

Review Article

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A review of coordination compounds: structure, stability, and biological significance

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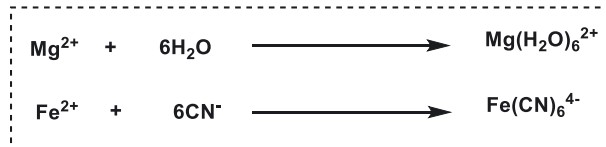
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Abstract: Coordination compounds are molecules that contain one or more metal centers bound to ligands. Ligands can be atoms, ions, or molecules that transfer electrons to the metal. These compounds can be charged or neutral. When charged, neighboring counter-ions help stabilize the complex. The metal ion is located at the center of a complex ion, surrounded by other molecules or ions known as ligands. Ligands can be thought of as covalently bonded to the core ion through coordination. Understanding coordination theory in chemistry provides insight into the geometric shape of complexes and the structure of coordination compounds, which consist of a central atom or molecule connected to surrounding atoms or compounds. Inorganic coordination compounds exhibit different properties and are used in synthesizing organic molecules. The coordination of chemicals is vital for the survival of living organisms. Metal complexes are also essential for various biological processes, with many enzymes, known as metalloenzymes, being composed of metal complexes. These metal complexes occur naturally.

Keywords: coordination compounds; ligands; metal complexes; coordination theory; metalloenzymes

1 Introduction

Ions or compounds classified as coordination complexes have a central metal atom or ion along with a collection of ions or molecules bound to it. Even in solution, such an ion or molecule usually maintains its identity, however partial dissociation could happen.¹ The charges of the coordinated groups and the central atom determine whether the coordinated species will have a positive, zero, or negative charge. These groups are called ligands. They are also referred to by various other names, including Werner complexes, coordinated complexes, chelation compounds, complex ions, and simple complexes. Coordination compounds have been recognized through experimental findings since the mid-18th century.² The chemistry of metals and metal ions in their interactions with other molecules or ions that lead to the creation of coordinate covalent bonds is often referred to as coordination chemistry. Lewis acid–base-type reactions, for instance, are shown in the reactions below. Coordination chemistry is a field of chemistry that builds coordination of complex ions or molecules.³



The benefit of having a vast library of trusted reactions at their disposal to build tiny molecules, mesoscopic structures, and polymers is enjoyed by synthetic organic chemists. In contrast, coordination chemists must contend with the reality that, when adjusted for the quantity of transition metals, there are very few high-yielding reactions in transition metal chemistry.⁴ It's also important to remember that hemoglobin is made up of iron-porphyrin structures, in which the oxygen molecules that the iron atom coordinates reversibly contribute to the iron's ability to carry oxygen.⁵ Vitamin B₁₂, a cobalt complex that contains the macrocyclic ligand corrin, and chlorophyll, a magnesium–porphyrin complex, are examples of coordination molecules that are

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not needed by the body and are found in vegetation and human cells.⁶ In contrast to carbon chemistry, which is capable of creating even the smallest molecular structures, coordination molecules such as cobalt complex with the macrocyclic ligand corrin and chlorophyll, which is a magnesium–porphyrin complex, are found in vegetation and human cells but are not essential for the body. Unlike the strong covalent bonds observed in organic molecules, coordination complexes exhibit weak metal–ligand interactions, highlighting the limited control over their formation. The weak metal links in coordination complexes and the directed bonding facilitated by metal centers are the focal points of certain research methods.⁷ The strong covalent bonds observed in organic molecules, the lack of control is a major characteristic of coordination complexes. The weak metal links and directed bonding facilitated by metal centers are the focal points of certain techniques.⁸

2 Complex compounds

2.1 Central atom

The coordination bond is typically formed through electron sharing. In this process, the ligand donor atom donates a lone pair of electrons from its orbit to the vacant orbital of the central atom, forming a coordinate covalent connection.⁹ Meanwhile, each neighboring species has at least one lone pair of electrons that can be used to fill a vacant orbital, with the central atom acting as the electron acceptor. When they engage, these donors of electron pairs are referred to as ligands. The center atom is an electron–pair acceptor, or Lewis acid, whereas the ligand is a donor of electron pairs. The compound of chemicals that emerges from the formation of bonds is known as a coordination substance, coordination complex, or frequently just a complex. The core atom consists of metals or metalloids, Figure 1 provides further details on these ideas.^{10–14}

Heteroatoms like nitrogen, oxygen, sulfur, and phosphor are commonly thought of as donor atoms in addition to halide ions. Ammonia, or NH_3 , is a usual and effective ligand that has just one lone pair. The accepting substance that a covalent bond with a coordinate develops is a metal or metalloid. Given that a metalloid always generates covalent bonds with an increasing number of groups or atoms bound to its core atom, this may assist with understanding how multiple-coordinate covalent links are formed.¹⁵

2.2 Ligands

In the field of coordination chemistry, a ligand is an anatomy or an ion with allowed donor groups and the capacity to bind (or coordinate covalent) to a central atom. Whereas a central metalloid atom can serve the same purpose, metals are often the central atom at the very core of ligand coordination. The term “ligand” was first coined earlier in the 20th century, and by the middle of the century, it was commonly used.^{16,17} If a ligand only occupies one coordination site ($\text{Mn}^+ \leftarrow \text{L}^-$) it is called monodentate. Usually, ligands are designated by the general symbol L. Prominent examples of monodentate ligands include ($:\text{NH}_3$), ($:\text{OH}_2$), and ($:\text{Cl}^-$) ion.^{18,19} Potential polydentate ligands are those that have many donor groups, each of which has a single pair that can bind to the same metal. Essentially all heteroatoms in organic molecules specifically, O, N, S, and P carry a few lone pairs of electrons. A molecule can take on the role of a ligand by providing a metal ion as many donor groups as possible in exchange for binding. Naturally, factors such as the position, surrounding environment, and position in relation of possible donors inside a molecule affect the total number of donor groups that can attach to a single metal ion.^{10,20–23}

2.2.1 Chelation

Ammonia is a typical simple ligand It can only make one coordinate covalent bond since it only provides one lone pair

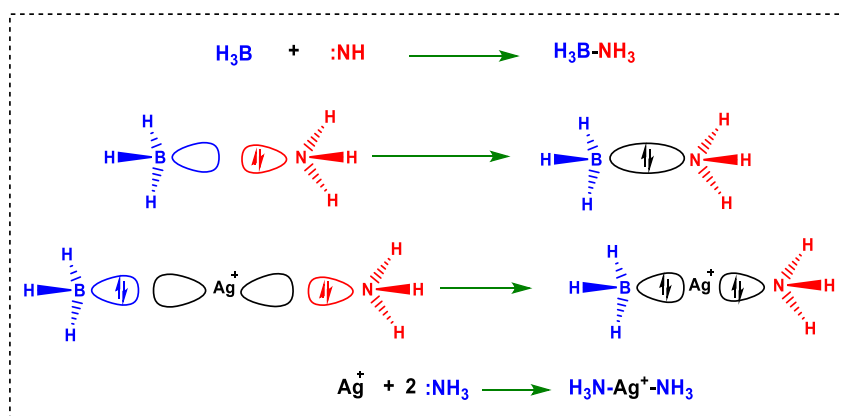


Figure 1: Reaction of metal and ligand as Lewis acid–base reaction.

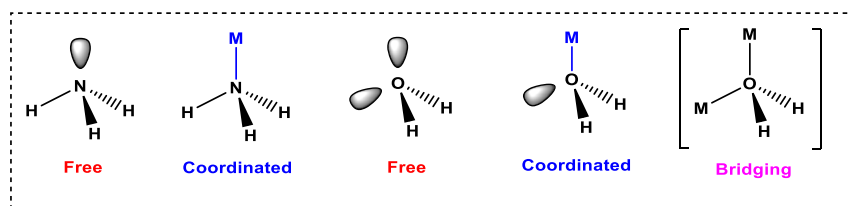


Figure 2: Coordinated ligands versus free ligands.

of electrons. A water molecule typically makes one coordinate covalent bond in addition to having two lone pairs of electrons on its oxygen. As seen in the image below Figure 2, the remaining lone pair points in a different direction to connect to the same metal ion. Only via attaching to a different metal, a process called ligand bridging, could this lone pair produce coordination.^{24,25}

2.3 Coordinate bond

Central atom coordination numbers in coordination compounds a comprehensive selection of 10,000 complexes with structural characterizations and X-ray diffraction data was made from databases to analyze the coordination numbers of their central atoms, or complexing agents. Coordination numbers differed according to an element's ordinal number in the periodic table.

