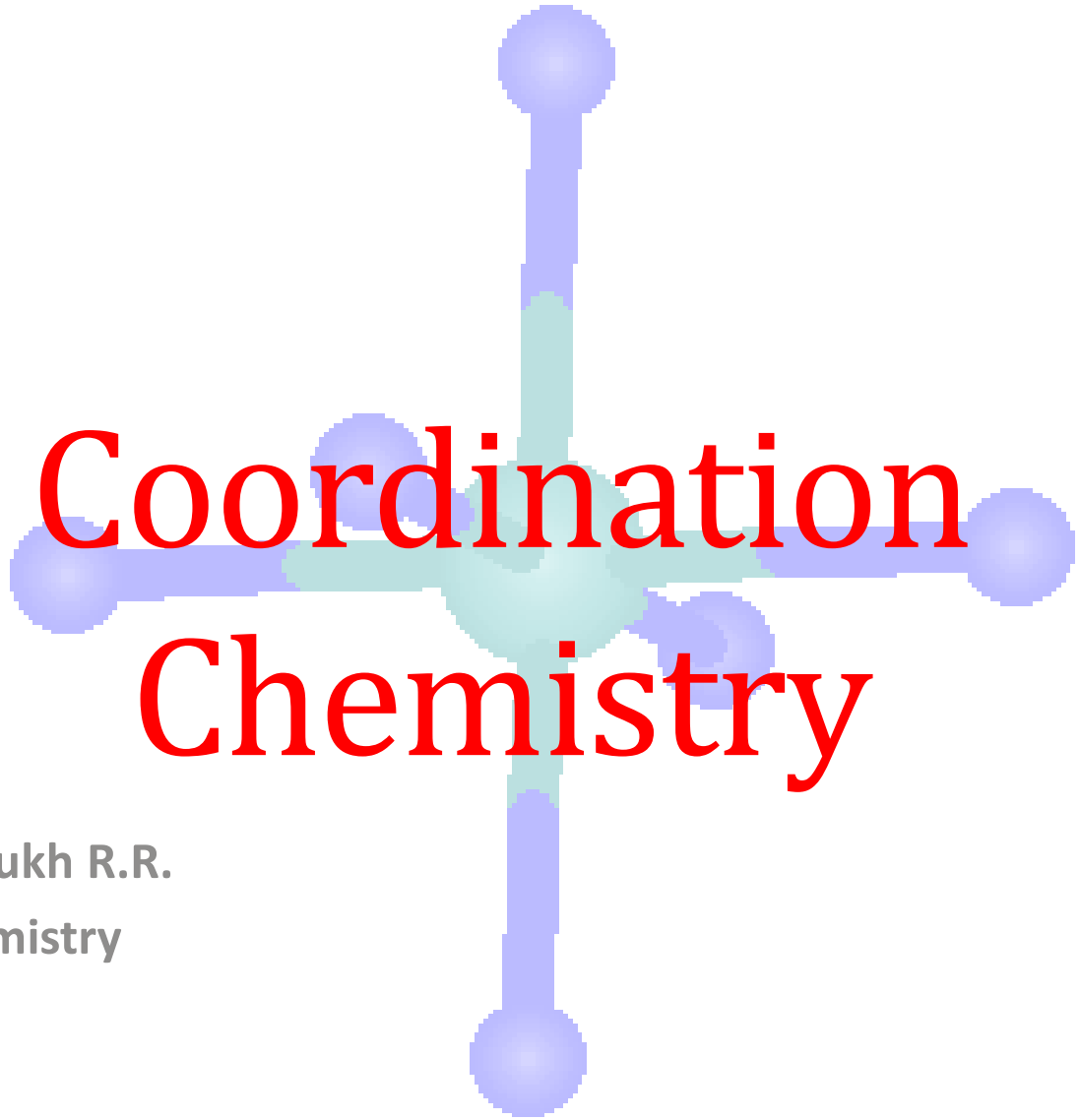


Coordination Chemistry

Prof.Deshmukh R.R.

Deft of Chemistry

Werner's Coordination Chemistry

- Performed systematic studies to understand bonding in coordination compounds.
  - Organic bonding theory and simple ideas of ionic charges were not sufficient.
- Two types of bonding
  - Primary – positive charge of the metal ion is balanced by negative ions in the compound.
  - Secondary – molecules or ion (ligands) are attached directly to the metal ion.
    - Coordination sphere or complex ion.
    - Look at complex on previous slide (primary and secondary)

Coordination Chemistry

- Transition metals act as Lewis acids
  - Form complexes/complex ions

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow Fe(CN)_6^{3-}(aq)$$

Lewis acid Lewis base Complex ion

$$Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq)$$

Lewis acid Lewis base Complex ion

Complex contains central metal ion bonded to one or more molecules or anions

Lewis acid = metal = center of coordination

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

Coordination Chemistry

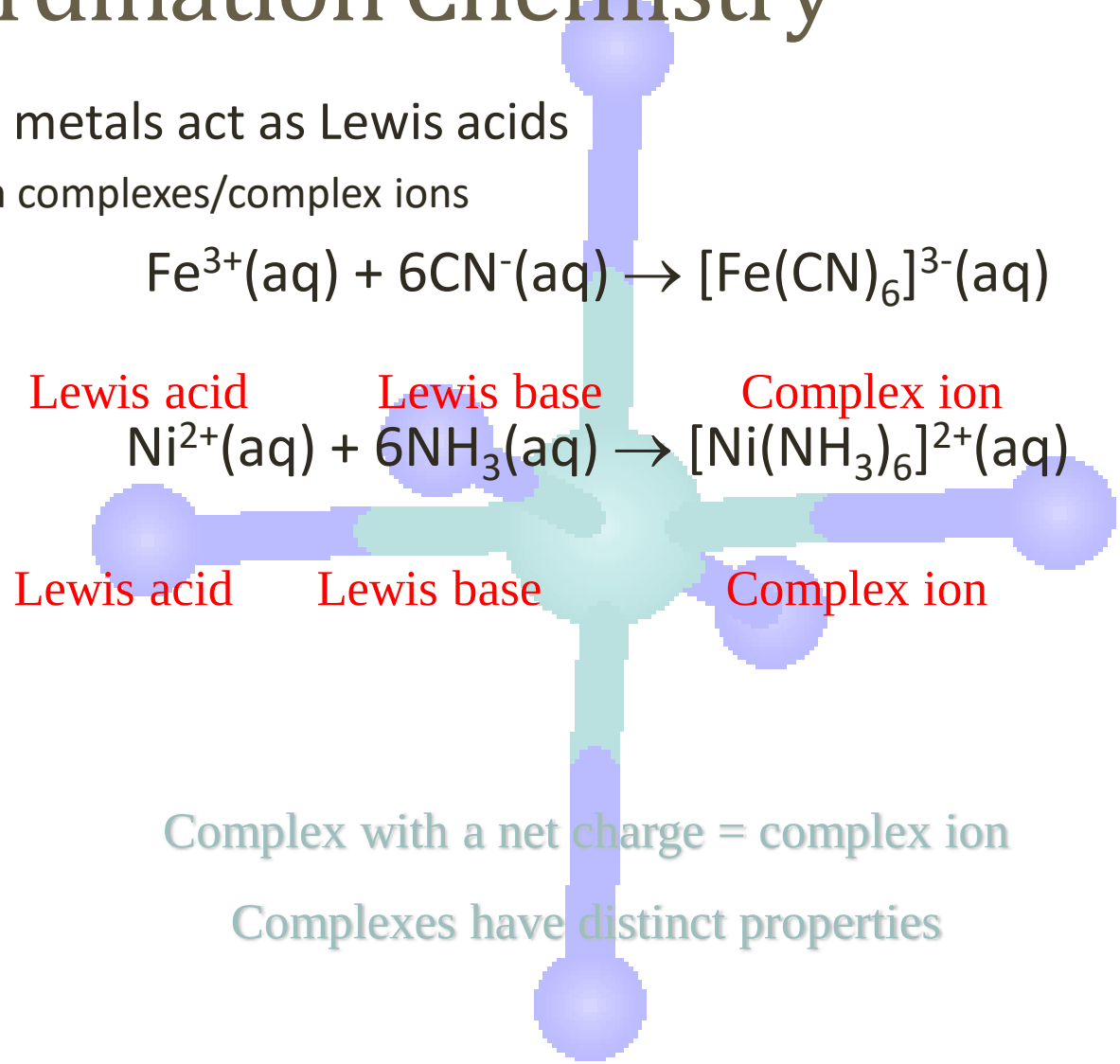
- Transition metals act as Lewis acids
  - Form complexes/complex ions

$$Fe^{3+}(aq) + 6CN^{-}(aq) \rightarrow [Fe(CN)_6]^{3-}(aq)$$

Lewis acid Lewis base Complex ion

$$Ni^{2+}(aq) + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq)$$

Lewis acid Lewis base Complex ion

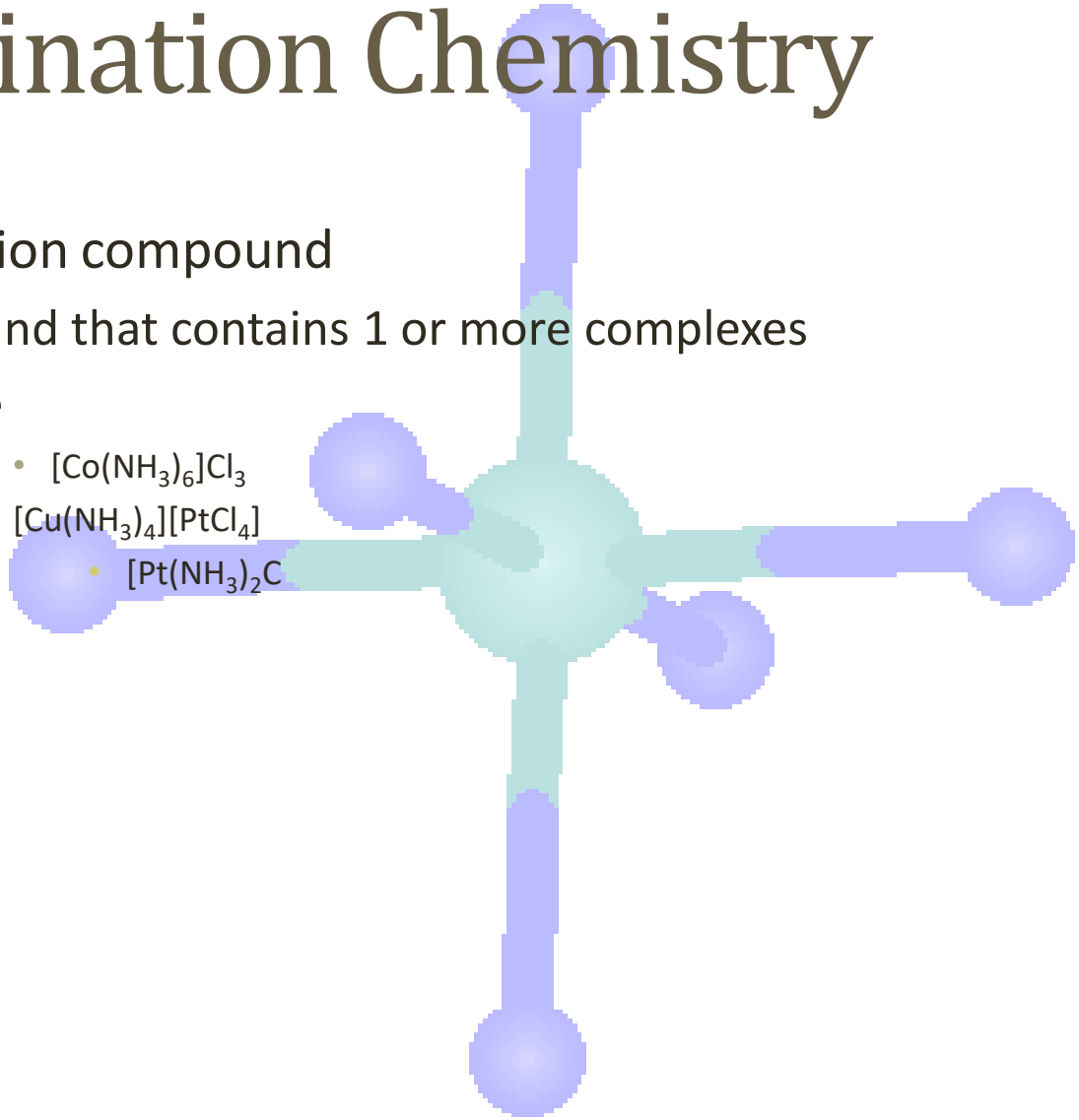


Complex with a net charge = complex ion

Complexes have distinct properties

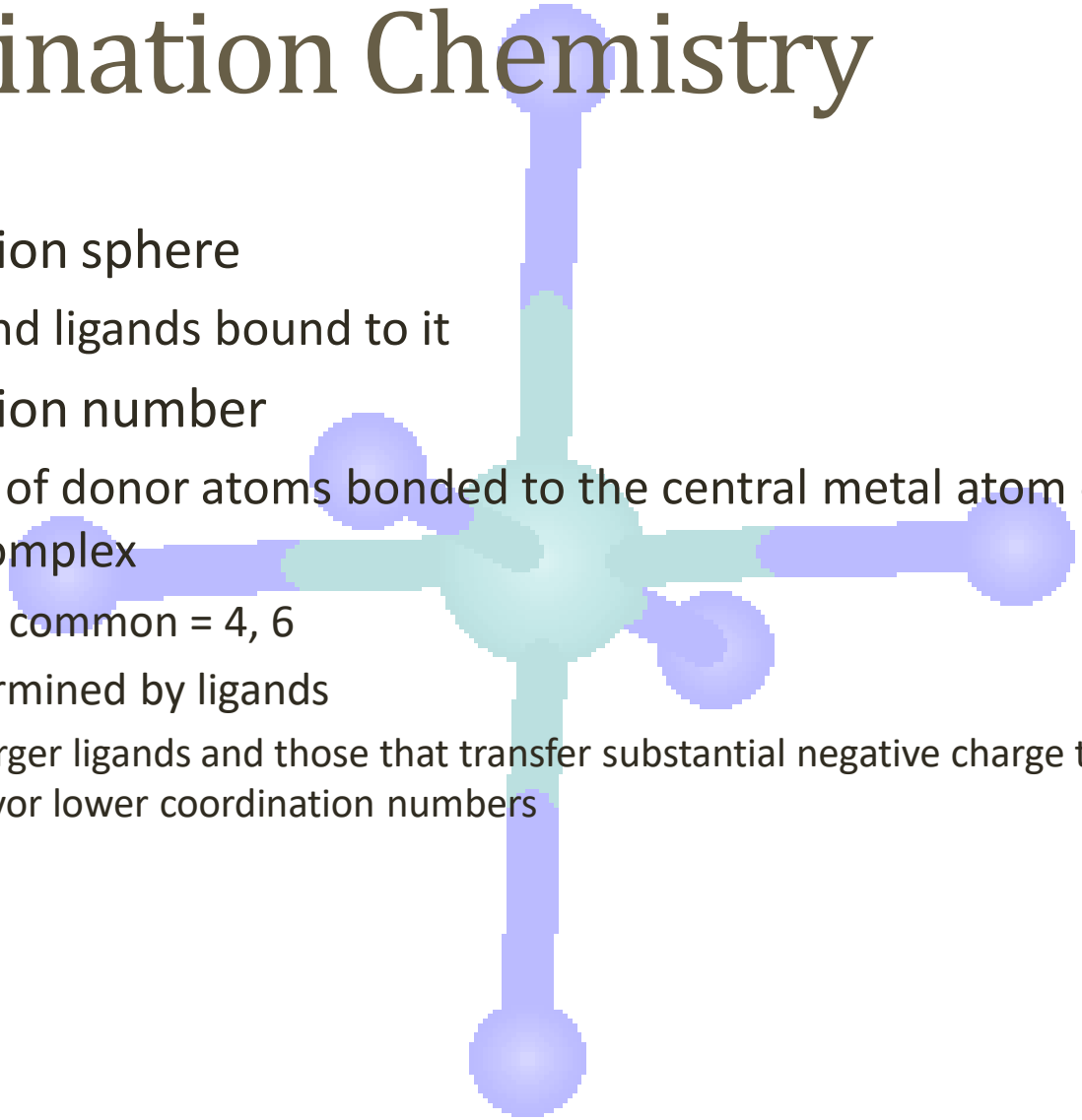
Coordination Chemistry

- Coordination compound
  - Compound that contains 1 or more complexes
  - Example
    - $[Co(NH_3)_6]Cl_3$
    - $[Cu(NH_3)_4][PtCl_4]$
    - $[Pt(NH_3)_2C$



