions relative to each other, geometric (*cis-trans*) isomerism occurs. Then we see whether the mirror image of an isomer is superimposable on the original. If it is *not*, optical isomerism also occurs.

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EXAMPLE 7.4 Identifying types of isomerism

When the four-coordinate square-planar complex $[IrCl(PMe_3)_3]$ (where PMe₃ is trimethylphosphine) reacts with Cl₂, two six-coordinate products of formula $[IrCl_3(PMe_3)_3]$ are formed. ³¹P-NMR spectra indicate one P environment in one of these isomers and two in the other. What isomers are possible?

Answer Because the complexes have the formula $[MA_3B_3]$, we expect meridional and facial isomers. Structures (70) and (71) show the arrangement of the three Cl⁻ ions in the *fac* and *mer* isomers, respectively. All P atoms are equivalent in the *fac* isomer and two environments exist in the *mer* isomer.

Self-test 7.4 When the glycinate anion, $H_2NCH_2CO_2^-$ (gly⁻), reacts with cobalt(III) oxide, both the N and an O atom of gly⁻ coordinate and two Co(III) nonelectrolyte *mer* and *fac* isomers of [Co(gly)₃] are formed. Sketch the two isomers. Sketch the mirror images of the two isomers: are they superimposable?



Ligand Chirality

- In certain cases, achiral ligands can become chiral on coordination to a metal, leading to a complex that is chiral.
- Usually, the achiral ligand contains a donor that rapidly inverts as a free ligand, but becomes locked in one configuration on coordination.
- ✤ An example is MeNHCH₂CH₂NHMe, where the two N atoms become chiral centres on coordination to a metal atom.
- For a square-planar complex, this imposed chirality results in four isomers: one pair of chiral enantiomers (72) and two complexes that are not chiral (73) and (74).



EXAMPLE 7.5 Recognizing chirality

Which of the complexes (a) [Cr(edta)]⁻, (b) [Ru(en)₃]²⁺, (c) [Pt(dien)Cl]⁺ are chiral?

Answer If a complex has either a mirror plane or centre of inversion, it cannot be chiral. If we look at the schematic complexes drawn in (75), (76), and (77), we can see that neither (75) nor (76) has a mirror plane or a centre of inversion; so both are chiral (they also have no higher S_n axis). Conversely, (77) has a plane of symmetry and hence is achiral. (Although the CH₂ groups in a dien ligand are not in the mirror plane, they oscillate rapidly above and below it.)

Self-test 7.5 Which of the complexes (a) cis-[CrCl₂(ox)₂]³⁻, (b) trans-[CrCl₂(ox)₂]³⁻, (c) cis-[RhH(CO)(PR₃)₂] are chiral?



Stereochemistry of coordination compounds

- Complexes of metal ions with the intermediate coordination numbers 4, 5, and 6 are the most important class of complex.
- They include the vast majority of complexes that exist in solution and almost all the biologically important complexes.
Four-coordination

- Tetrahedral complexes (T_d) are favored if the central atom is small or the ligands large.
- ✤ With small central atom and large ligands (such as Cl⁻, Br⁻, and I⁻), the ligand-ligand repulsions prevail over the energy advantage of forming more metal-ligand bonds.
- Four-coordinate s- and p-block complexes with no lone pair on the central atom, such as [BeCl₄]²⁻, [AlBr₄]⁻, and [AsCl₄]⁺ are almost always tetrahedral
- Tetrahedral complexes are common for oxoanions of metal atoms on the left of the d block in high oxidation states, such as [MoO₄]²⁻.
- Some tetrahedral complexes of 3d-metals are $[VO_4]^{3-}$, $[CrO_4]^{2-}$, $[MnO_4]^{-}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[NiBr_4]^{2-}$ and $[CuBr_4]^{2-}$.