Both the sample complexes' overall distribution across the central atom's coordination numbers and their distributions for specific oxidation numbers are shown. When creating compounds with rich and distinctive features, anticipating the properties of complexes, building their stability, and developing retrieval and visual tools for chemical databases, a general pattern of the observed changes in the coordination number of chemical substances might be helpful.²⁶ The nature of the coordinate bond has been explained by three different ideas. These three theories are the molecular orbital theory, the crystal field theory, and the valence bond theory. At now, the molecular orbital theory is the only application of the theory.²

2.3.1 Valence bond theory

Linus Pauling was primarily responsible for developing the valence bond theory for metal complexes. Based on this concept, the connection is essentially covalent and the pair of electrons on the ligand join the metal's hybridized atomic orbitals.² This idea can account for a number of these compounds' characteristics. For instance, the picture below represents cobalt (III) complexes in Figure 3. $[\text{Co}(\text{NH}_3)_6]^{3+}$ orbital hybridization is referred to as $d_2 sp^3$, and the complex is called an inner orbital complex. Since all of the electrons in

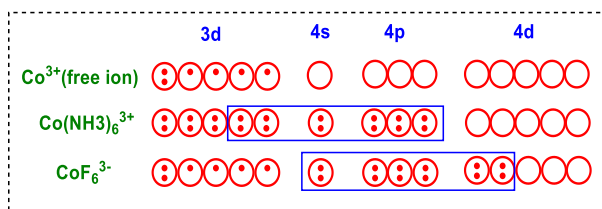


Figure 3: Complex (III) complexes.

this representation are connected, it is compatible with the diamagnetic characteristics of this cation.² $[\text{CoF}_6]^{3-}$ orbital hybridization of this complex is known as an outer orbital complex and is assigned the designation $sp^3 d_2$. The four unpaired electrons in the third orbital are consistent with the ion's known paramagnetic nature. When d orbitals with a different quantum number than s and p orbitals are utilized in bonding, the system is referred to as outer orbital; in contrast, systems where d orbitals with the same quantum number as s and p orbitals are referred to as inner orbitals.²

2.3.2 Crystal field theory

The 1929 proposal by Bethe, referred to as transition metal complexes (CFT), reduces complicated species to those that only participate in ionic bonding and have point charges. The fivefold energy deviation of the d subgroup is a central realization of the theory, which orbits around the usually partly occupied valence level d sub-shell.^{10,27–29} This hypothesis, which has lately been expanded to metal complexes, has helped explain to physicists the properties of ionic crystalline solids. For non-transition metals, the parameters needed to compute the strength of the metal–ligand bond are the sizes and charges of the core ions as well as the ligands' charges, dipole moments, polarizabilities, and sizes.² Nevertheless, despite their seeming structural differences, it is noteworthy in the following image that the dx^2-y^2 orbital and dz^2 orbital likewise eventually degenerate Figure 4.^{10,27–29} (d_{xy} , d_{yz} , and d_{xz}) have smaller energy, which is called t_{2g} , reflects triplet degeneracy. The more energetic set (dx^2-y^2 and dz^2) is known e.g., as a doublet level. The gap in energy between these stages is referred to as the splitting of crystal fields, and it is calculated by a metric called Δ_o , where 'o' indicates an octahedral. The two sets of orbitals balance

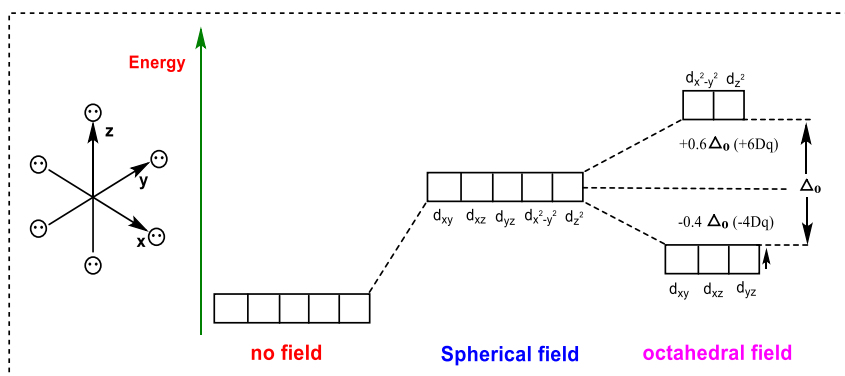


Figure 4: An octahedral field's crystal field controls a set of d orbitals.

each other out, with the top two phases being $+0.6 \Delta_o$ higher and the three lower ones being $-0.4 \Delta_o$ lower than the spherical field location, which is called the zero reference point. The difference in energy Δ_o gets referred to as $10Dq$ in certain sources. The regulation of electrons in the d -orbital energy levels can take on unique configurations where very tiny energy gaps cause electrons that are unpaired to either be maximized (high-spin) or decreased (low-spin). Various characteristics arise from this.^{10,27–29} In our ML6 model, the metal initially had nine orbitals with equivalent energies (five d , one s , and three p), but only six are needed to make bonds with six ligand orbitals. This indicates that three are called nonbonding orbitals since they are not engaged in making bonds with the ligands Figure 5.^{10,27–29} The image as a whole displays 15 significant orbitals with a maximum electron count of 30.

Therefore, the cobalt (III) complexes mentioned above are identified in Figure 6 below based on the crystal field theory. While $[\text{CoF}_6]^{3-}$ is referred to as spin-free, or high-spin, the $[\text{Co}(\text{NH}_3)_6]^{3+}$ is referred to as a spin-paired, or low-

spin, complex. This alludes to the fact that in the former, due to a bigger crystal field splitting, Δ_o , all of the electrons are coupled, but in the latter, Δ_o is minimal and there are no paired electrons. This theory provides a sufficient explanation of the visible spectra of metal complexes, in addition to describing their structure and magnetic characteristics.²

Each coordinate covalent bond between a metal ion and a donor atom will display some polarization since the two atoms joined are not equal. Ionic bonds are the most intense type of polar bonds. An approach to understanding

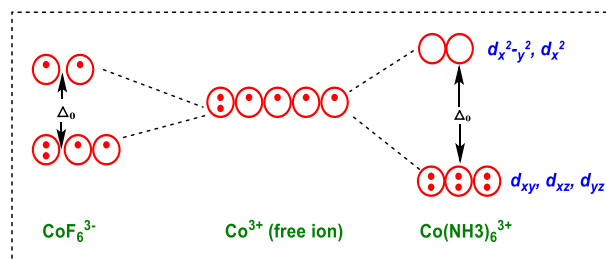


Figure 6: Crystal field theory drives cobalt (III) complexes.

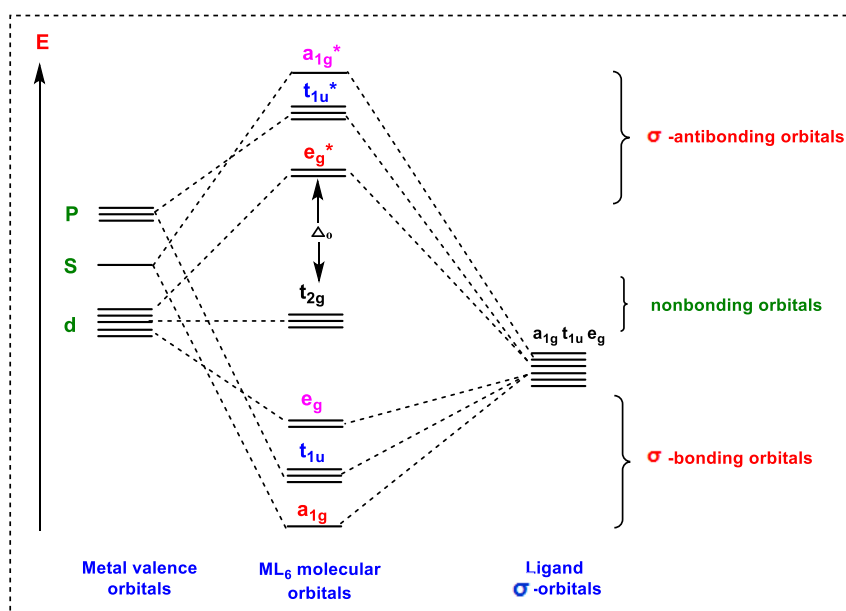


Figure 5: Diagram showing the molecular orbitals of an octahedral complex.

'SOFT' - <i>increasing electronegativity</i> → 'HARD'									
CN ⁻	S ²⁻	RS ⁻	I ⁻	Br ⁻	Cl ⁻	NH ₃	-OH	OH ₂	F ⁻

Figure 7: Pearson's concept of hard and soft acids and base.

experimentally observed metal–ligand preference that is both straightforward and surprisingly successful is Pearson's concept of hard and soft acids and bases (HSAB) (Figure 7).^{10,27–29}

From the standpoint of the metal ion, the hard-soft idea is frequently recast in terms of the following two kinds of metal ions:

Category A: Atoms from hard metals Ti⁴⁺, Fe³⁺, Co³⁺, and Al³⁺ are among the more strongly charged and lighter metal ions in this group, along with alkali and alkaline earth metal ions. These ions are small, compact, and not easily polarized. Smaller, less polarizable ligands, or bases, are what they seem to prefer.