Coordination Chemistry

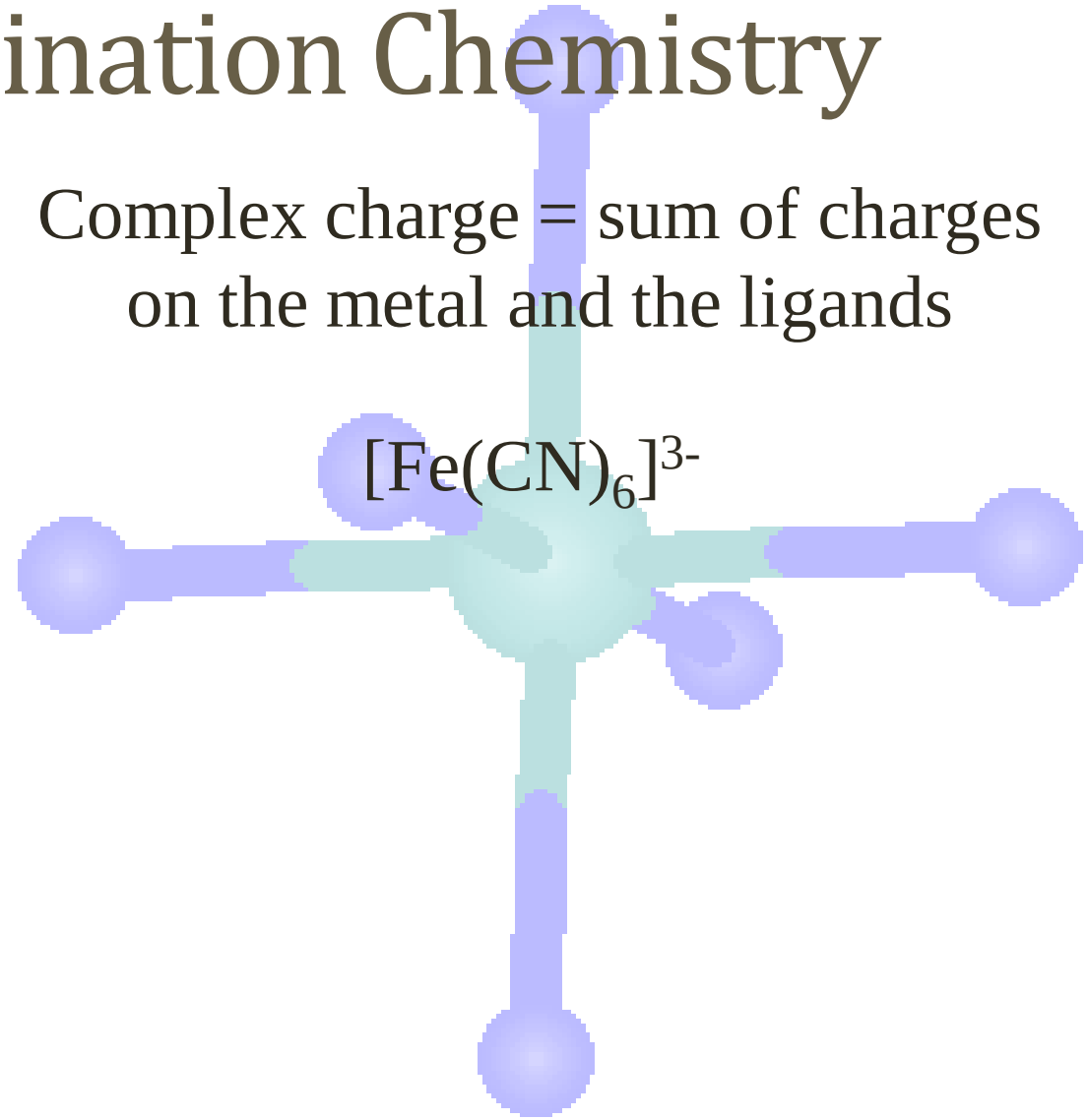
- Coordination sphere
  - Metal and ligands bound to it
- Coordination number
  - number of donor atoms bonded to the central metal atom or ion in the complex
    - Most common = 4, 6
    - Determined by ligands
      - Larger ligands and those that transfer substantial negative charge to metal favor lower coordination numbers



Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands

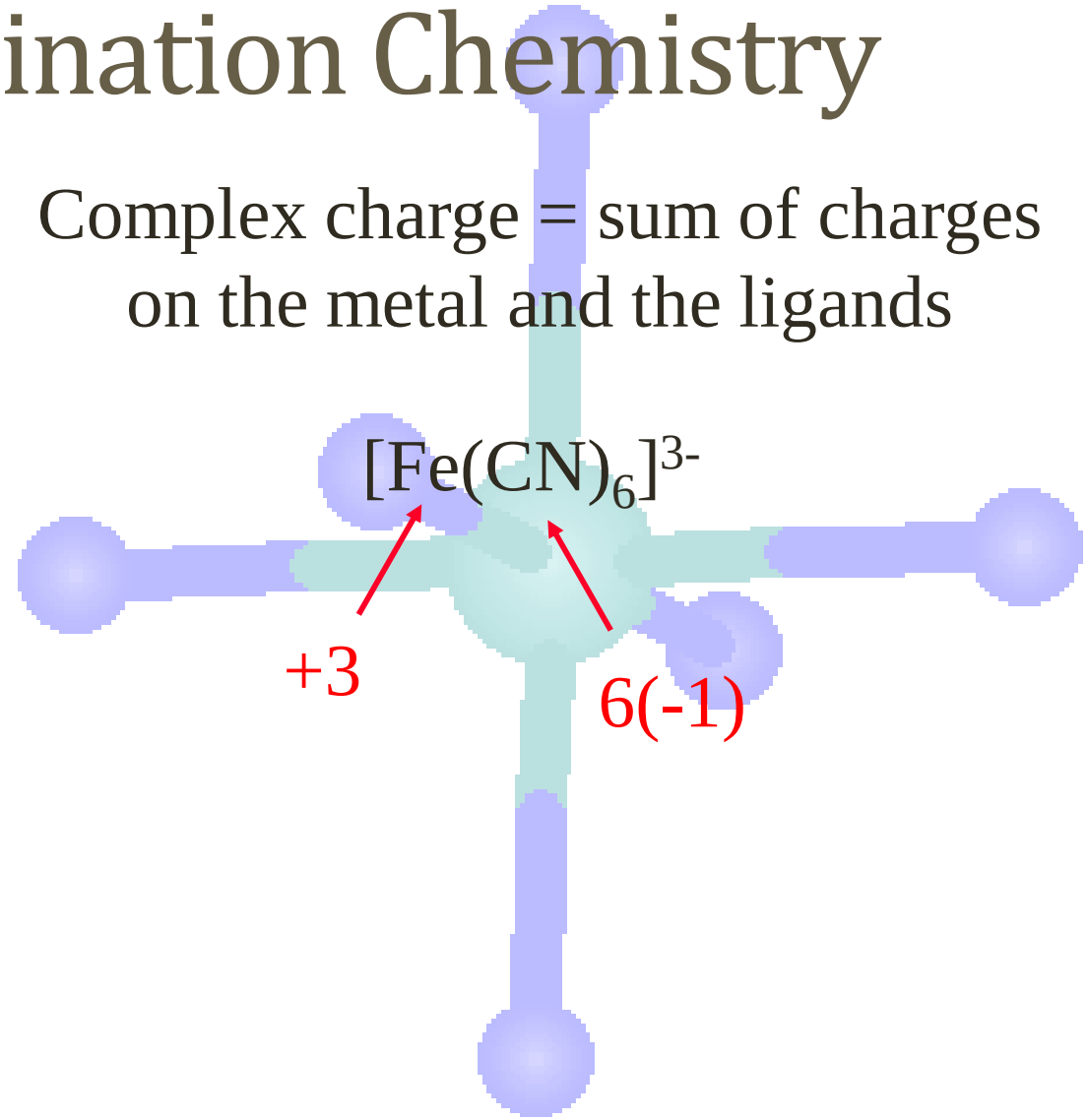
$[Fe(CN)_6]^{3-}$



Coordination Chemistry

Complex charge = sum of charges on the metal and the ligands

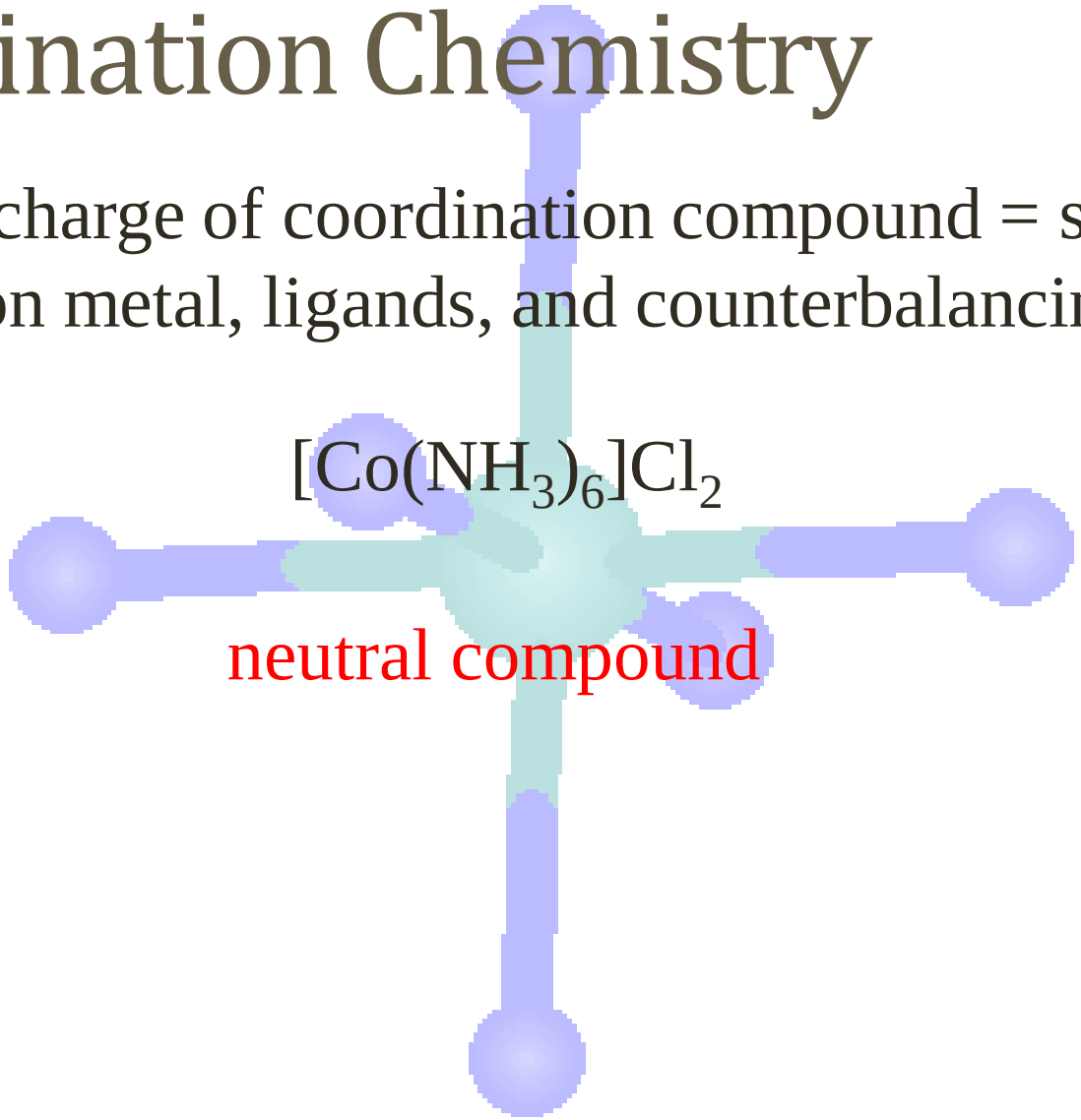
$[Fe(CN)_6]^{3-}$



Coordination Chemistry

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions

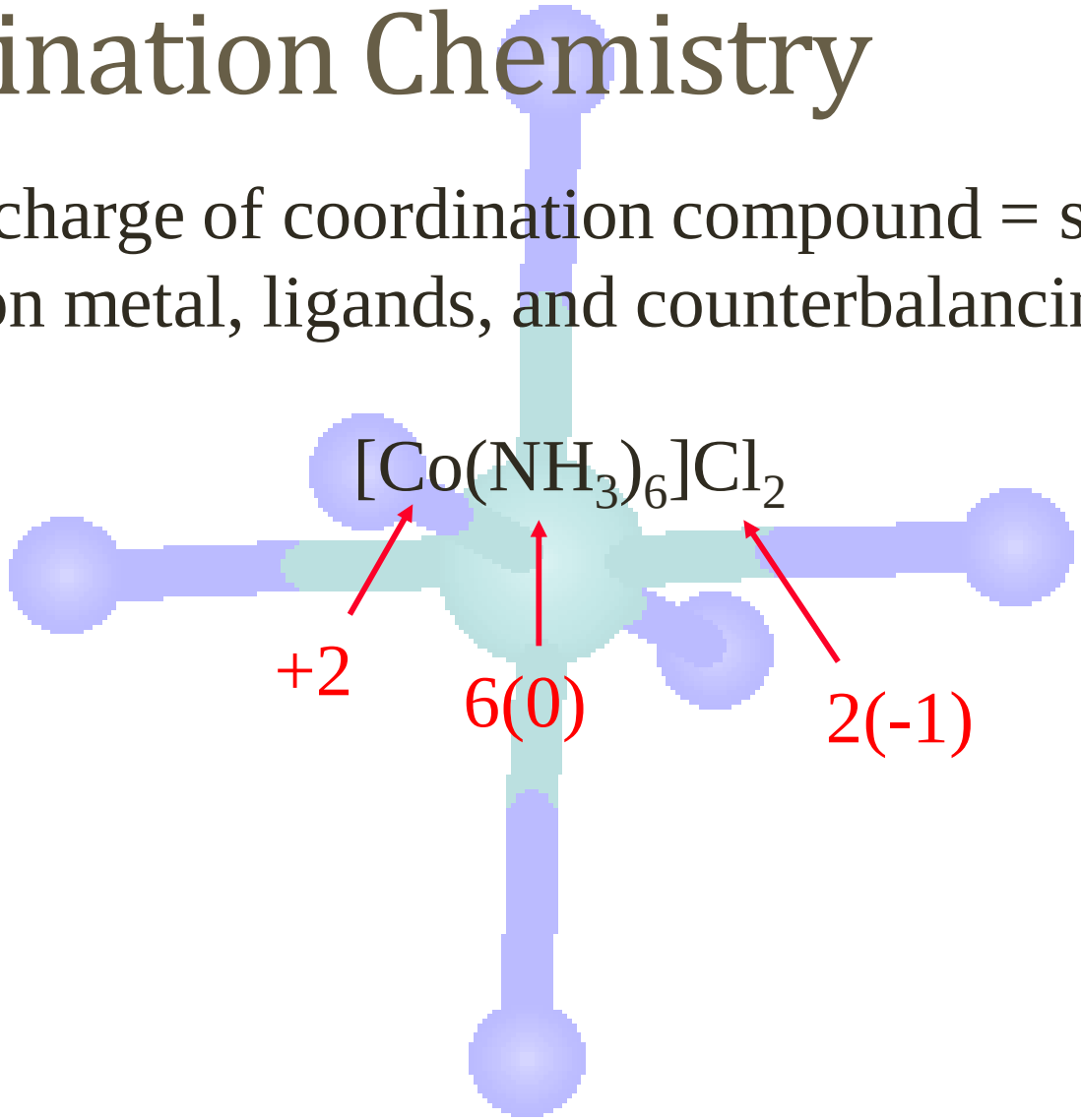
$[Co(NH_3)_6]Cl_2$



neutral compound

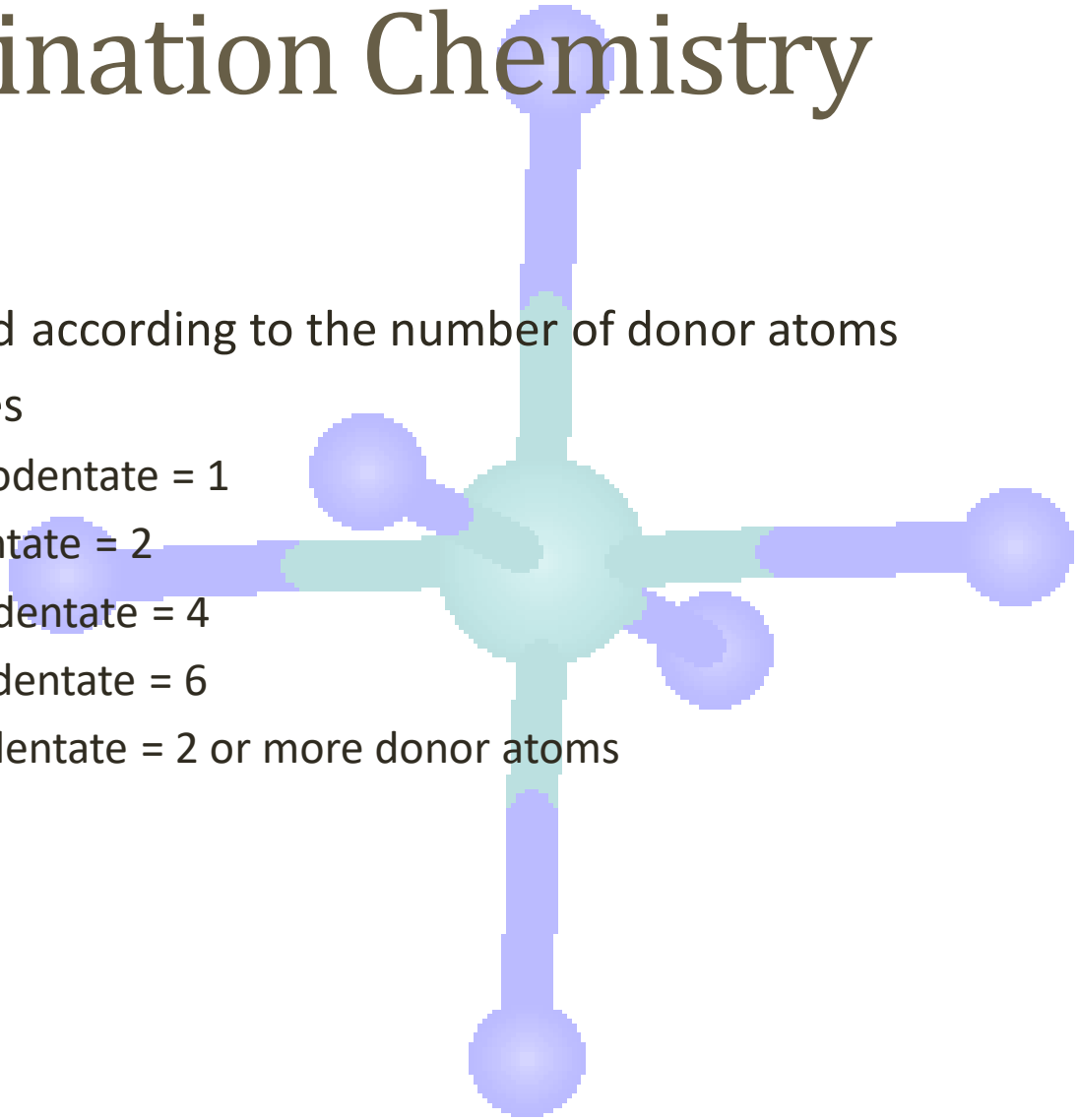
Coordination Chemistry

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions



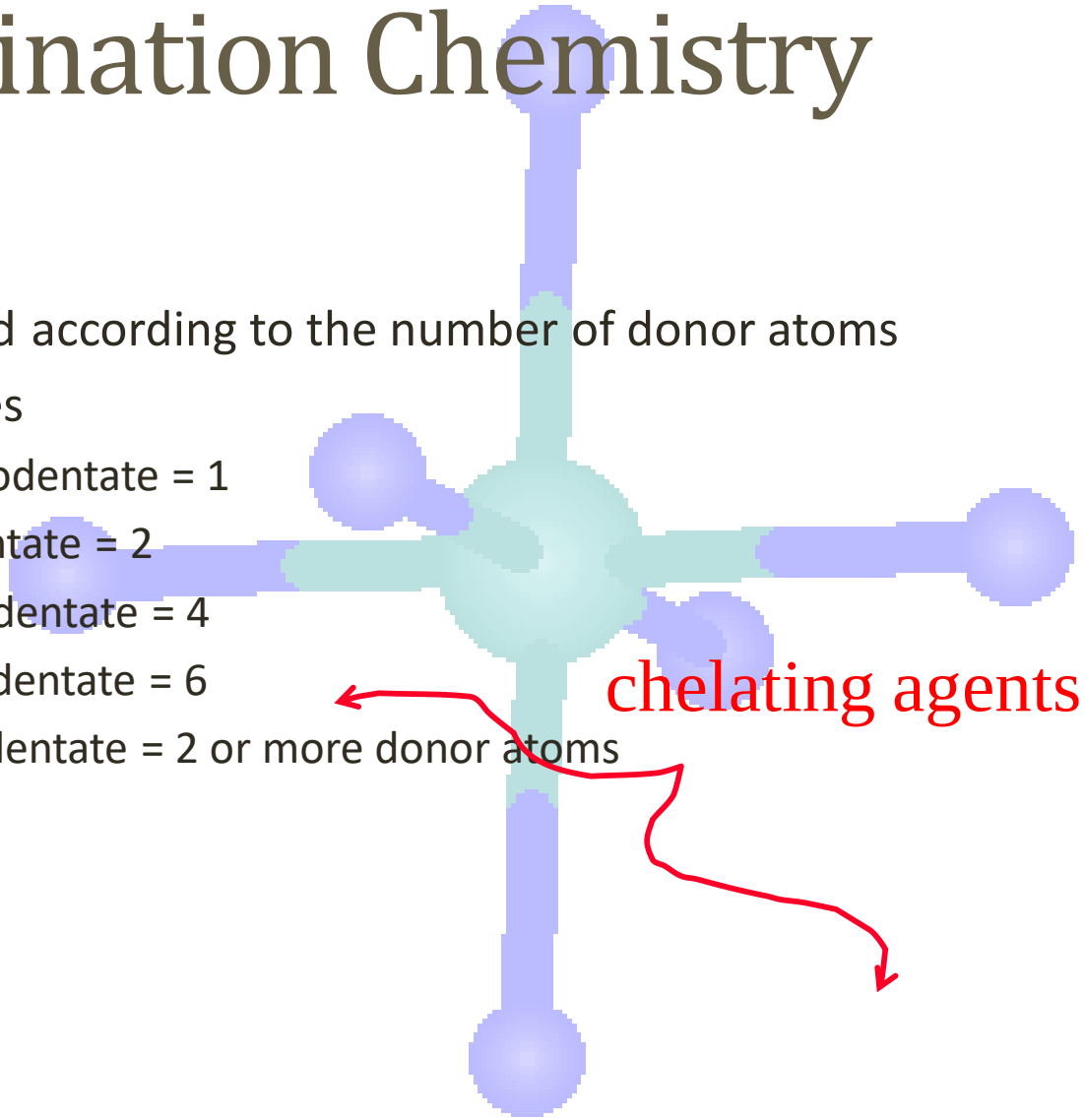
Coordination Chemistry

- Ligands
  - classified according to the number of donor atoms
  - Examples
    - monodentate = 1
    - bidentate = 2
    - tetradentate = 4
    - hexadentate = 6
    - polydentate = 2 or more donor atoms



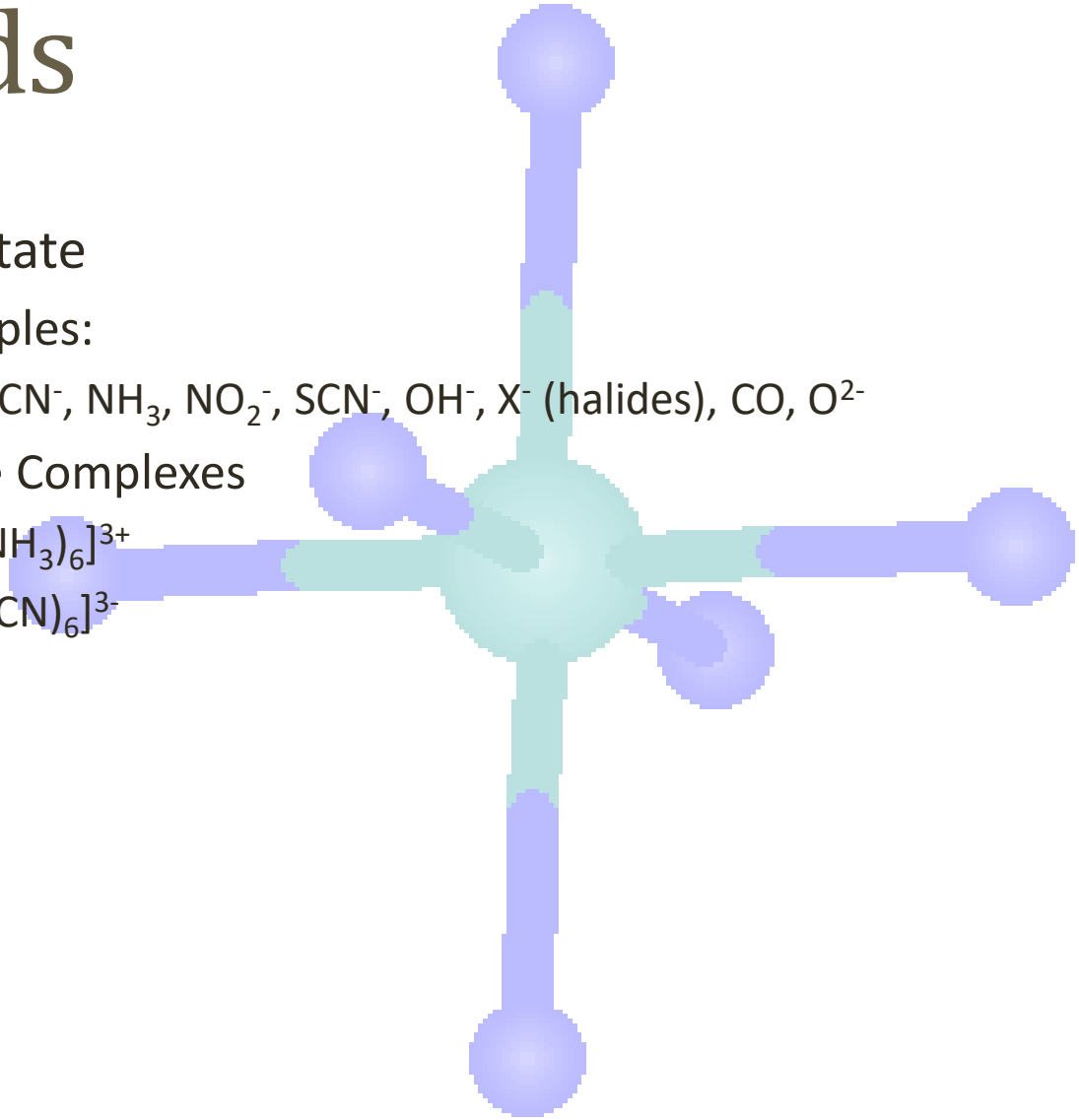
Coordination Chemistry

- Ligands
  - classified according to the number of donor atoms
  - Examples
    - monodentate = 1
    - bidentate = 2
    - tetradentate = 4
    - hexadentate = 6
    - polydentate = 2 or more donor atoms



