

Werner's Theory of Coordination Compounds

Decoding the structural mystery of complex ions, primary and secondary valences, and coordination polyhedra.

Section 5.1

Alfred Werner (1898)

H2: The Cobalt-Ammonia Puzzle

Alfred Werner reacted cobalt(III) chloride with varying amounts of ammonia, then added cold silver nitrate (AgNO_3).

Unexpectedly, the amount of AgCl precipitated **varied wildly** despite similar baseline ingredients.

**Yellow
Complex**

(1 mol $\text{CoCl}_3 \cdot 6\text{NH}_3$)
→ Yields 3 mol AgCl

**Purple
Complex**

(1 mol $\text{CoCl}_3 \cdot 5\text{NH}_3$)
→ Yields 2 mol AgCl

**Green / Violet
Complexes**

(1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$)
→ Yields 1 mol AgCl

**Why do some chloride ions precipitate while others
others remain locked in the solution?**

H2. Formulating the Complexes

Color	Modern Formula	Ions Precipitated	Conductivity
Yellow Complex	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	3 Cl^-	1:3 electrolyte
Purple Complex	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	2 Cl^-	1:2 electrolyte
Green Complex	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1 Cl^-	1:1 electrolyte
Violet Complex	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1 Cl^-	1:1 electrolyte (Isomer)

Notice how the atoms inside the square brackets act as a single, unbreakable entity.



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$$E=mc^2$$



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Werner's Postulates: The Dual Valence Model

Primary Valence (Oxidation State)

- Ionisable linkages.
- Satisfied by negative ions only.
- Determines the overall charge of the complex.

Secondary Valence (Coordination Number)

- Non-ionisable linkages.
- Satisfied by neutral molecules OR negative ions.
- Fixed for a specific metal; dictates spatial geometry.

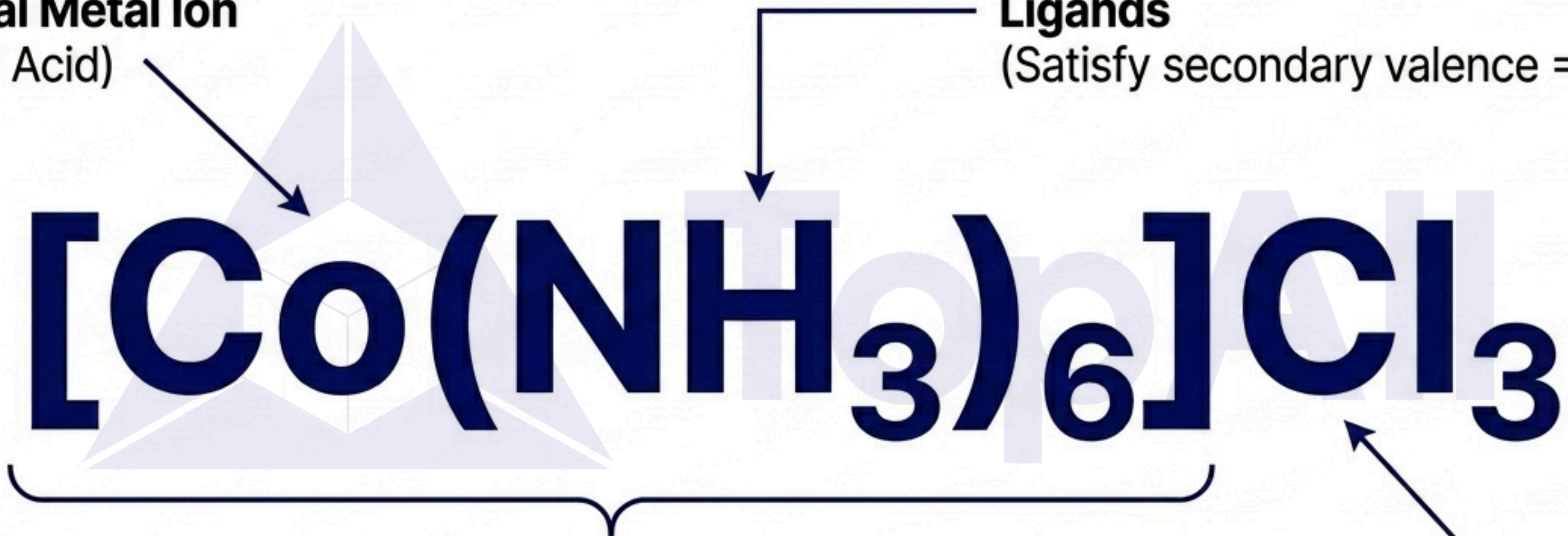
Werner's Rule: Metals always strive to satisfy BOTH their primary and secondary valences.