Category B: Soft Metal Ions These transition metal ions, which include heavier ones like Ag⁺, Pt²⁺, and Hg²⁺, are bigger and more polarizable. They also show a predilection for larger, polarizable ligands. As a result, the preference pattern is seen in the below Table 1.^{10,27–29}

2.3.3 Molecular orbital theory

According to the molecular orbital hypothesis, electrons travel in molecular orbitals that pass through each of the metal–ligand system's nuclei. It utilizes both the crystal field theory and the valence bond theory in this way. Since the molecular orbital theory is sufficiently flexible to allow for both covalent and ionic bonding as well as the splitting of *d* orbitals into different energy levels, it is consequently the best estimate of the nature of the coordinate bond. The molecular orbital energy diagrams in Figure 8 may be used to describe the complexes [CoF₆]³⁻ and [Co(NH₃)₆]³⁺.²

These diagrams of molecular orbitals show that this theory incorporates the best aspects of the crystal field theory with the valence bond theory. As the sigma (σ) bonded molecular orbitals, σ_s , σ_p , and σ_d , the covalent bonding of the valence bond theory is shown. The energy differential between the antibonding sigma orbital σd^* and the

Table 1: A few illustrations of soft and hard Lewis bases and acids.

Character	Lewis acids	Lewis bases
Hard	H ⁺ , Li ⁺ , Na ⁺ , Mg ²⁺ , Cr ³⁺ , Ti ⁴⁺	F ⁻ , HO ⁻ , H ₂ O, H ₃ N, CO ₃ ²⁻ , PO ₄ ³⁻
Intermediate	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺	Br ⁻ , NO ₂ ⁻ , SCN ⁻
Soft	Cu ⁺ , Ag ⁺ , Au ⁺ , Hg ⁺ , Cd ²⁺ , Pt ²⁺	I ⁻ , CN ⁻ , CO, H ⁻ , <u>SCN</u> ⁻ , R ₃ P, R ₂ S

nonbonding *d* orbitals d_{xy} , d_{xz} , and d_{yz} is also known as the crystal field splitting (Δo) in crystal field theory. A more intricate representation of molecular orbitals would incorporate the role of π bonding in these configurations.²

3 Nomenclature

Alchemists have named substances from the dawn of time. This problem was solved in the last decade of the nineteenth century thanks to the early stages of “updated” chemistry, and it was from these early attempts that the current naming developed. In the area of coordination chemistry, the counter-ions (if the structure of complex is ionic), the ligands (which may be of different sorts), the metal at the center (or metals, depending on the situation), and the ligand distributions surrounding the metal(s) are all extremely important variables. A formula, a verbal term, or a molecular structure can all be used to explain molecules. Let us examine these options for two very simple cases, as shown in Figure 9.^{30–32}

3.1 The molecular drawing

- (1) The cobalt-centered species is designated as the coordination complex unit by the set of square brackets that surround it and divide it from the other parts of the figure.
- (2) The metal ion is six-coordinate and a 3+ cation based on the octahedral form of the illustration.
- (3) Six NH₃ (ammonia) molecules are attached to it, all of which seem to be evenly across the N atom.
- (4) Considering that the complex is an ionic complex, the presence of additional molecules in this scenario that are not bound to the metal suggests that the complex may carry these molecules as counterions. The cation and anion are charged as shown above.
- (5) If there are no ion charges, one must deduce from enough chemical understanding to identify ‘NO₃’ as a nitrate monoanionic that (NO₃)₃ denotes three NO₃-anions.
- (6) From the above, a second, less obvious inference is that the total charge of the complex unit has to be 3+ in order to balance the charges of the three NO₃⁻ anions.
- (7) In addition, the fact that ammonia is a neutral chemical may be used to deduce that the 3+ charge is positioned at the cobalt center. This suggests that any metal that has a 3+ charge on it has an oxidation state of three, which indicates that we are dealing with a cobalt (III) ion.^{30–32}

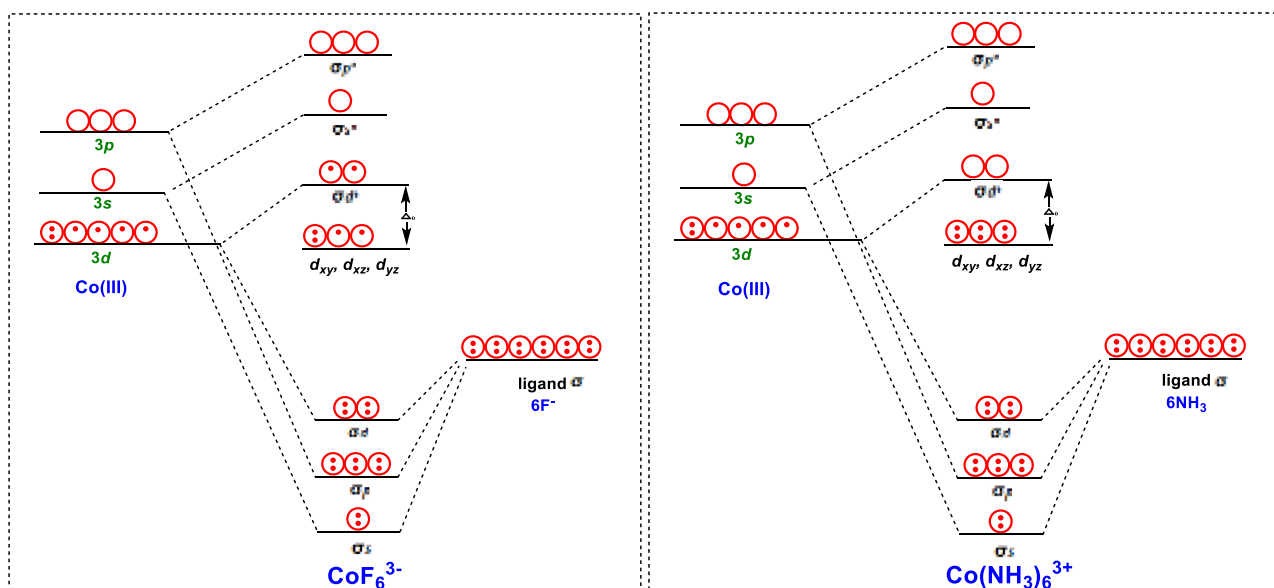


Figure 8: Cobalt complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ according to molecular orbital theory.

Molecular drawing	Molecular formula	Molecular name
	$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$	Hexaamminecobalt(III) nitrate
	$\text{cis-}[\text{PtCl}_2(\text{NH}_2\text{CH}_3)_2]$	cis-dichlorobis(methanamine)platinum(II)

Figure 9: Examples of nomenclature of complexes.

3.2 The chemical formula

At last, we are able to identify the metal as cobalt (III), working with a $[\text{Co}(\text{NH}_3)_6]^{3+}$ cation and three NO_3^- anions. This is similar to the crystal structure.^{30–32}

3.3 The molecular name

- (1) Notably, there are two terms in this instance – one for the cation and another for the anions.
- (2) There is a precise definition of the metal and its oxidation state.
- (3) A prefix related to the quantity of ligands is defined along with the ligand name.
- (4) It is clear what the anion is called, but figuring out how much of it there is on the cation requires knowing how charged or uncharged the ammonia ligands are. Note that while certain other components are the same in both

formulations, the metal occurs last in the written name and first in the mathematical representation of the complex unit. The explanation is shown in Figure 10 below.^{30–32}

3.4 Polydentency

In coordination chemistry, where polydentate ligands are often encountered, denticity plays a significant role in the nomenclature. Denticity means the number of donor groups that any ligand has bound to the metal ion, Table 2.^{30–32}

As seen in Table 3. These are only necessary for written names.

3.5 Naming coordination compounds

This is a short, fundamental set of rules for coordinating complicated names. The complete set of naming rules is a little lengthy.^{30–32}

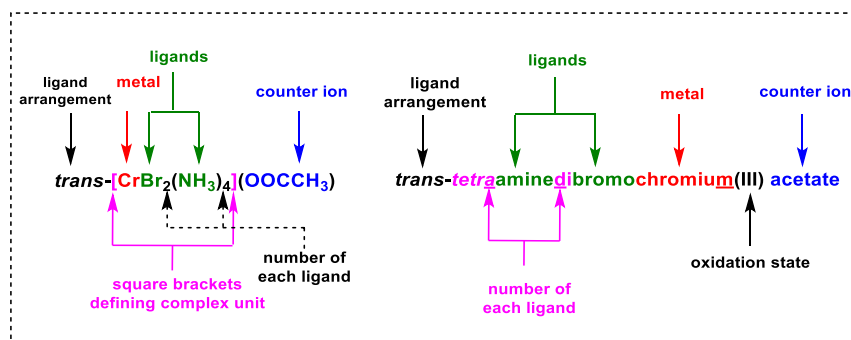


Figure 10: Some fundamental guidelines for naming substances.

Table 2: Polidenticity of ligands.

Number of donor groups coordinated	Name	Number of donor groups coordinated	Name
0	Free ligand	6	Hexadentate
1	Monodentate	7	Heptadentate
2	Didentate	8	Octadentate
3	Tridentate	9	Enneadentate
4	Tetradentate	10	Decadentate
5	Pentadentate	Many	Polydentate

Table 3: Name of monodentate versus polydentate ligands.

Number of monodentate	Prefix to ligand name	Number of polydentate ^a	Prefix to ligand name
1	No prefix	1	No prefix
2	Di	2	Bis
3	Tri	3	Tris
4	Tetra	4	Tetrakis
5	Penta	5	Pentakis
6	Hexa	6	Hexakis

^aAlso used for large and or complicated monodentate ligands, or where ambiguity may arise.