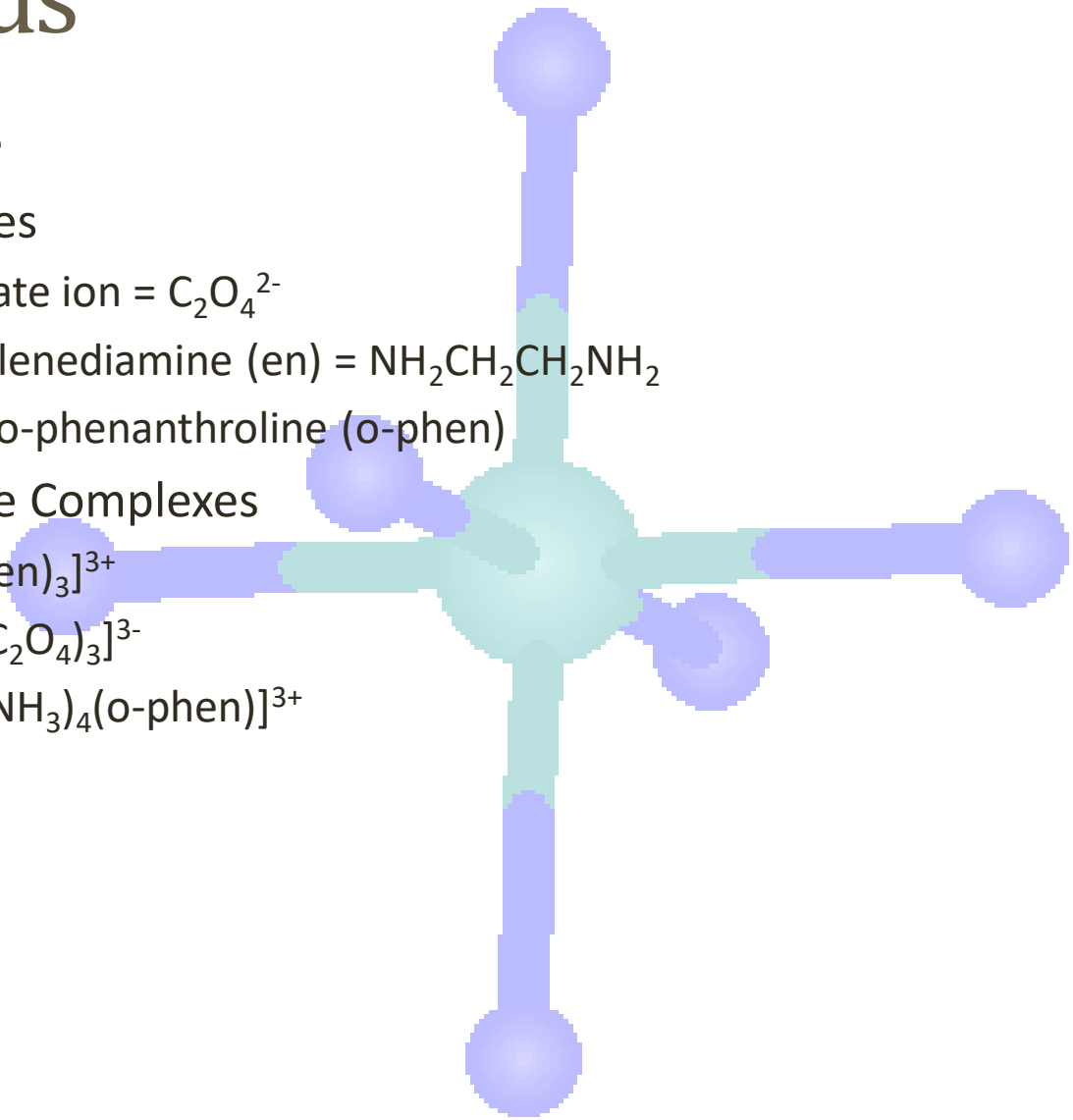
Ligands

- Monodentate
  - Examples:
    - H_2O, CN^-, NH_3, NO_2^-, SCN^-, OH^-, X^- (halides), CO, O^{2-}
  - Example Complexes
    - $[Co(NH_3)_6]^{3+}$
    - $[Fe(SCN)_6]^{3-}$



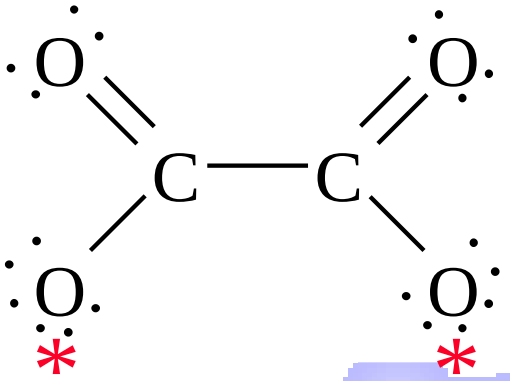
Ligands

- Bidentate
  - Examples
    - oxalate ion = $C_2O_4^{2-}$
    - ethylenediamine (en) = $NH_2CH_2CH_2NH_2$
    - ortho-phenanthroline (o-phen)
  - Example Complexes
    - $[Co(en)_3]^{3+}$
    - $[Cr(C_2O_4)_3]^{3-}$
    - $[Fe(NH_3)_4(o\text{-}phen)]^{3+}$