- Square-planar (D_{4h}) complexes are usually observed for metals with d⁸-configurations
- Square planar complexes can lead to different isomers which bear the formula MX_2L_2 .
- Square-planar complexes are rarely found for s- and p-block complexes.
- Such complexes are abundant for d⁸ complexes of 4d- and 5d-series transition metals (Rh+, Ir⁺, Pd²⁺, Pt²⁺, and Au³⁺).
- ✤ For 3d metals with d⁸ configurations (Ni²⁺), square-planar geometry is favored by ligands that can form π-bonds by accepting electrons from the metal atom ([Ni(CN)₄]^{2−})
- Some example of square-planar complexes are [RhCl(PPh₃)₃], *trans* -[Ir(CO)Cl(PMe₃)₂], [Ni(CN)₄]²⁻, [PdCl₄]²⁻, [Pt(NH₃)₄]²⁺, and [AuCl₄]⁻.
- Square-planar geometry can also be forced on a central atom by complexation with a ligand bearing a rigid ring of four donor atoms (formation of a porphyrin complex)





Five-coordination

- The energies of the various geometries of five-coordinate complexes differ little from one another and such complexes are often fluxional.
- Five-coordinate complexes (less common than four- or six-coordinate complexes), are normally either square pyramidal or trigonal bipyramidal.
- A square-pyramidal have C_{4V} (with all identical ligands) and the trigonal-bipyramidal complex have D_{3h} symmetry with identical ligands.
- ✤ Distortions from these geometries are very common
- A trigonal-bipyramidal shape minimizes ligand-ligand repulsions, but steric constraints on ligands that can bond through more than one site to a metal atom can favor a square pyramidal structure.



Six-coordination

- Six-coordination is the most common arrangement for metal complexes and is found in s-, p-, d-, and (more rarely) f-metal coordination compounds.
- ✤ Almost all six-coordinate complexes are octahedral
- ✤ A regular octahedral (O_h) arrangement of ligands is highly symmetrical
- It is especially important because it is the starting point for discussions of complexes of lower symmetry.
- ★ The simplest deviation from O_h symmetry is tetragonal (D_{4h}) , and occurs when two ligands along one axis differ from the other four; these two ligands, which are *trans* to each other, might be closer in than the other four or, more commonly, further away.



20 Trigonal prism, Dah

- For the d⁹ configuration (for Cu²⁺ complexes), a tetragonal distortion may occur even when all ligands are identical because of an inherent effect known as the Jahn Teller distortion.
- Rhombic (D_{2h}) distortions, in which a *trans* pair of ligands are close in and another *trans* pair are further out, can occur.
- Trigonal (D_{3d}) distortions occur when two opposite faces of the octahedron move away and give rise to a large family of structures that are intermediate between regular octahedral and trigonal-prismatic (sometimes referred to as rhombohedral)



Distortions of a regular octahedron: (a) and (b) tetragonal distortions, (c) rhombic distortion, (d) trigonal distortion

Berry pseudorotation: Trigonal-bipyramidal and square-pyramidal complexes

- The energies of the various geometries of five-coordinate complexes often differ marginally from one another.
- The delicacy of this balance is underlined by the fact that [Ni(CN)₅]³⁻ can exist as both square-pyramidal (51) and trigonal-bipyramidal (52) conformations in the same crystal.
- In solution, trigonal-bipyramidal complexes with monodentate ligands are often highly fluxional (able to twist into different shapes), so a ligand that is axial at one moment becomes equatorial at the next moment
- The conversion from one stereochemistry to another may occur by a Berry pseudorotation (Fig. 7.6).
- Thus, although isomers of five-coordinate complexes do exist, they are commonly not separable.
- It is important to be aware that both trigonal-bipyramidal and square-pyramidal complexes have two chemically distinct sites: axial (a) and equatorial (e) for the trigonal bipyramid (
 53) and axial (a) and basal (b) for the square pyramid (54).

Certain ligands have preferences for the different sites because of their steric and electronic requirements.