3.5.1 Basic ligands

The nomenclature of coordination compounds with neutral ligands often don't change. For example, a few notable outliers affect the use of a few commonly utilized ligands, with the two primary ones being:

- (1) Water (H₂O) turns into aqua.
- (2) Ammonia (NH₃) is converted to ammine.

Coordinated anions now have names that always finish in (o). A Table 4 of common anionic ligand examples is provided below.^{30–32}

3.5.2 Complexes

A neutral complex has only one word for a name. An ionic compound's cation and anion names are written as two

Table 4: Names used for anionic ligands according to (IUPAC) nomenclature.³³

Ligand	Name	Ligand	Name	Ligand	Name
F [−]	Fluoro	OH [−]	Hydroxo	O ₂ ^{2−}	Peroxo
Cl [−]	Chloro	CN [−]	Cyano	CH ₃ O [−]	Methoxo
Br [−]	Bromo	HS [−]	Thiolo	C ₅ H ₅ [−]	Cyclopentadienyl
I [−]	Iodo	S ^{2−}	Thio	C ₆ H ₅ [−]	Phenyl
H [−]	Hydrido	O ₂ [−]	Superoxo	O ^{2−}	Oxo

“words,” one for each. The cation of ionic complexes is always mentioned first and afterward the anion. These basic rules state that a neutral, cation, or anion name must constantly flow through each of its constituent parts. We will now go into detail about these parts.^{30–32} An alphabetical list of the names of the ligands and the name of the central atom to which they are connected results in the name of a coordination entity. The names of the ligands are once more stated first in alphabetical order in the case of polynuclear compounds or those including more than one central atom.³⁴ Following the metal name after the name, the number of oxidations of the central metal atom is shown as a numeral in Roman letters enclosed in brackets. One method is to replace the oxidation state (metal (II)) (metal (+2)) with the complex's total charge, which is shown in quotation marks at the end.

The metal name is left unaffected in a neutral or positive ion substance. However, the anionic nature of the complex unit can be detected by the addition of a -ate suffix to the metal's name (such as if zinc becomes zincate or molybdenum becomes molybdate), following the opening square bracket for establishing the formula representation of a complex, it should be noticed.

Next, the ‘word’ name is typed in the same alphabetic order as previously mentioned. By using common acronyms or the first letter of their respective formulae, ligands are sorted alphabetically.^{30–32}

3.5.3 Bridging ligands

A specific type of ligand, referred to as a bridge ligand due to its many lone pairs of electrons, can bind two metals

simultaneously to generate polynuclear structures. In the case of these ligands, the number of the metal atoms that the ligand interacts to is given by the subscript n (but only when $n > 2$), and the Greek letter mu (μ) indicates that the ligand is bridging together. As a demonstration:^{30–32}

$[\text{Fe}_2(\text{CN})_{10}(\mu\text{-CN})]^{5-}$	μ -Cyano-bis(pentacyanidoferrate(III))
$[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_3]$	Tri- μ -carbonyl-bis(tricarbonyliron(0))
$[\{\text{Co}(\text{NH}_3)_4\}_2(\mu\text{-Cl})(\mu\text{-OH})]^{4+}$	μ -Chloro- μ -hydroxido-bis(tetraamminecobalt(4+))

4 Stability of complexes

Metal complex stability is dependent on both the ligand and the metal ion; generally speaking, metal complex stability rises as the central ion becomes more charged, gets smaller, and has a higher electron affinity. Hence, transition-metal ions that are strongly polarizing have the highest tendency to form complexes, whereas alkali-metal ions have the lowest inclination. For instance, the stability of complexes of bivalent transition metals is $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} > \text{Cu} > \text{Zn}$, independent of the kind of ligand. The crystal field theory explains this so-called natural order of stability.²

4.1 Effect of ligand

There are several ligand properties that are known to affect the stability of complexes: (1) a basicity; (2) the number of metal-chelate rings per ligand; (3) size of the bind to ring; (4) steric effects; (5) the resonance effects; and (6) ligand atom. Because coordination compounds are formed by reactions between acids and bases in which the ligand is the base and the metal ion is the acid, the more basic ligand will typically form the more stable complex. Additionally, polydentate ligands – those that are linked to the metal ion multiple times – are known to form more stable complexes than monodentate ligands. As seen in Figure 11 below.²

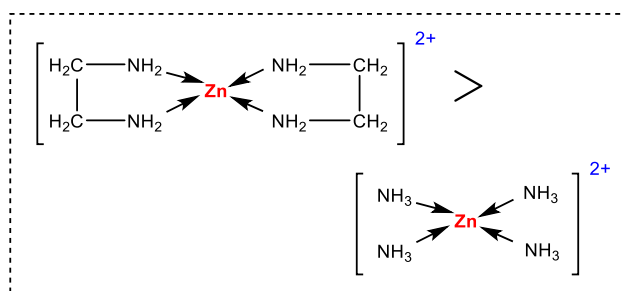


Figure 11: Ethylenediamine for instance generates more stable compounds than ammonia.

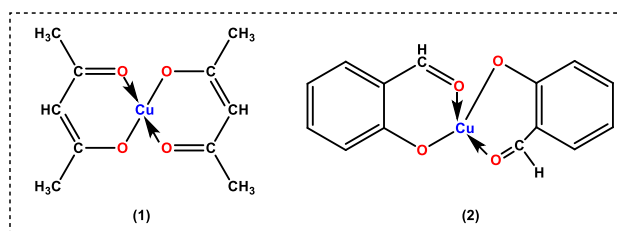


Figure 12: Size the chelate ring of the ligand effect on stability of the complex.

Another significant element is the chelate ring's size. Five-membered rings are the most stable for saturated ligands like ethylenediamine, whereas six-membered rings are the most stable for chelates that include one or more double bonds, like Figure 12 below (1) and (2).²

Steric variables frequently have a significant impact on metal complex stability. This is most commonly seen when ligands have a big group that is either connected to or close to the ligand atom. Lastly, a major factor influencing the stability of metal complexes is the ligand atom itself. The ligand atom with the highest electron density and the shortest size will form the most stable complex for the majority of the metal ions. This indicates that compared to other members of the same group, such as $\text{N} > \text{P} > \text{As} > \text{Sb}$, $\text{O} > \text{S} > \text{Se} > \text{Te}$, and $\text{F} > \text{Cl} > \text{Br} > \text{I}$, the second-period elements form more stable metal–ligand connections. It is also known that the stability order for this same class of metal ions is $\text{N} > \text{O} > \text{F}$.²

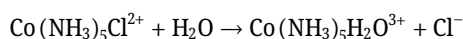
4.2 Stability and reactivity

Most of the time, the least reactive or most inert complex is also the most stable. As a result, the cobalt (III) and chromium (III) complexes, together with the platinum metal complexes, often react extremely slowly. The electronic structure of the central metal ion, its coordination number, and the degree of chelation are some of the variables that significantly impact a compound's rate of reaction.² It is evident from experimental data that the transition metals in the first row favor oxidation state +II and +III. Elevated and decreased formal oxidation states: The primary idea behind oxidation states is that each metal has a unique chemistry at each oxidation state. When it comes to ligand substitution, for instance, cobalt (III) is slow which cobalt (II) is quick; each have distinct tastes in terms of stereo chemical composition and ligand class.^{10,27–29} Most first-row transition metals in the two most common oxidation states generate stable complex ions, commonly with formula $[\text{M}(\text{OH}_2)_6]^{n+}$ ($n = 2$ or 3), when they mix with water as a ligand. The potential of these ions for the M(III)/(II) and M(II)/(0) redox

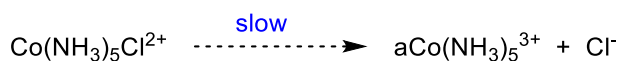
pairs varies substantially, and they are frequently colored. This is so that the physical properties of the ions, such as their color and redox potential, may be altered by substituting other ligands for coordinated water ligands.^{10,27–29}

5 Reactions of complexes

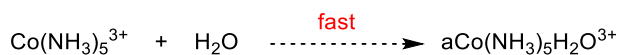
The aforementioned reactions are acid–base reactions, such as the one below, in which a less basic ligand coupled to the acidic metal ion is replaced by a more basic ligand.²



This kind of reaction is known as a nucleophilic substitution reaction and is represented by the letter SN. Such a response can occur via at least two fundamentally distinct mechanisms. The first stage of an SN¹ reaction is a gradual unimolecular heterolytic dissociation that occurs underneath the reaction.

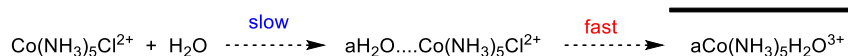


The swift synchronization of the advancing group came next, the response below.



As the reaction below illustrates, an SN² reaction has a bimolecular rate-determining phase where one nucleophilic reagent displaces another.