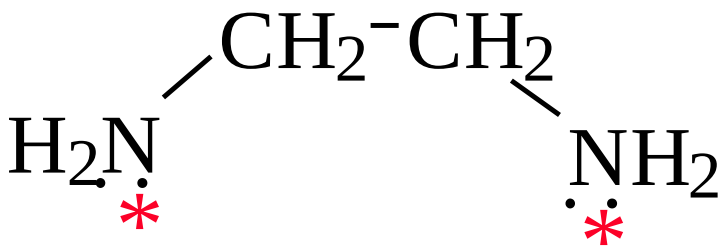


Ligands

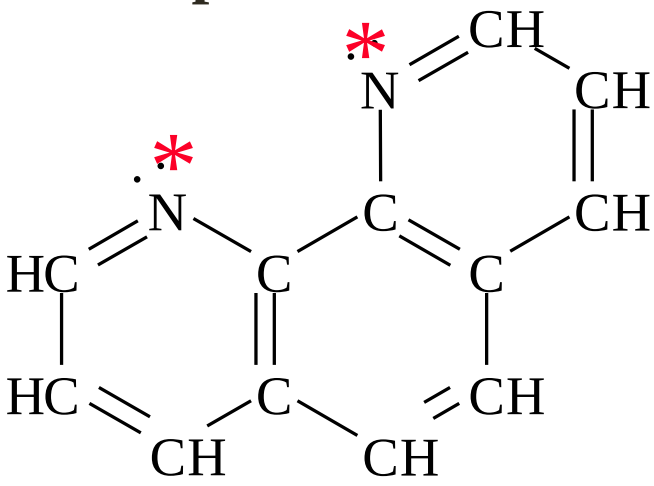
oxalate ion



ethylenediamine



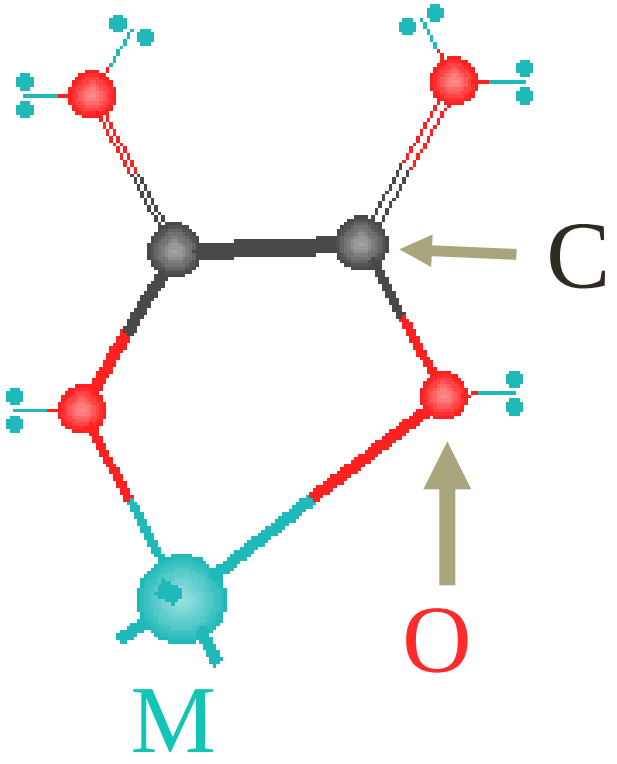
ortho-phenanthroline



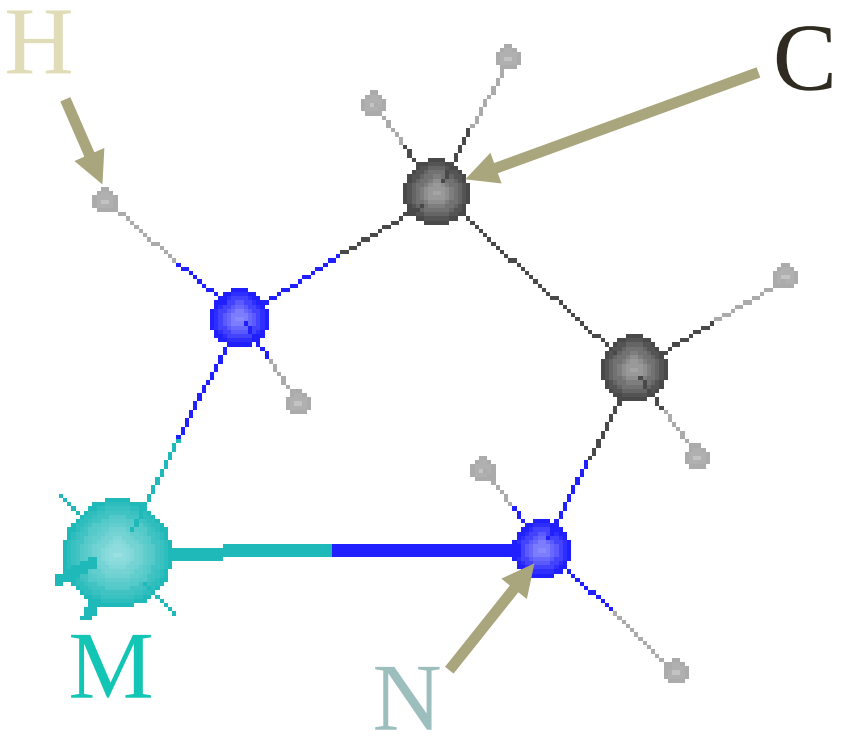
Donor Atoms

Ligands

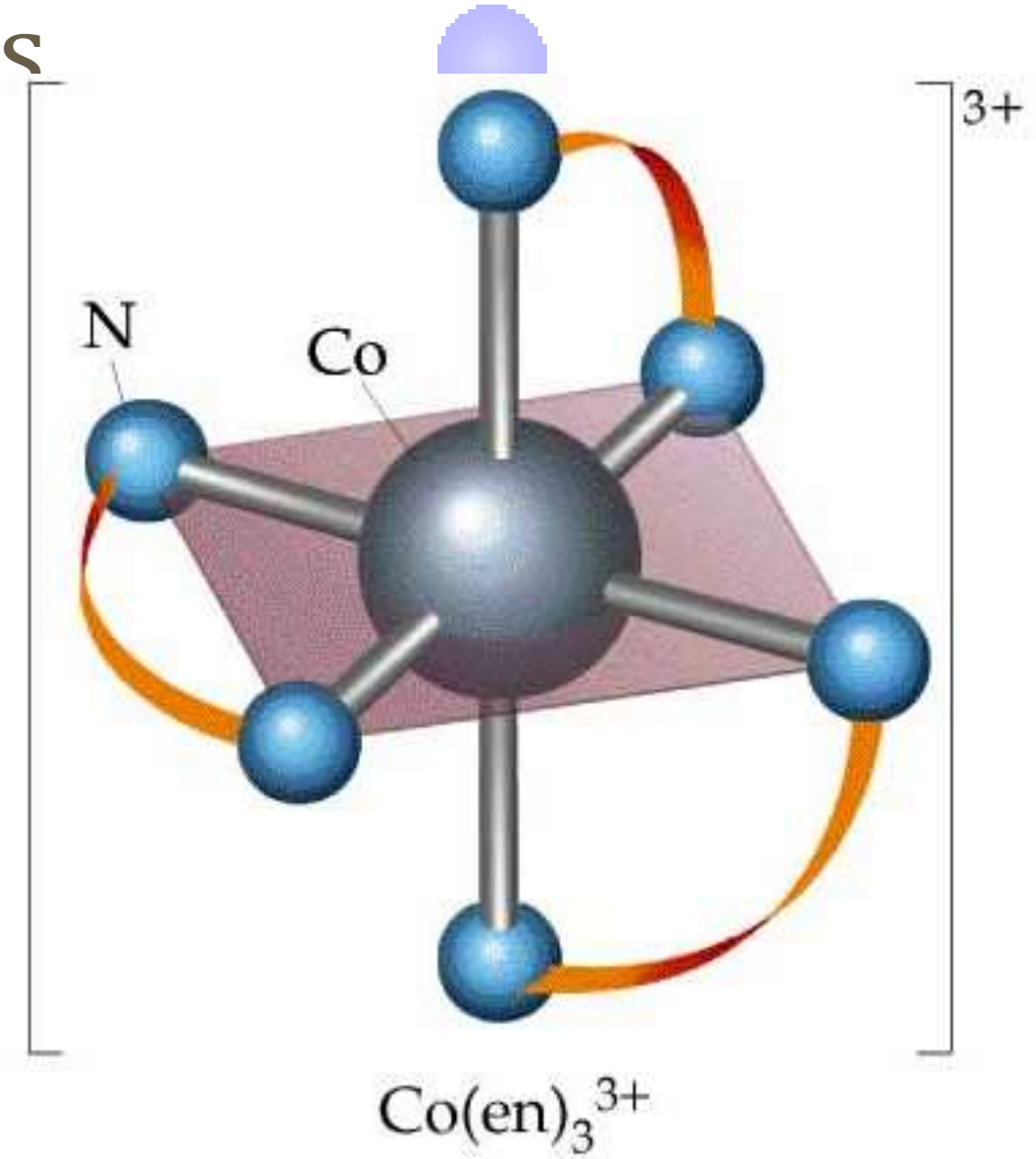
oxalate ion



ethylenediamine

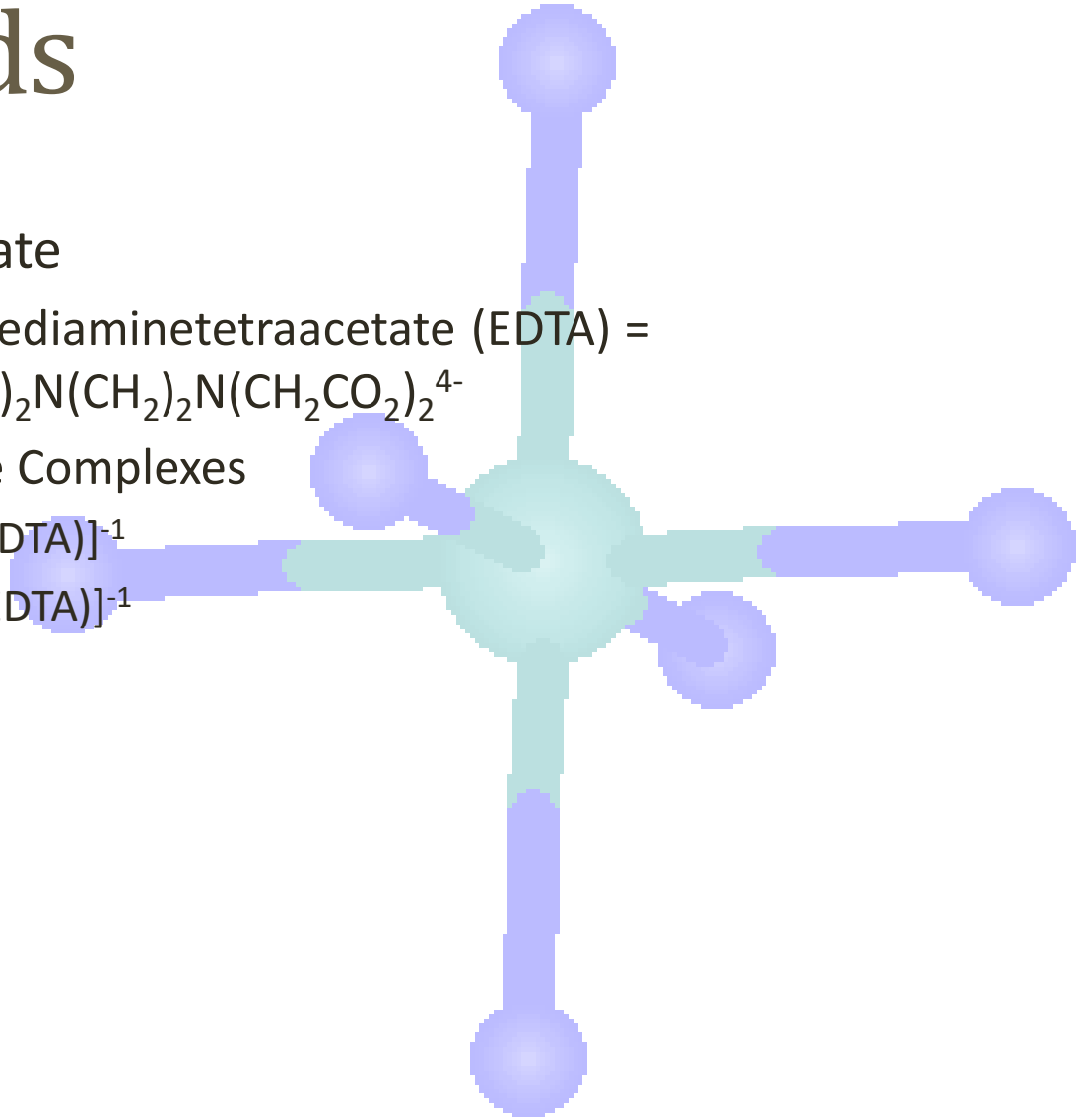


Ligands



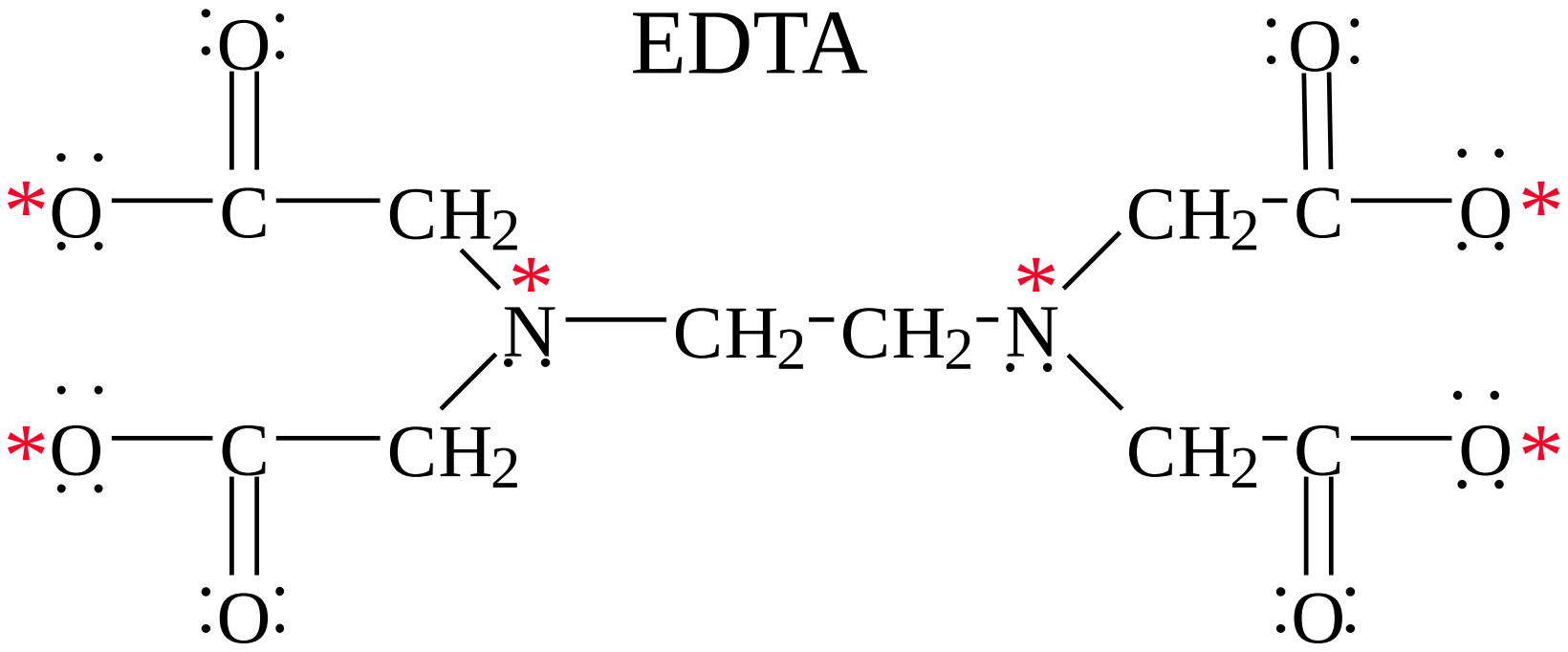
Ligands

- Hexadentate
  - ethylenediaminetetraacetate (EDTA) = $(O_2CCH_2)_2N(CH_2)_2N(CH_2CO_2)_2^{4-}$
  - Example Complexes
    - $[Fe(EDTA)]^{-1}$
    - $[Co(EDTA)]^{-1}$