H2. Decoding the Chemical Notation



Central Metal Ion
(Lewis Acid)

Ligands
(Satisfy secondary valence = 6)



Coordination Entity
(Non-ionisable inner sphere)

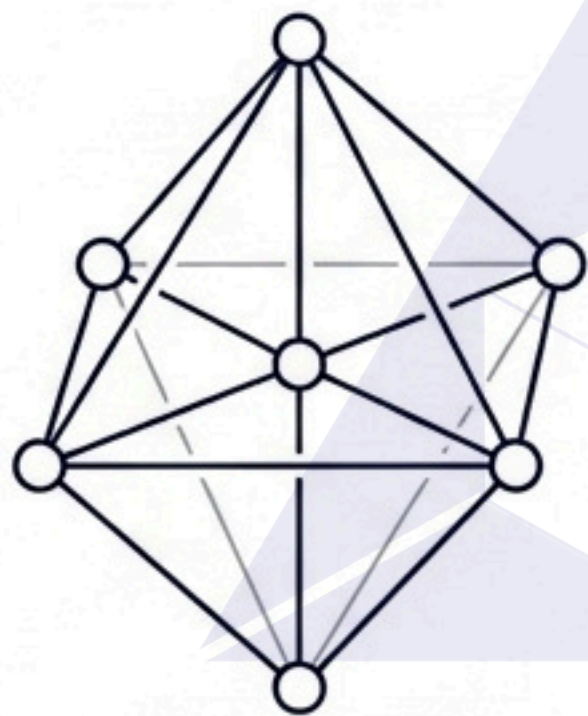
Counter Ions
(Ionisable primary valence)

Species inside the bracket form a single complex. Species outside are free to dissociate in water.

H2. Characteristic Spatial Arrangements

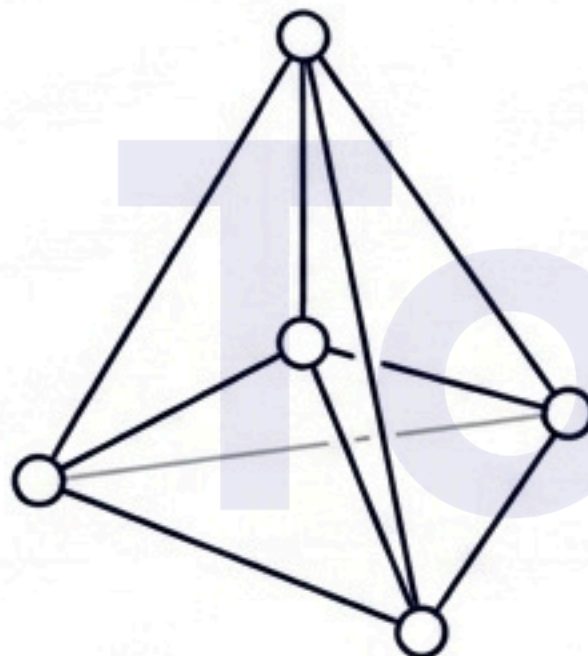


Octahedral



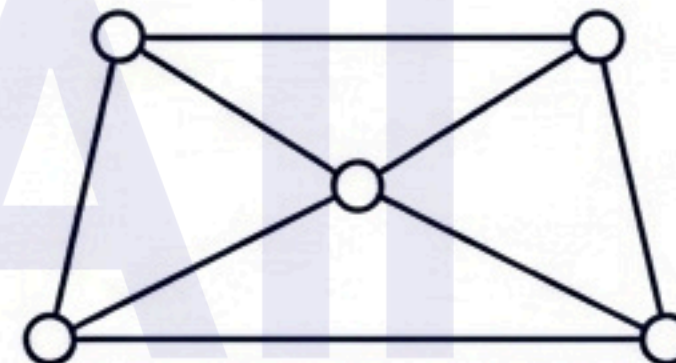
Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$
Coordination Number: 6

Tetrahedral



Example: $[\text{Ni}(\text{CO})_4]$
Coordination Number: 4

Square Planar



Example: $[\text{PtCl}_4]^{2-}$
Coordination Number: 4

Werner correctly postulated that these three shapes are the most common in transition metal coordination compounds.

H2. Key Takeaways & Recall

- **Coordination compounds** feature metals bound to neutral molecules/anions.
- **Primary Valence** = Ionisable (Oxidation state).
- **Secondary Valence** = Non-ionisable (Coordination number & Geometry).
- **Brackets []** denote the unbreakable Coordination Entity.



Quick Recall 1

Q: What type of valence dictates the spatial shape of the complex?

A: Secondary

Quick Recall 2

Q: In $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$, how many moles of AgCl will precipitate?

A: 2 moles

Quick Recall 3

Q: Are the ions outside the square brackets ionisable or non-ionisable?

A: Ionisable



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