Examples of both substitution types are seen in metal complex reactions.²



6 Coordination number and shape

The number of valence electrons on the metal ion, its size, preferred coordinate bond lengths, inter-ligand repulsions, and the stiffness and shape of the ligand all affect the coordination number and form of complexes. Coordination complexes have a predictability component.^{10,35–39} Over two centuries have passed since Wollaston's 1808 study, which suggested that the different (3D) three-dimensional form of chemical compounds, was published. Stereochemistry in action: Lawrence and William Bragg employed single crystal X-ray diffraction for the first time in the early 1900s. In the

1920s, it became the gold standard for precisely describe the shape of solid-state molecules.^{10,27–29}

6.1 Jorgensen and Werner's theory

It was not until the latter part of the nineteenth century that transition metal compound shapes attracted much attention. Cobalt (III) is explained by Jorgensen's chain theory, which defines a connection between the metal oxidation state and multiple bonds, hence assuming three direct bonds to the cobalt. The image below depicts three representations. One important finding was that NH₃–Cl bonds were thought to be able to ionize in solution, but Co–Cl binds were not thought to be able to do so.^{10,27–29} Nevertheless, this model did not suit the nonelectrolyte CoCl₃(NH₃)₃, considering its three-bond barrier to cobalt (III); an electrolyte of at most one to one was suggested. His formula for CoCl₃(NH₃)₃ adopts the modern structure, which structural studies have already firmly shown, and it satisfies the compound's non-electrolytic feature, as seen in the following Figure 13.^{10,27–29} Most people agree that Werner's idea marked the beginning of contemporary chemistry of complexes. The primary layer (ionizing; linked to oxidation grade) and secondary layer (nonionizable; related to coordination number) valencies of metal ions are the two valencies he suggested. Most elements meet all of their primary and secondary valencies, and neutral or anionic molecules can supply the latter (usually four or six).^{10,27–29}

A second (outer) coordination sphere was also proposed by Werner in 1912; it would be made up of species arranged in an outside shell around the primary coordination circuit, with focused but less strong connections between groupings in the initial (inner) coordination sphere.^{10,27–29}

6.2 A single coordination (ML)

Since the metal would remain highly exposed even if there was just one donor associated with it, this improbable coordination number is the outcome. This would almost definitely encourage the attachment of more ligands, which would increase the coordination number. The metal-bonded benzene anion of indium(I) and thallium(I) complexes is depicted below. It has a single M–C bond and two sizable tri-substituted benzene substituents positioned orthogonally, Figure 14. The form has been defined using an X-ray crystal structure, a linear ML configuration.^{10,35–39}

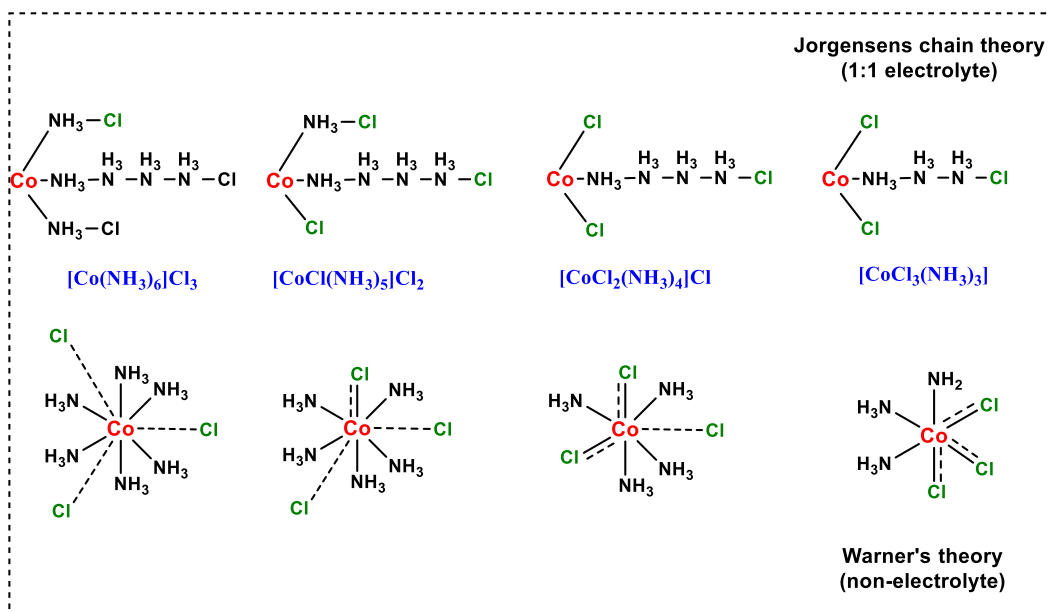


Figure 13: Jorgensen's chain theory compared with the Werner's theory.

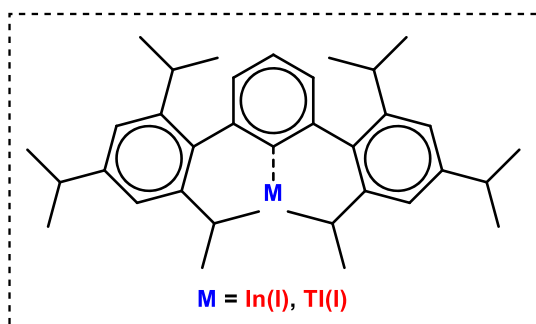


Figure 14: A very uncommon complex with only one coordinate.

6.3 Two coordination (ML₂)

This coordination number that has been lowest stable, thoroughly documented is two coordination. The typical bond angle is 180° (L-M-L) expected to be lowered to $<180^\circ$ by bending Figure 15 in an ML₂ molecule, which is expected to be linear. The linear form is preferred by both basic steric considerations and electron pair repulsion. When this kind

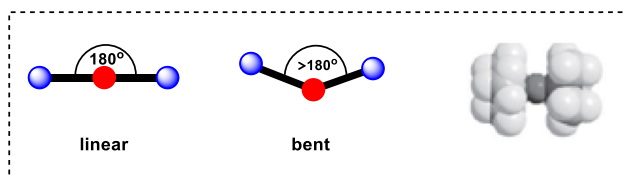


Figure 15: Potential two-coordination forms, and an illustration of a linear complex cation, $[\text{Au}(\text{PR}_3)_2]^+$, with $\text{R}=\text{CH}_3$, on the right.

of bending is observed in metal complexes, it is frequently attributed to a form with a larger pseudo coordination number in which nonbonding orbitals are present that contribute by occupying a certain area of space.^{10,35–39}

Two-coordinate complexes consist of the d_{10} cations Ag(I) and Au(I) . For instance, the $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{CN})_2]^-$ complexes contain linear N-Ag-N and C-Au-C cores, respectively. The top figure shows a comparable example with a larger PR_3 ligand. There are not many examples of bent complexes. One of the easiest is $\text{Ag}(\text{SCN})_2$, which, as seen in Figure 16 below, forms a polymer with the SCN-Ag-SCN character in the solid state.^{10,35–39}

6.4 Three coordination (ML₃)

This rather uncommon coordination number is well-represented by the VSEPR-predicted trigonal planar geometry. Similar to ML₂, transition metal ions with a large number of d electrons (d_8 , d_9 , d_{10}) favor ML₃. Nonetheless, two more forms are recognized: the T-shape and the trigonal pyramidal. As seen in the Figures 17 and 18, the last two results from distortions of the basic trigonal planar structure.^{10,35–39}

6.5 Four coordination (ML₄)

Four-coordination appears to have a tetrahedral organization, however we know that square planar, a plane geometry

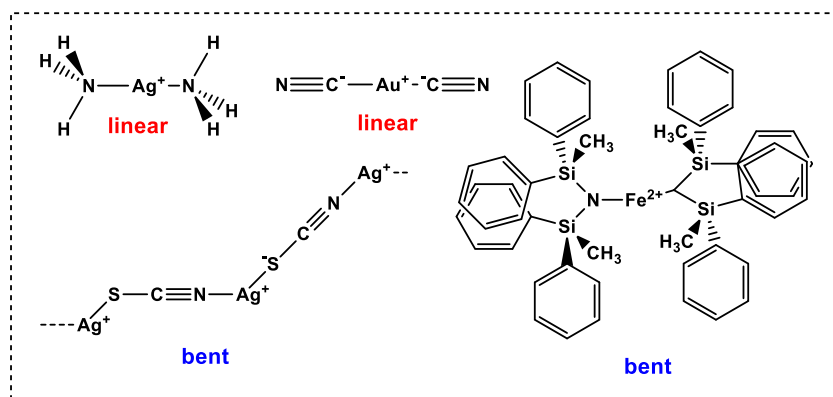


Figure 16: Examples of complexes with two coordination include both linear and bent species.

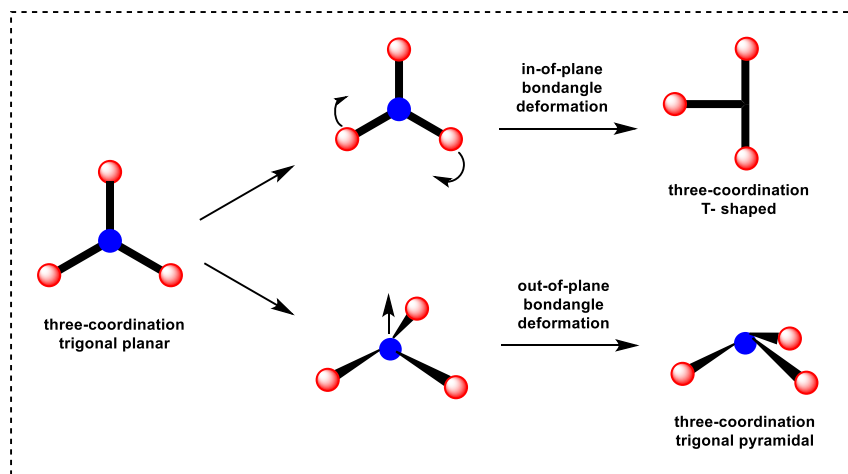


Figure 17: Trigonal planar geometry.