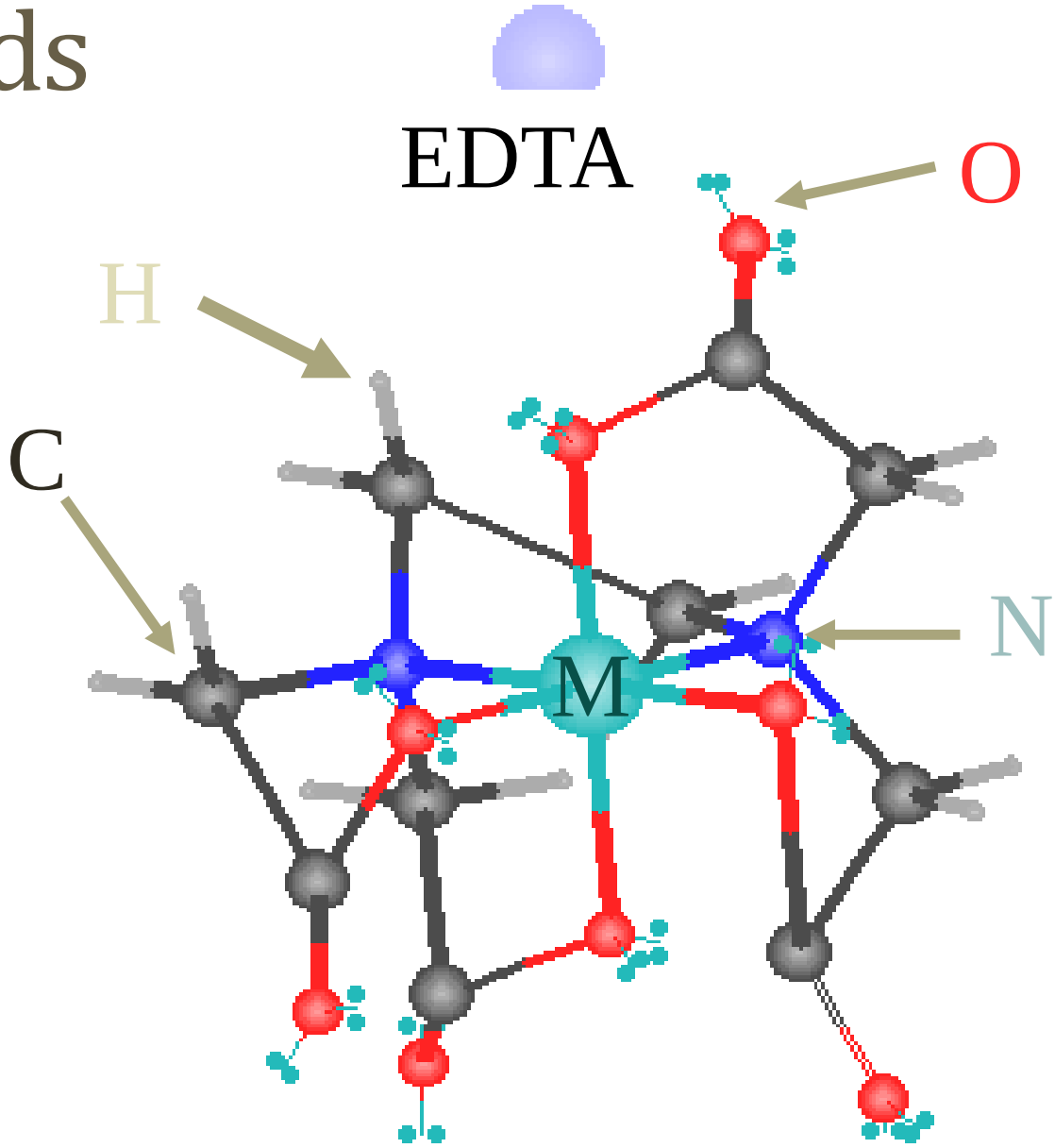
Ligands

EDTA

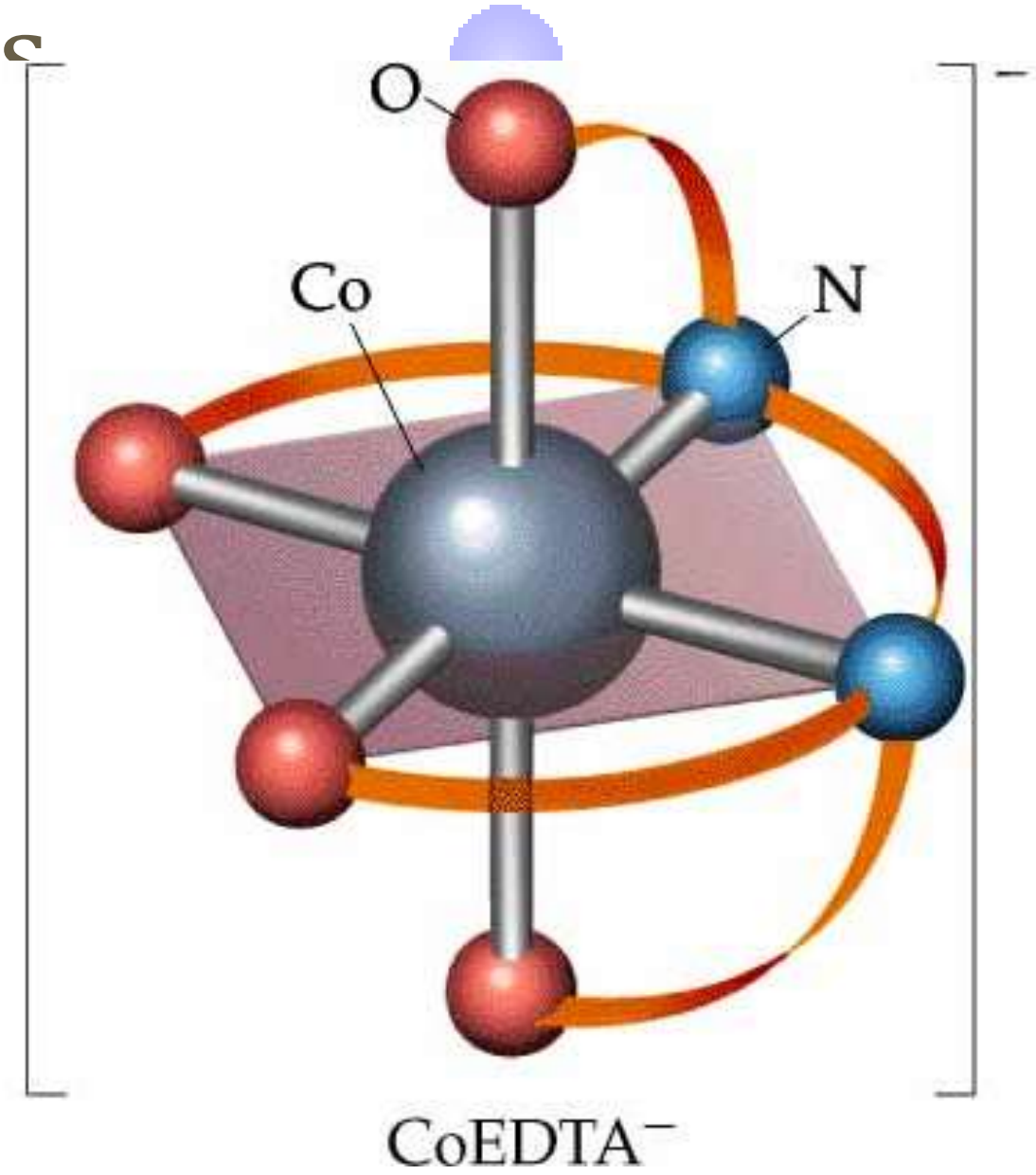


Donor Atoms

Ligands

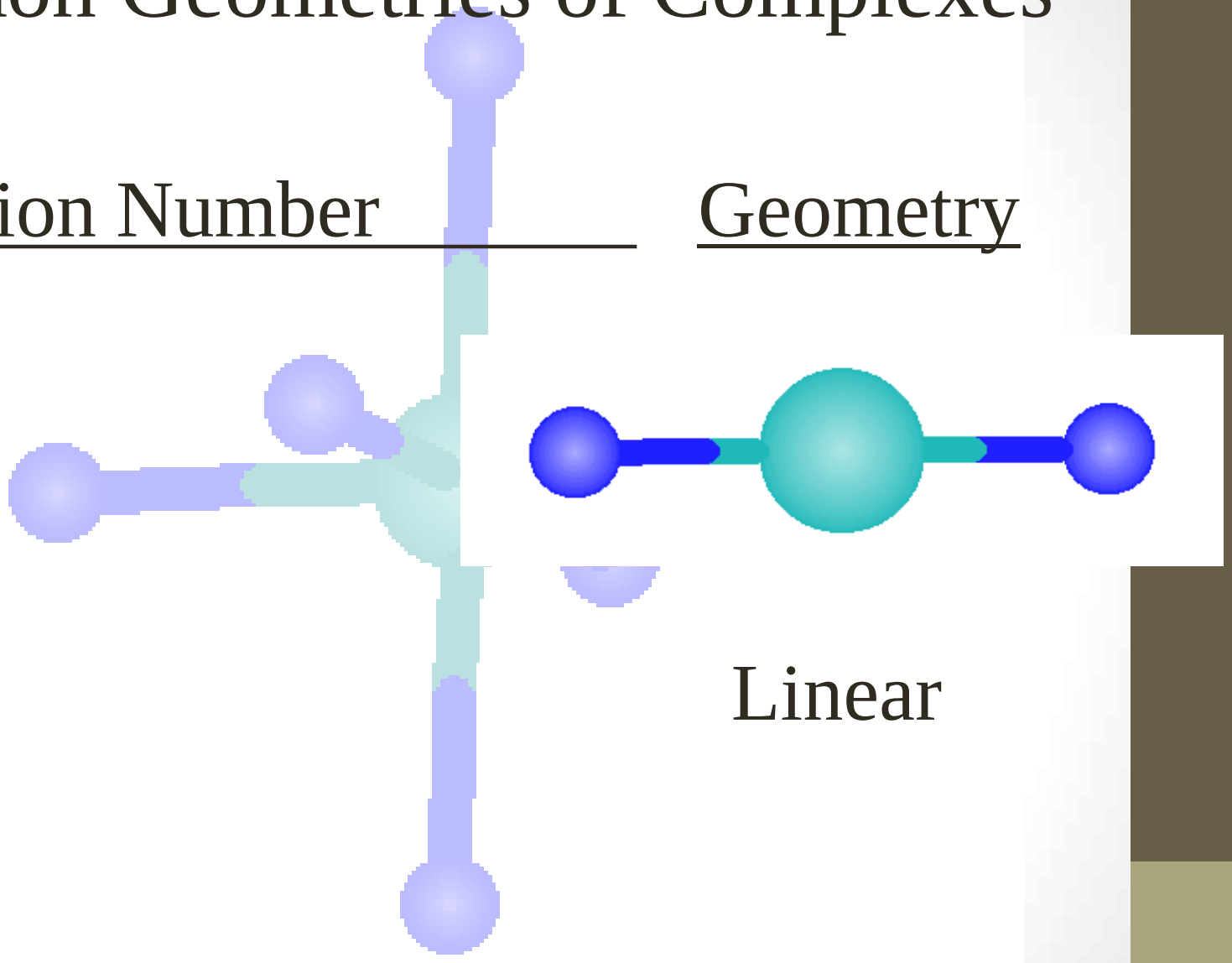


Ligands



Common Geometries of Complexes

Coordination Number	Geometry
2	Linear



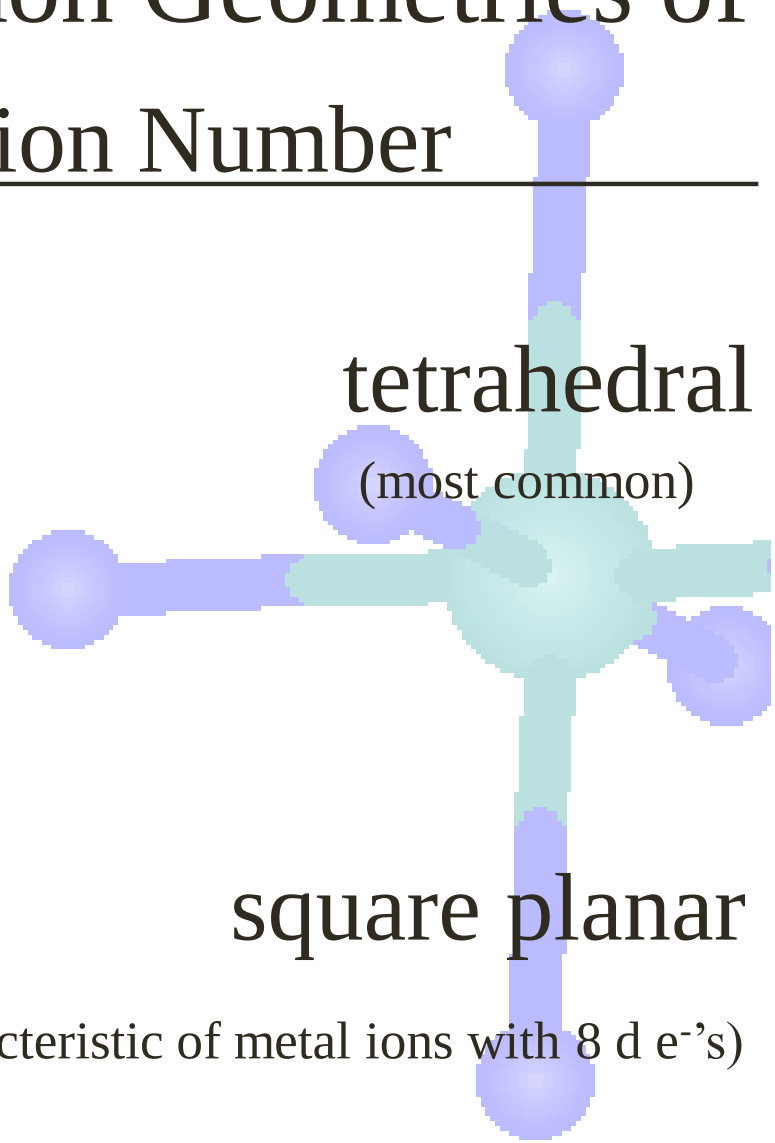
Common Geometries of Complexes

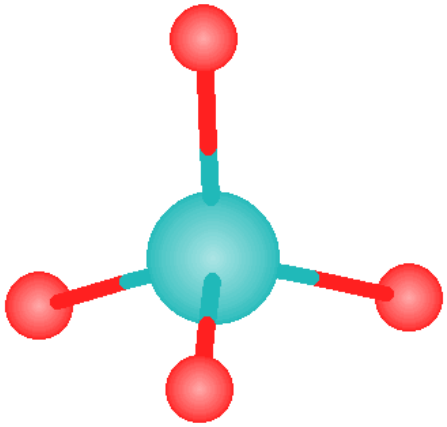
Coordination Number	Geometry
2	Linear

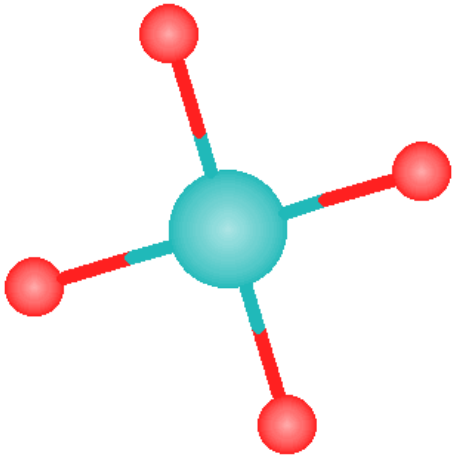
Example: $[Ag(NH_3)_2]^+$

Common Geometries of Complexes

Coordination Number	Geometry
4	tetrahedral (most common)
	square planar (characteristic of metal ions with 8 d e⁻'s)