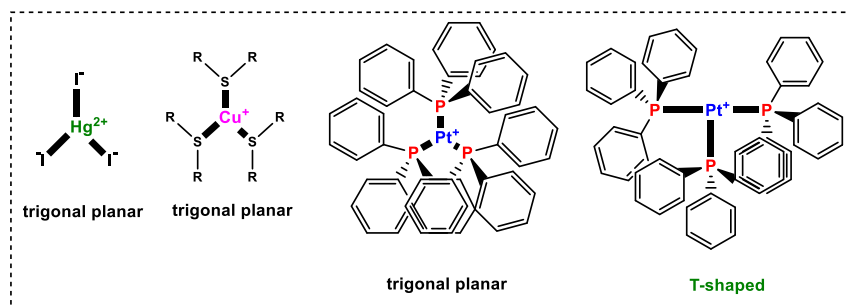


Figure 18: Examples of trigonal planar or the rarer T-shaped geometry.

in which all four ligands are positioned in a rectangular shape with the metal ion at the middle, is a significant form for four-coordination in metal complexes.^{10,27–29} There are two main types of coordination number four (ML₄), which is widely used. The Figure 19 illustrate the forms of the two limiting and intermediate geometry. For simple $[\text{MCl}_4]^{2-}$ ions, for instance, d_7 Co (II) is tetrahedral, d_8 Ni (II) is an intermediate geometry, and d_9 Cu (II) is square planar.^{10,35–39}

Tetrahedral crystals are primarily found in complexes that are neutral or anionic overall, according to experimental data. $[\text{CuX}_4]^{2-}$, $[\text{FeX}_4]^{2-}$, and $[\text{CoX}_4]^{2-}$ are a few basic examples (where X is a halogen anion). Elsewhere, compounds that trend toward tetrahedral geometry are d_0 (like $[\text{TiCl}_4]$)

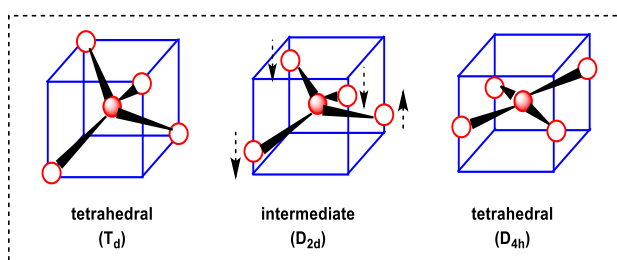


Figure 19: The two limiting shapes for four coordination.

or d_{10} (like $[\text{Ni}(\text{PF}_3)_4]$ and $[\text{Ni}(\text{CO})_4]$). Limited examples are found for other d_n configurations (apart from d_3), and generally just for the first-row transition metals.^{10,35–39}

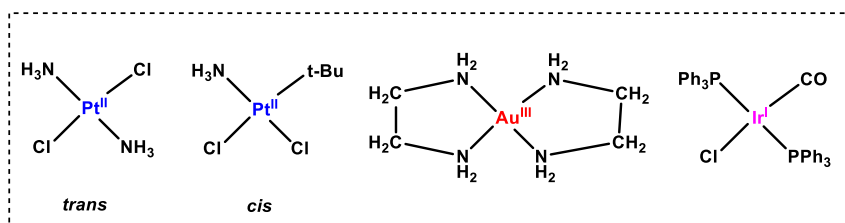


Figure 20: Examples of four coordination square planar complexes.

Square planar complexes with a d_8 metal ion, such as Rh(I), Ir(I), Pd(II), Pt(II), and Au(III), are the most common types utilized as examples. Several instances are displayed in Figure 20. These examples demonstrate an obvious effect of square planarity: the possibility of structural isomers. The geometric isomers of the neutral $[\text{PtCl}_2(\text{NH}_3)_2]$ are *trans*, in which each pair of groups is on the opposite side of the molecule, and *cis*, in which the two pairs occupy neighboring positions.^{10,35–39}

The examples of d_8 nickel (II) complexes exhibit either a tetrahedral or square planar geometry, contingent upon the nature of the ligand. The tetrahedral complex has two unpaired electrons (paramagnetic), but the square planar complex has none (diamagnetic). This difference makes the identification of the two complexes simple (energy splitting diagrams not to scale), which is described below in Figure 21.^{10,35–39}

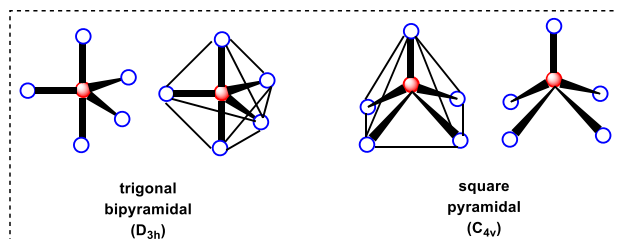


Figure 22: The two shapes for five coordination.

complexes of metal ions from the s and p blocks of the periodic table. The most prevalent type of geometry is octahedral geometry, which is represented by the six-coordinate geometries in the Figures 24 and 25.^{10,35–39}

7 Synthesis

Chemistry is primarily concerned with the synthesis, or creation, of novel and potentially valuable molecules, which is what interests most chemists. Coordination chemistry is still in its infancy since every novel chemical has difficulties during both preparation and isolation. Explain how to construct complexes.^{10,22,40–48}

7.1 Ligand substitution reactions in aqueous solution

Although chemistry carried out in an aqueous or nonaqueous solution is usually included in synthetic processes, solvent-free reactions are also used. In coordination chemistry, the most used synthetic technique is ligand replacement in an aqueous medium. It has the benefit of

6.6 Five coordination (ML5)

There are instances of ML5 in all first-row transition metal ions and in a few other metal ions. Finding that five-coordination also has matching status, at least for lighter, smaller metal ions, may not come as a huge surprise. Complexes of the heavier transition metals seldom meet five coordination. The limiting structures in these cases are square pyramidal and trigonal bipyramidal Figures 22 and 23.^{10,35–39}

6.7 Six coordination (ML6)

When it comes to transition metal elements (found in all configurations from d_0 to d_{10}), ML6 is by far the most often met coordination type. It is also frequently met for

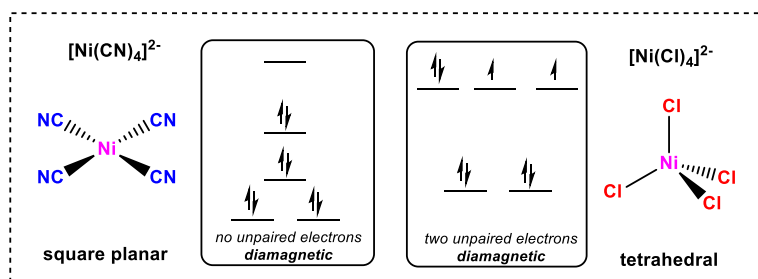


Figure 21: The examples of d_8 nickel (II) complexes exhibit either a tetrahedral or square planar geometry.

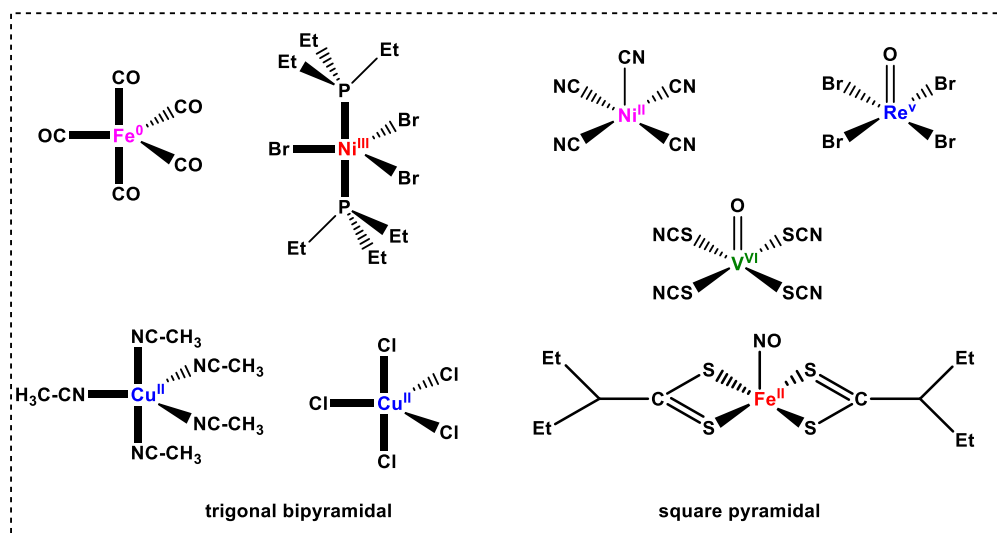


Figure 23: Examples of complexes of the two shapes of five coordination.

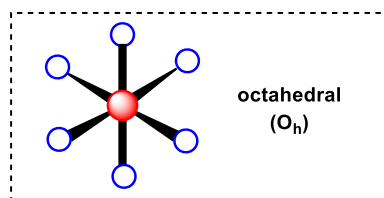


Figure 24: Six-coordinate geometries.

being comparatively inexpensive, using the safest solvent, and having reactants that are frequently well soluble in water because many chemicals and complexes are ionic. A suitable example of anion exchange reaction is the complex

cation $[\text{Ni}(\text{py})_4](\text{SO}_4)$, which is created in water when Ni (SO_4) reacts with pyridine. On the other hand, when too much sodium nitrite is added, the much less soluble $[\text{Ni}(\text{py})_4](\text{NO}_2)_2$ complex precipitates quickly; this is the only process in which the counter ion has changed, as shown in the Figure 26.^{10,22,40–48}

An additional instance of a substitute of a ligand other than coordinated water can be seen in the reaction below Figure 27 which shows us that ligand exchange does frequently limit what the leaving and arriving group could be. When the end result turns from red anionic $[\text{PtCl}_4]_2$ to yellow neutral $[\text{PtCl}_2(\text{NH}_3)_2]$, it might naturally have less solubility than an ionic product because two neutral

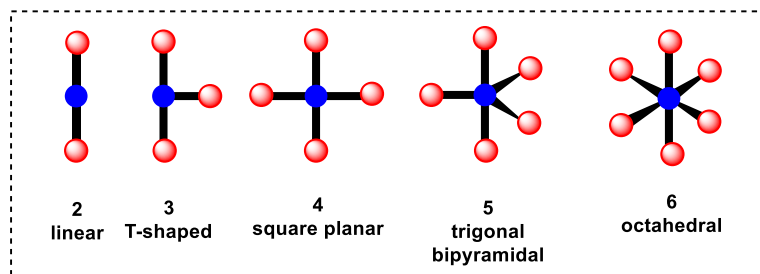


Figure 25: Shapes for coordination numbers from two to six.

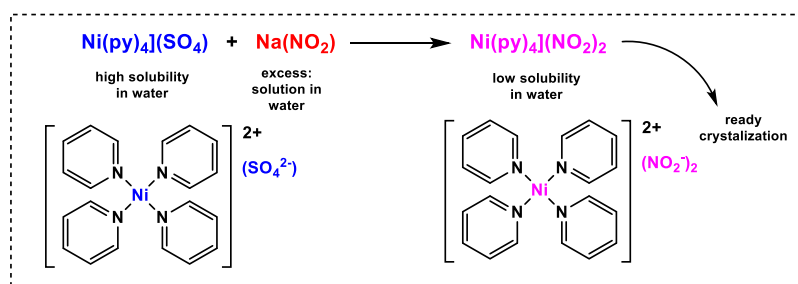
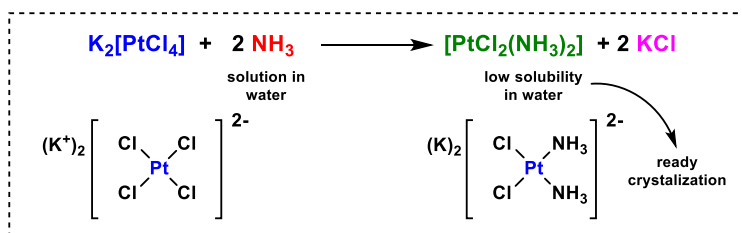


Figure 26: Formation of $[\text{Ni}(\text{py})_4](\text{NO}_2)_2$ compound.

Figure 27: Formation yellow neutral $[\text{PtCl}_2(\text{NH}_3)_2]$ complex.

ammonia ligands have replaced the two chloride anions.^{10,22,40–48}

In actuality, there is no limitation on the kind of ligand that may be changed out in a single reaction. For example, when purple $[\text{CoCl}_3(\text{NH}_3)_3]$ was heated to generate yellow $[\text{Co}(\text{en})_3]^{3+}$, it interacted with 1,2-ethylenediamine (en), substituting both ammonia and chloride generated above, as seen in Figure 28 below, has a high degree of stability, which drives this reaction.^{10,22,40–48}

7.2 Reactions of nonaqueous solvent substitution

Because of the reactant's the insoluble nature, major inertness, which necessitates using a solvent with a greater point of boiling for the reaction, or its high degree of stability of undesired hydroxo or oxo different species that obstruct or interfere with the formation of the desired products, water can sometimes not be the best solvent. The formation of powerful M–O linkages is an essential component of the aquatic chemical of chrome (III), iron (III), and aluminum (III). In basic aqueous solutions, hydroxide species – also known as unreactive oligomers – usually precipitate preferentially and rapidly because many extra ligands are strong bases that increase the pH of the solution. Fe (III) behavior is

best shown by the reaction shown in the Figure 29 in a little a simple basic watery mixture.^{10,22,40–48}

7.3 Catalyzed reactions

With catalysis, one may conveniently drive exceedingly slow reactions that would otherwise only be possible by raising the time to reaction, pressure, and heat. The idea behind catalysis is that by lowering a reaction's activation barrier, a catalyst can enable it to go forward more quickly. A heterogeneous catalyst would stay as a solid whereas a homogeneous catalyst would dissolve in the reaction solution. After a ligand attaches and reacts to produce a product, the product departs and is replaced by a regenerated compound that could carry on the reaction. This reaction becomes more rapid and is referred to as a metal-catalyzed reaction.^{10,22,40–48} Metals, metal oxides, various easy salts, and metal complexes are the general categories into which catalysts exist. In one example, the ligand substitution procedure required to create platinum(IV) complexes proceeds extremely slowly. In contrast, the process is effectively catalyzed when a little quantity of a platinum(II) compound is introduced to the reaction mixture. These intermediates are referred to as mixed oxidation state bridging ones because they facilitate ligand transfer.^{10,22,40–48}

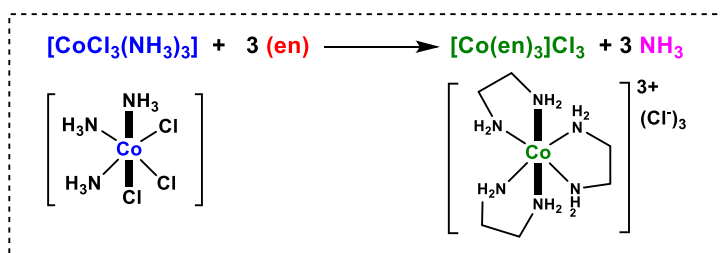
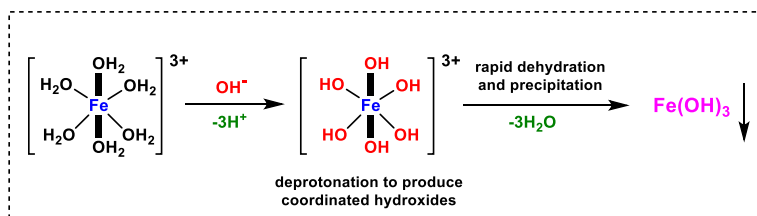
Figure 28: $[\text{Co}(\text{en})_3]^{3+}$ complex formation.

Figure 29: Illustration of Fe (III) behavior in an aqueous solution with a little basicity.

8 Properties

8.1 Methods and outcomes

One important physiological technique that offers a precise three-dimensional image of crystallized structures in their rigid state is single-crystal X-ray crystallographic analysis. The architectures of solid-state phenomena and their solutions don't have to coincide. Important techniques for physical analysis in coordination chemistry include mass spectrometers, UV–Vis spectrophotometry, nuclear magnetic resonance, infrared and ultraviolet-Vis spectroscopy.^{10,49–57}

Occasionally, characteristics associated with the primary form of assessment include physical methods like diffraction (X-ray diff, neutron diffraction), ionization-driven (MS and photoelectron spectroscopy), absorption spectroscopy (ultraviolet-visible, infrared light and Raman), and resonance

techniques (NMR technology, the effect of ESR and Mossbauer spectroscopy). A thorough summary of frequently utilized methods is given in Tables 5, and includes elements such as elemental auto analysis, the ultraviolet (UV) spectrophotometry, IR spectrum analysis, NMR analysis, single crystal XRD, and MS. The fundamental list that each chemist uses will vary depending on the kind of substances that they work with. These easily available methods differ according to the aim and objective of the study. Instrument unavailability and price are challenges. For example, a high-field NMR spectroscopy nowadays may cost a hundred times as much as a costly UV–Vis spectrophotometer.^{10,49–57}

8.2 Para magnetism and diamagnetism

An alternate arrangement for electrons in the octahedral *d* sublevel may be obtained by looking at the orbits of

Table 5: Important physical techniques for sophisticated separation and isolation as well as obtaining fundamental details about the isolated chemical.