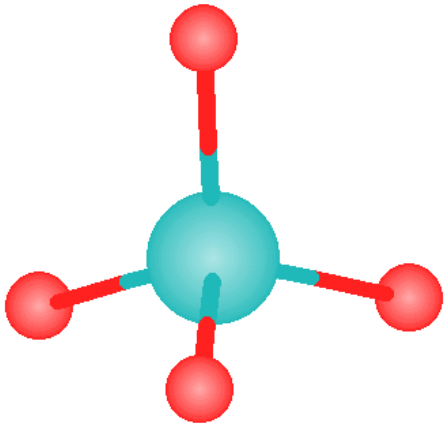


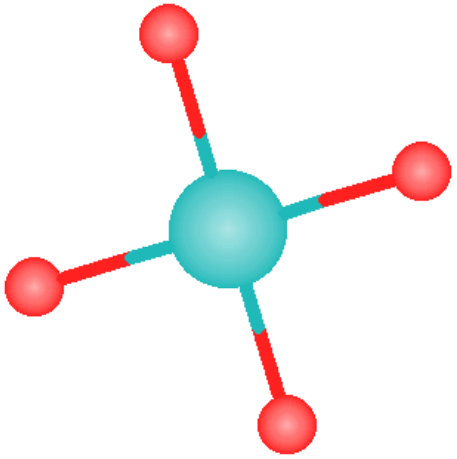
Common Geometries of Complexes

Coordination Number	Geometry
4	tetrahedral
	square planar

Examples: $[Zn(NH_3)_4]^{2+}$, $[FeCl_4]^-$

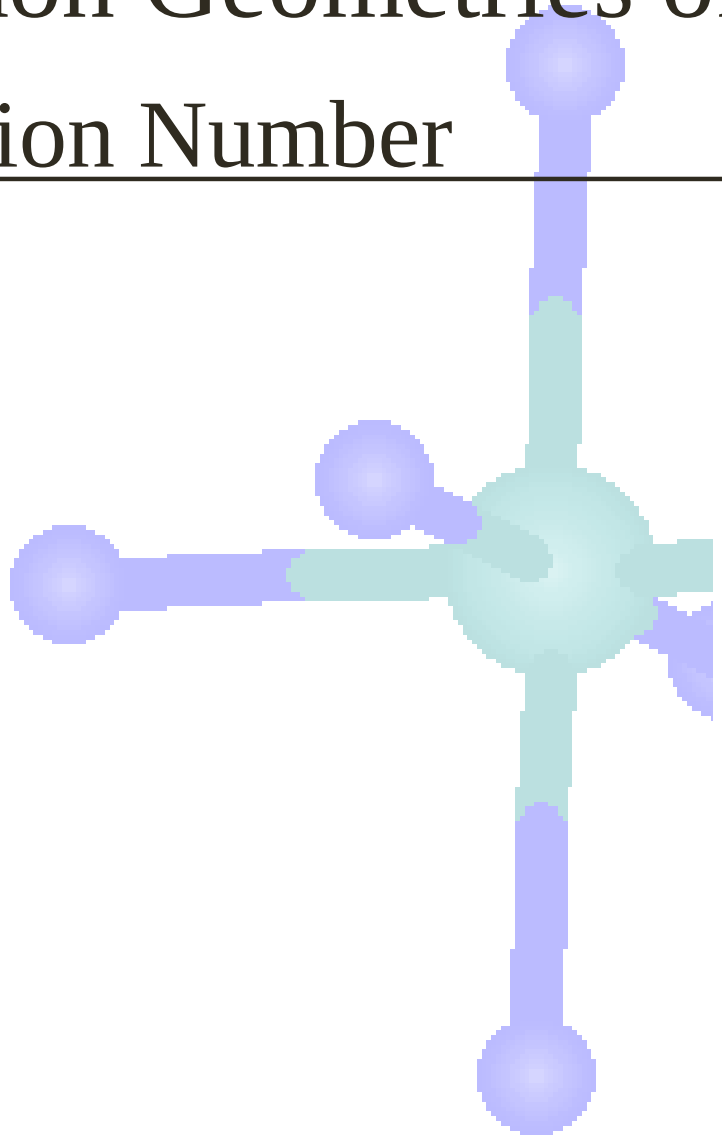
Example: $[Ni(CN)_4]^{2-}$

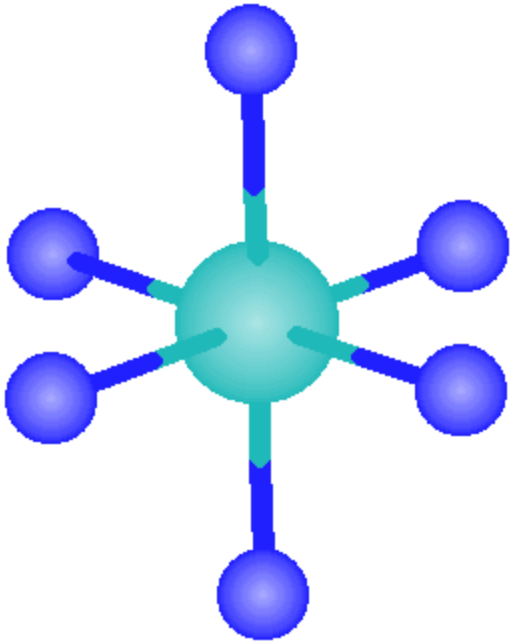




Common Geometries of Complexes

Coordination Number	Geometry
6	octahedral

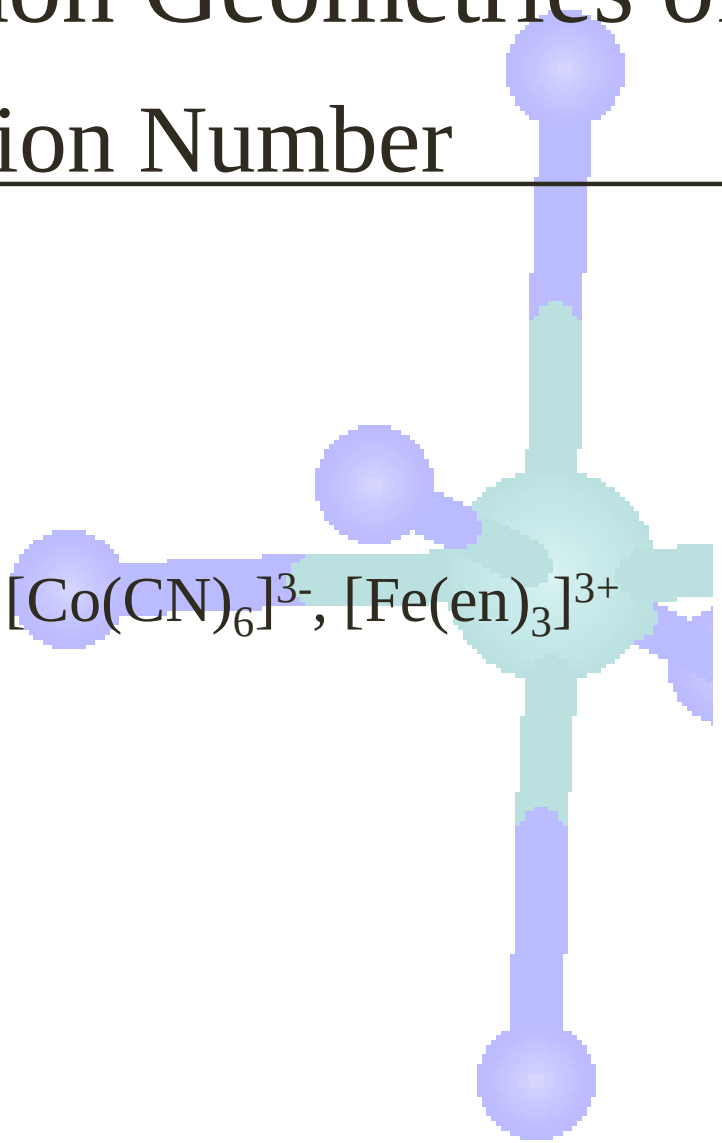


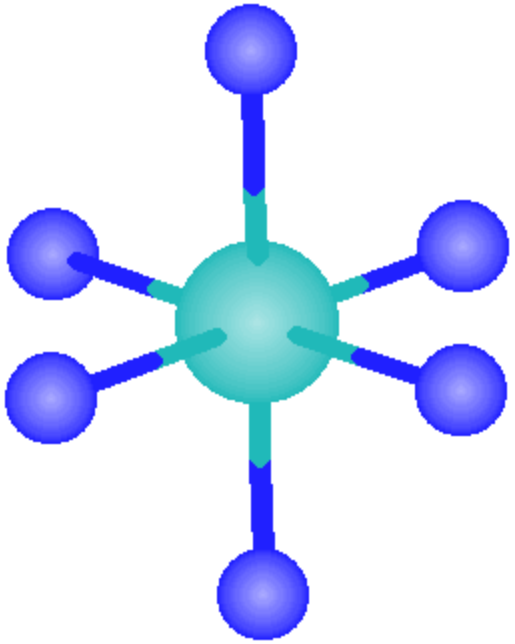


Common Geometries of Complexes

Coordination Number	Geometry
6	octahedral

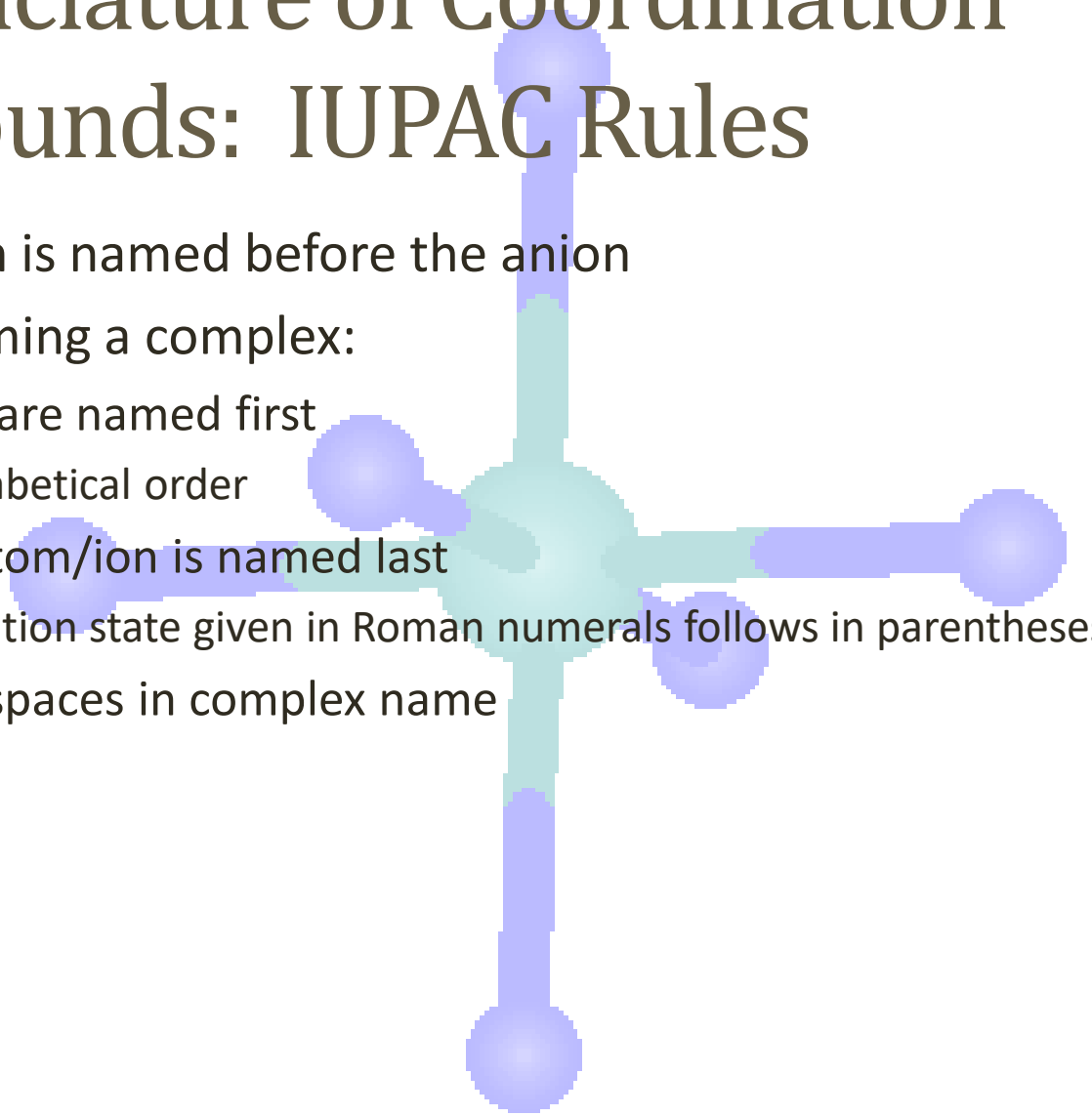
Examples: $[Co(CN)_6]^{3-}$, $[Fe(en)_3]^{3+}$





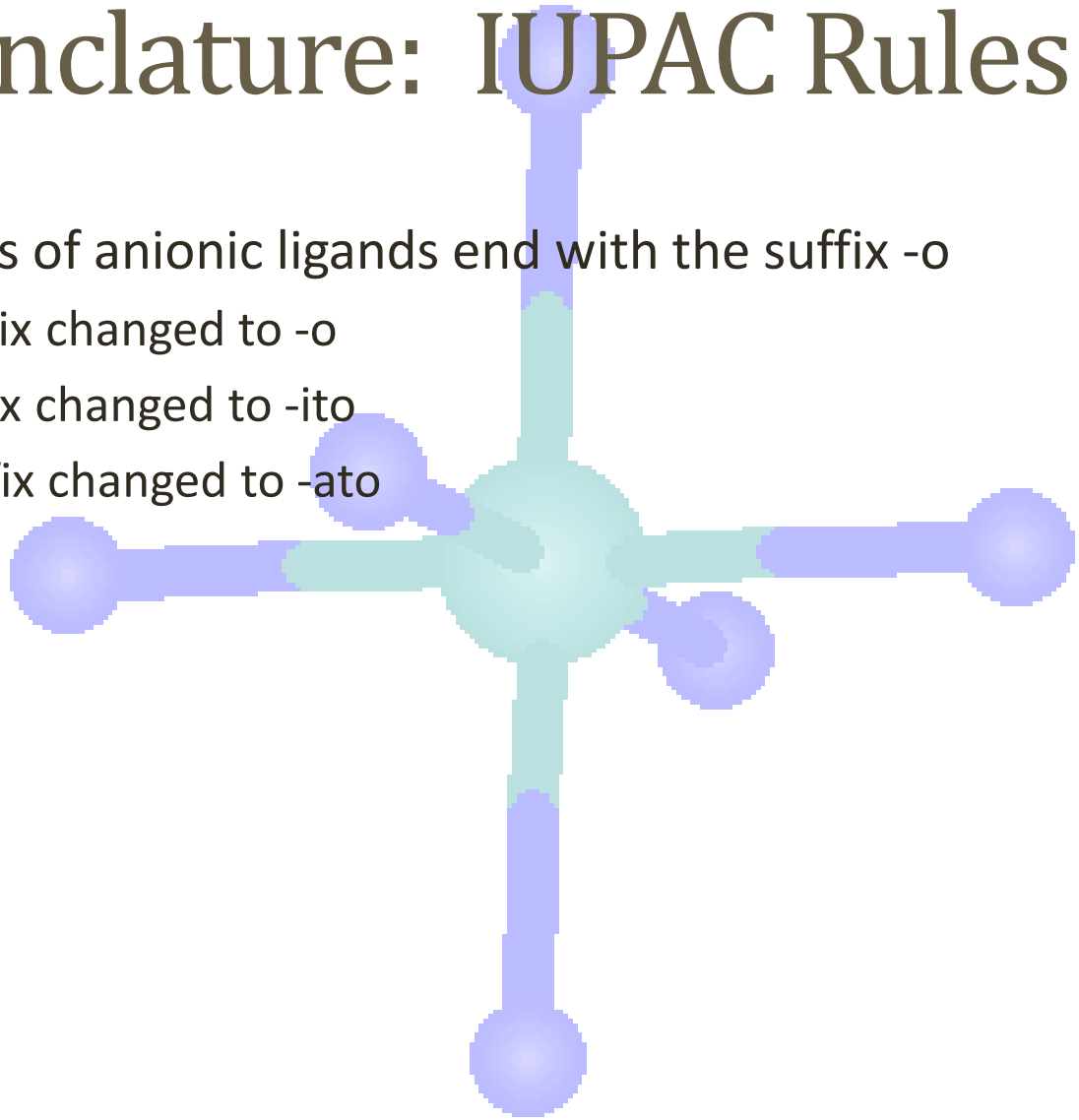
Nomenclature of Coordination Compounds: IUPAC Rules

- The cation is named before the anion
- When naming a complex:
  - Ligands are named first
    - alphabetical order
  - Metal atom/ion is named last
    - oxidation state given in Roman numerals follows in parentheses
  - Use no spaces in complex name



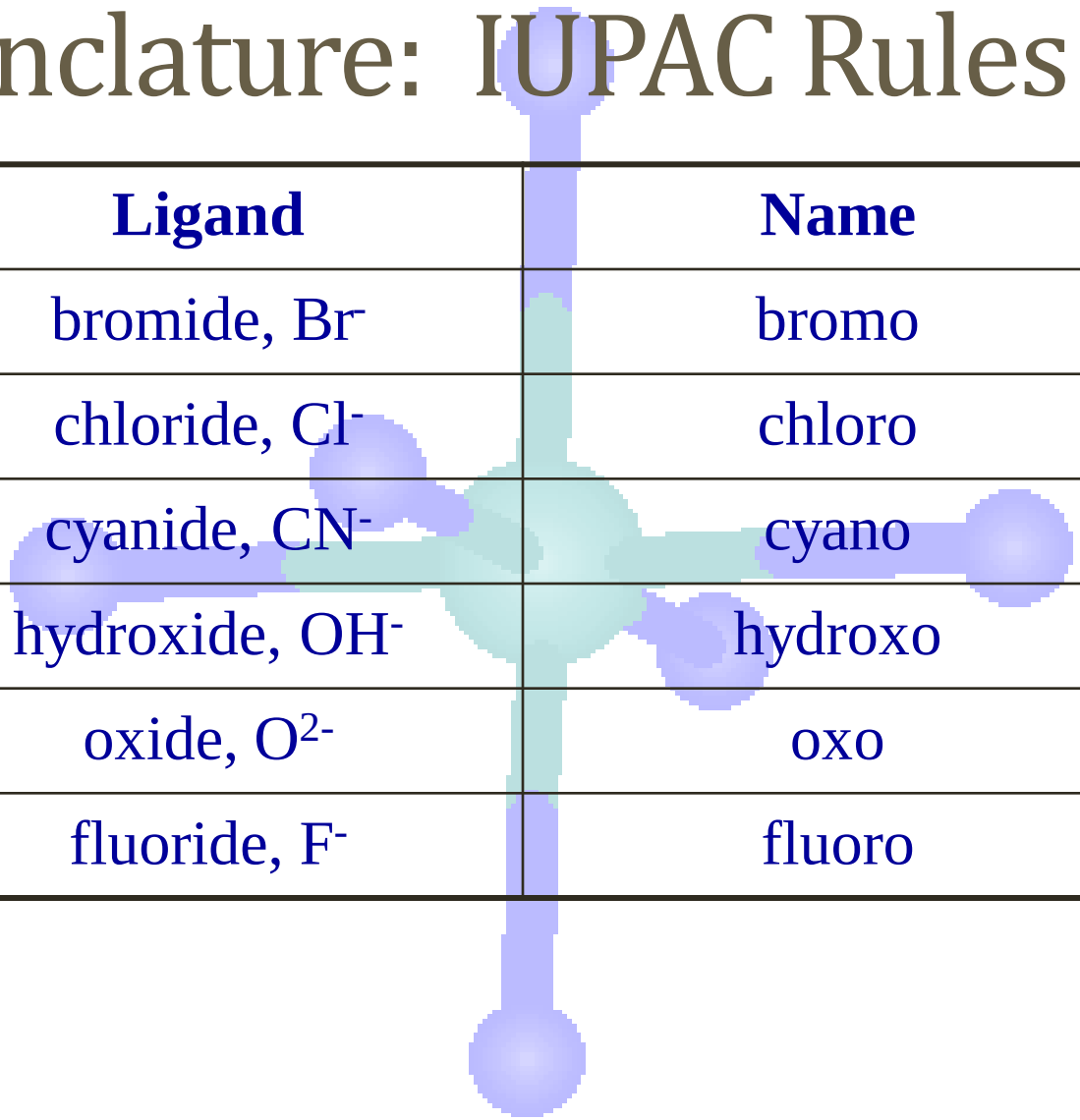
Nomenclature: IUPAC Rules

- The names of anionic ligands end with the suffix -o
  - -ide suffix changed to -o
  - -ite suffix changed to -ito
  - -ate suffix changed to -ato



Nomenclature: IUPAC Rules

Ligand	Name
bromide, Br^-	bromo
chloride, Cl^-	chloro
cyanide, CN^-	cyano
hydroxide, OH^-	hydroxo
oxide, O^{2-}	oxo
fluoride, F^-	fluoro