Method	Sample and device requirements	Outcome expected
Separation techniques		
Crystallization	A solution of either the pure complex or a mixture of complex species	Selective crystallization of a pure complex; this may, but need not, follow chromatographic separation of solution species
Ion chromatography	Solutions of soluble ionic complexes <i>Ion chromatography columns packed with appropriate cationic or anionic polymer resin</i>	Separation of ions mainly according to charge, and possibly assignment of charge. (Examination of separated bands of compounds directly as they exit the column by tandem instrumental methods is also possible.)
High pressure liquid chromatography (HPLC)	Liquids or solutions <i>Commercial HPLC instrument with appropriate packed columns</i>	Separation of neutral and/or ionic species
Gas chromatography	Gaseous or volatile liquid samples <i>Gas chromatograph instrument with capillary or packed columns</i>	Separation of volatile samples, usually applicable only to some neutral low molecular weight complexes Identification by comparison with known standards is possible
Basic analytical procedures		
Elemental analysis	Pure compound, as liquid, solid or solution of known concentration <i>Elemental autoanalyser</i> (for C, H, N, S, O only usually) or else <i>atomic absorption (AAS)</i> or <i>atomic emission (ICP-AES) spectrometers</i> (for other elements)	Percentage composition of elements determined, allowing component elements and the empirical formula to be defined
Thermal analysis Techniques [Thermogravimetric analysis, differential thermal analysis]	Solid or liquid sample <i>Thermogravimetric analyser</i>	Mass change with temperature; information on number of waters of crystallization, ligand loss and complex transformation with increasing temperature obtained
Conductivity	A solution of a pure compound of known concentration <i>Conductivity meter and probe</i>	Ionic or neutral character of complex, and possibly the overall charge of the complex ion
Magnetic measurements	Solid or concentrated solution <i>Magnetobalance or magnetometer.</i> (A limited NMR-based method is also available.)	Defines dia- or para-magnetism; number of unpaired electrons, and some inferences about gross symmetry possible Variable-temperature behaviour provides information on metal–metal interactions in polymetallic species

Table 6: Comparison of (P) versus (Δo).

d^n	Ion	Ligands	P	Δo	Spin state
d^4	Cr^{4+}	$(\text{OH}_2)_6$	282	166	High ($P > \Delta o$)
	Mn^{3+}	$(\text{OH}_2)_6$	335	252	High ($P > \Delta o$)
d^5	Mn^{2+}	$(\text{OH}_2)_6$	306	94	High ($P > \Delta o$)
	Fe^{3+}	$(\text{OH}_2)_6$	360	164	High ($P > \Delta o$)
d^6	Fe^{2+}	$(\text{OH}_2)_6$	211	125	High ($P > \Delta o$)
		$(\text{CN}^-)_6$	211	395	Low ($P > \Delta o$)
	Co^{3+}	$(\text{F}^-)_6$	252	156	High ($P > \Delta o$)
		$(\text{NH}_3)_6$	252	272	Low ($P > \Delta o$)
		$(\text{CN}^-)_6$	252	404	Low ($P > \Delta o$)

Low spin and high spin arrangements exemplified for d^6 [Δo (low spin) $> \Delta o$ (High spin)]:

d electrons for d_4 to d_7 . The possibilities for high- and low-spin electron pairings are shown in these designs.^{10,49–57} Low spin configurations are favored by large Δo . The differentiation is contingent upon the size of (Δo) in relation to the amount of spin (P). The amount of Δo is depend on ligand, precisely based on the kind of donor atom and the metal ion's charge; P alone is mostly dependent on the metal's center and its oxidation state. When P is lesser than Δo , the complex tends to have low spin and high spin when P is more than Δo , as Table 6 below shows.^{10,49–57}

8.3 Complexes as drugs (kill or care?)

We are very interested in health concerns as we strive to attain and maintain the highest quality of life possible, which is one reason why medicine is a field with a lot of activity and interest. Drugs, which might be synthetic coordination complexes, natural products, or synthetic organic molecules, are often used in the treatment and recovery of sickness. Drugs that include metal complexes are frequently referred to as metallodrugs to differentiate them from the more widely used organic drugs. Metals have been exploited for medical purposes for thousands of years, at least going back to the Chinese and ancient Egyptians who made use of gold and copper compounds in their concoctions.^{58–64}

8.3.1 Metallodrugs

In recent decades, there has been a notable increase in the quantity and variety of uses of coordination compounds containing metals that demonstrate the ability to treat or

Table 7: Several uses of metal coordination complexes in medicine.

Function	Compounds
Bioassay	
Fluoroimmunoassay	Europium(III) complexes
Diagnostic imaging	
Gamma radiolysis contrast agents	Radioactive $^{99\text{m}}\text{Tc}$ complexes
Magnetic resonance contrast agents	Gadolinium(III) complexes
Radiopharmaceuticals	Short half-life radioactive metal salts and complexes
Anticancer drugs	Platinum complexes; titanium complexes; photosensitive porphyrin complexes
Other selected treatments	
Wilson disease and Menkes disease	Copper complexes
Arthritis	Gold complexes
Blood pressure control	Iron complexes
Diabetes – insulin mimics	Vanadium complexes
Antimicrobials	Ag, Hg, Zn and Bi compounds
Ligands as drugs	
Metal intoxication treatment	Polydentate ligands (such as EDTA)

manage diseases. They come in a variety of forms that include ligands, stereochemistries, and metal ions. A few instances are provided in Table 7.^{58–64}

8.3.2 Anticancer drugs

As one of the most serious illnesses we face today, cancer is the subject of extensive research and development on a global scale for new treatments. The recent finding that platinum-based medicines for chemotherapy rank among the most well-liked and effective therapeutic treatments for a variety of deadly cancers is significant.^{58–64} One of the most popular medications on the market, diamminedichloroplatinum(II), often known as cisplatin in medicine, was the first to be used therapeutically and is seen in Figure 30. It was Peyrone who first reported on this ancient coordination complex in 1845. Rosenberg identified cisplatin's possible anticancer effects in 1965, and the medication was first used in clinical settings in 1971. Among other disorders, it is widely and often used to treat small-cell lung cancer, testicular, bladder, head, and neck cancer, as well as ovarian cancer.^{58–64}

Another type of compounds being studied as anticancer medications is other metallodrugs, which are made of titanium. Budotitane ($[\text{Ti}(\text{bzac})_2(\text{OEt})_2]$) is one titanium (IV) anticancer medication that has been approved for clinical testing; ruthenium complexes are also being researched as possible anticancer medications.^{58–64}

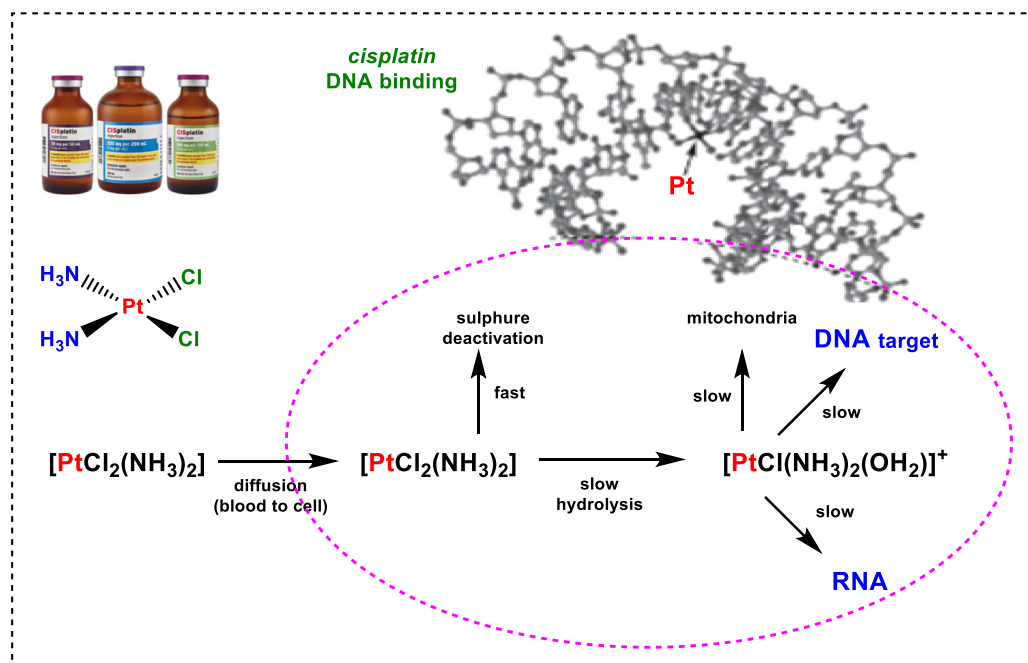


Figure 30: The chemical cisplatin, its intracellular reaction pathways, and an illustration of coordination to DNA resulting in double helix deformation (cisplatin-DNA binding picture retrieved from the Protein Data Bank).

9 Conclusion

To sum up, coordination compounds are chemical compounds composed of a variety of anions or neutral molecules united to a central atom by the formation of covalent bonds as a result of the coordination of the anions or neutral molecules. Coordination compounds, sometimes referred to as coordination complexes, are substances with a certain structure. Coordination compounds have a wide range of uses in industry due to their various beneficial qualities. They are also utilized in medicine and pharmaceuticals as anticancer treatments, among their many other diverse applications in chemistry. Certain coordination compounds are desirable as dyes due to their high color content and vibrant, eye-catching hues. The International Union of Pure and Applied Chemistry (IUPAC) system is used for identifying various complexes.

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