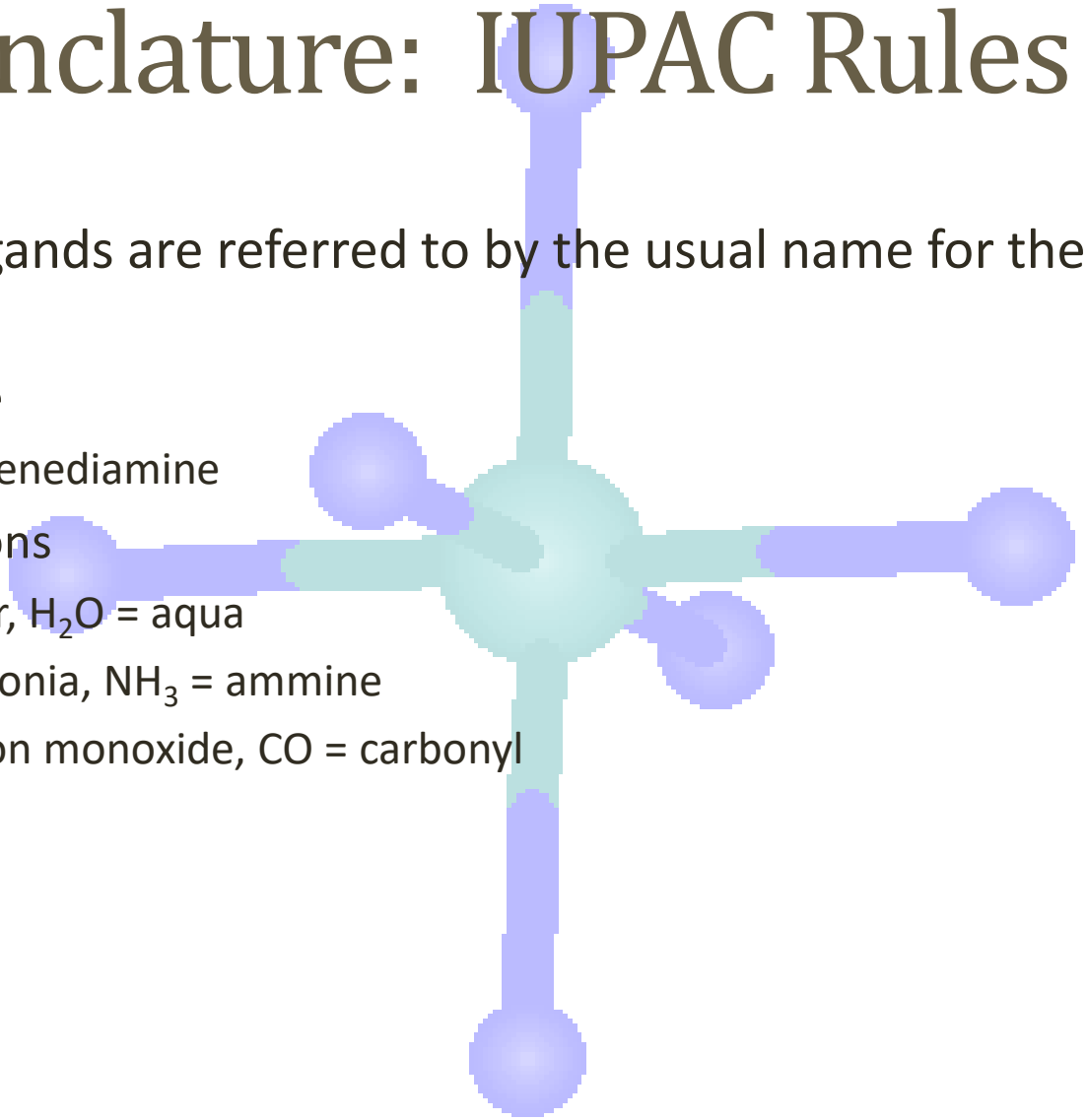


Nomenclature: IUPAC Rules

Ligand	Name
carbonate, CO_3^{2-}	carbonato
oxalate, $C_2O_4^{2-}$	oxalato
sulfate, SO_4^{2-}	sulfato
thiocyanate, SCN^-	thiocyanato
thiosulfate, $S_2O_3^{2-}$	thiosulfato
Sulfite, SO_3^{2-}	sulfito

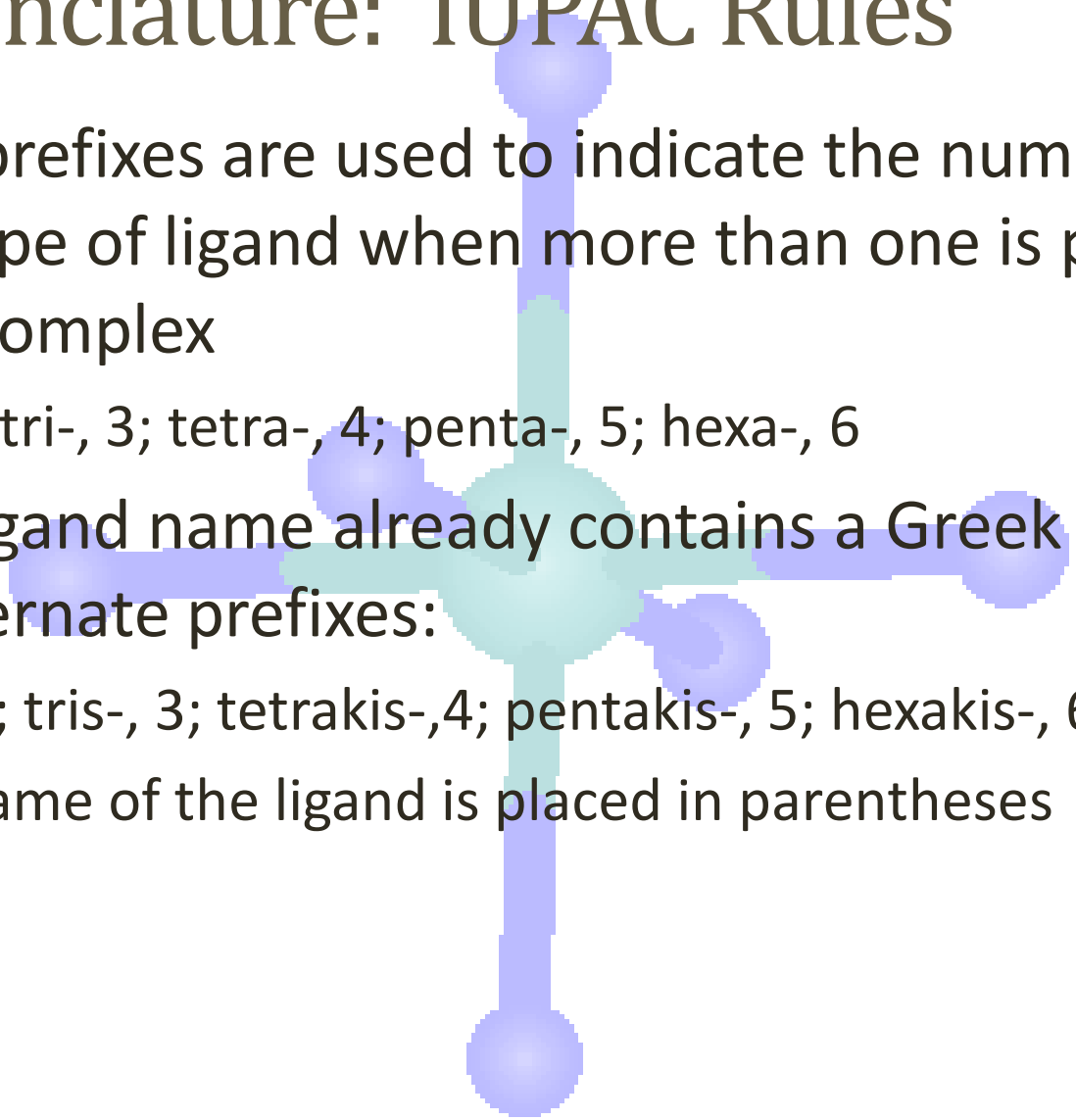
Nomenclature: IUPAC Rules

- Neutral ligands are referred to by the usual name for the molecule
  - Example
    - ethylenediamine
  - Exceptions
    - water, H_2O = aqua
    - ammonia, NH_3 = ammine
    - carbon monoxide, CO = carbonyl



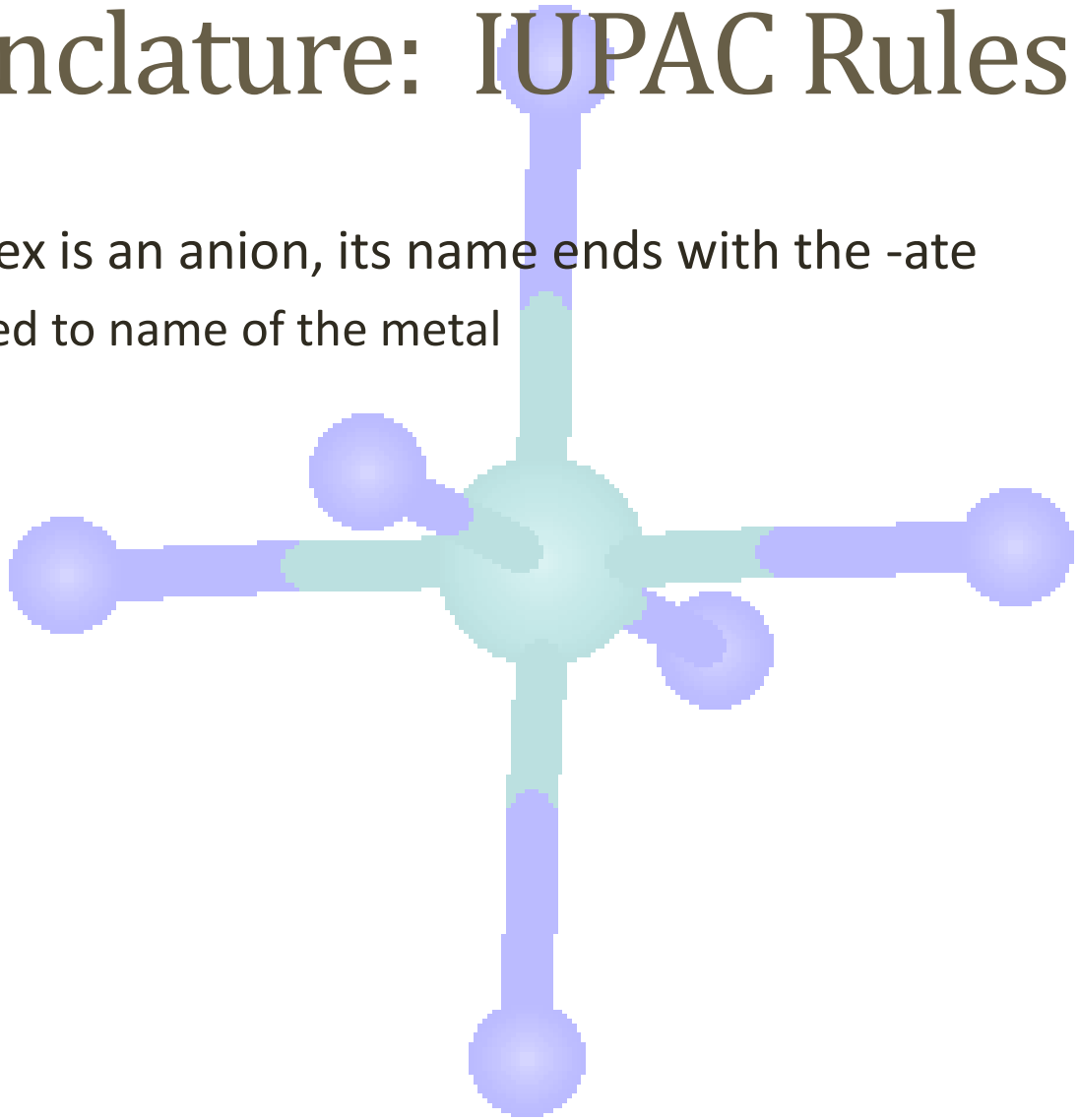
Nomenclature: IUPAC Rules

- Greek prefixes are used to indicate the number of each type of ligand when more than one is present in the complex
  - di-, 2; tri-, 3; tetra-, 4; penta-, 5; hexa-, 6
- If the ligand name already contains a Greek prefix, use alternate prefixes:
  - bis-, 2; tris-, 3; tetrakis-,4; pentakis-, 5; hexakis-, 6
  - The name of the ligand is placed in parentheses



Nomenclature: IUPAC Rules

- If a complex is an anion, its name ends with the -ate
  - appended to name of the metal

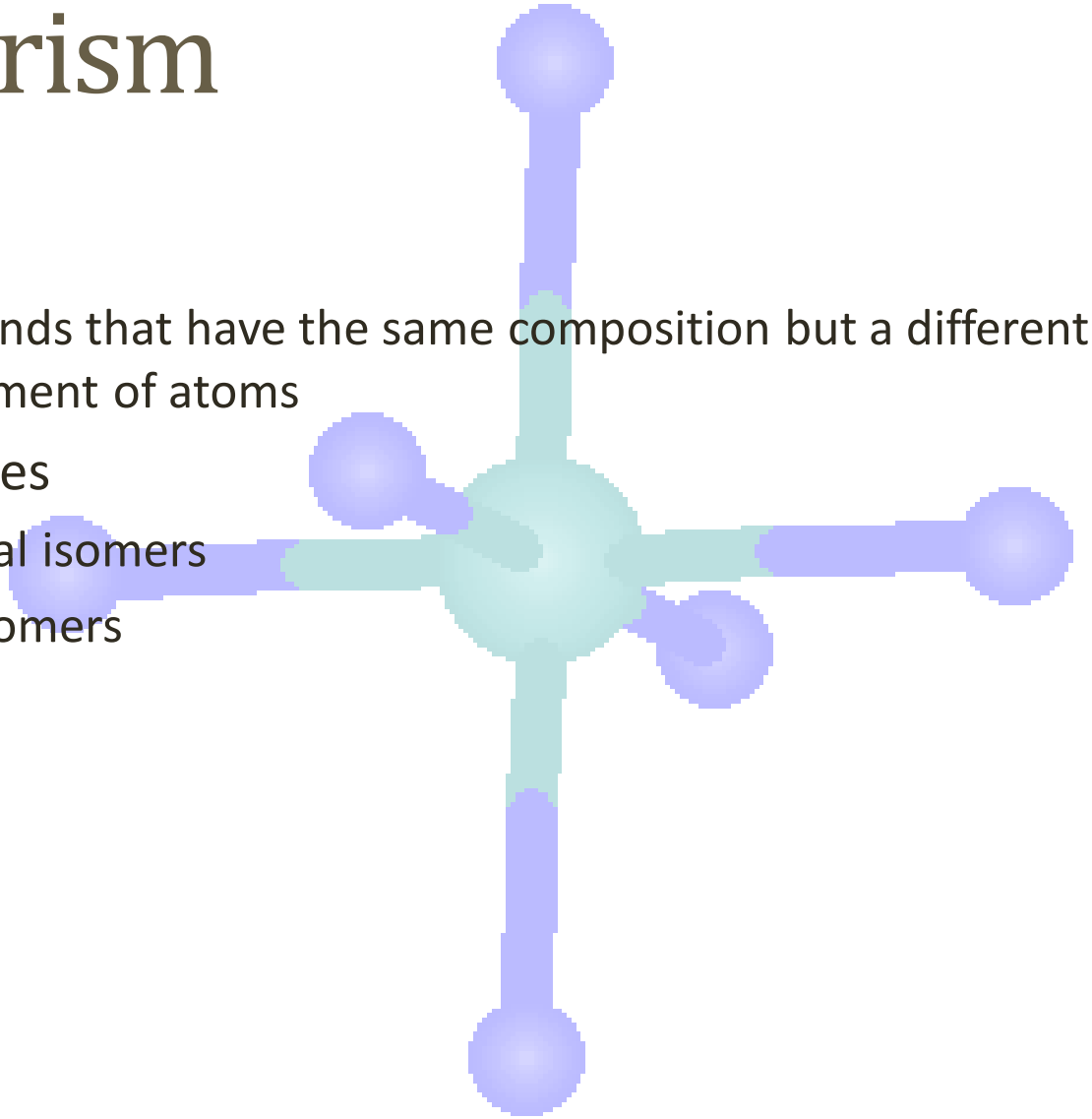


Nomenclature: IUPAC Rules

Transition Metal	Name if in Cationic Complex	Name if in Anionic Complex
Sc	Scandium	Scandate
Ti	titanium	titanate
V	vanadium	vanadate
Cr	chromium	chromate
Mn	manganese	manganate
Fe	iron	ferrate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Cu	Copper	cuprate
Zn	Zinc	zincate

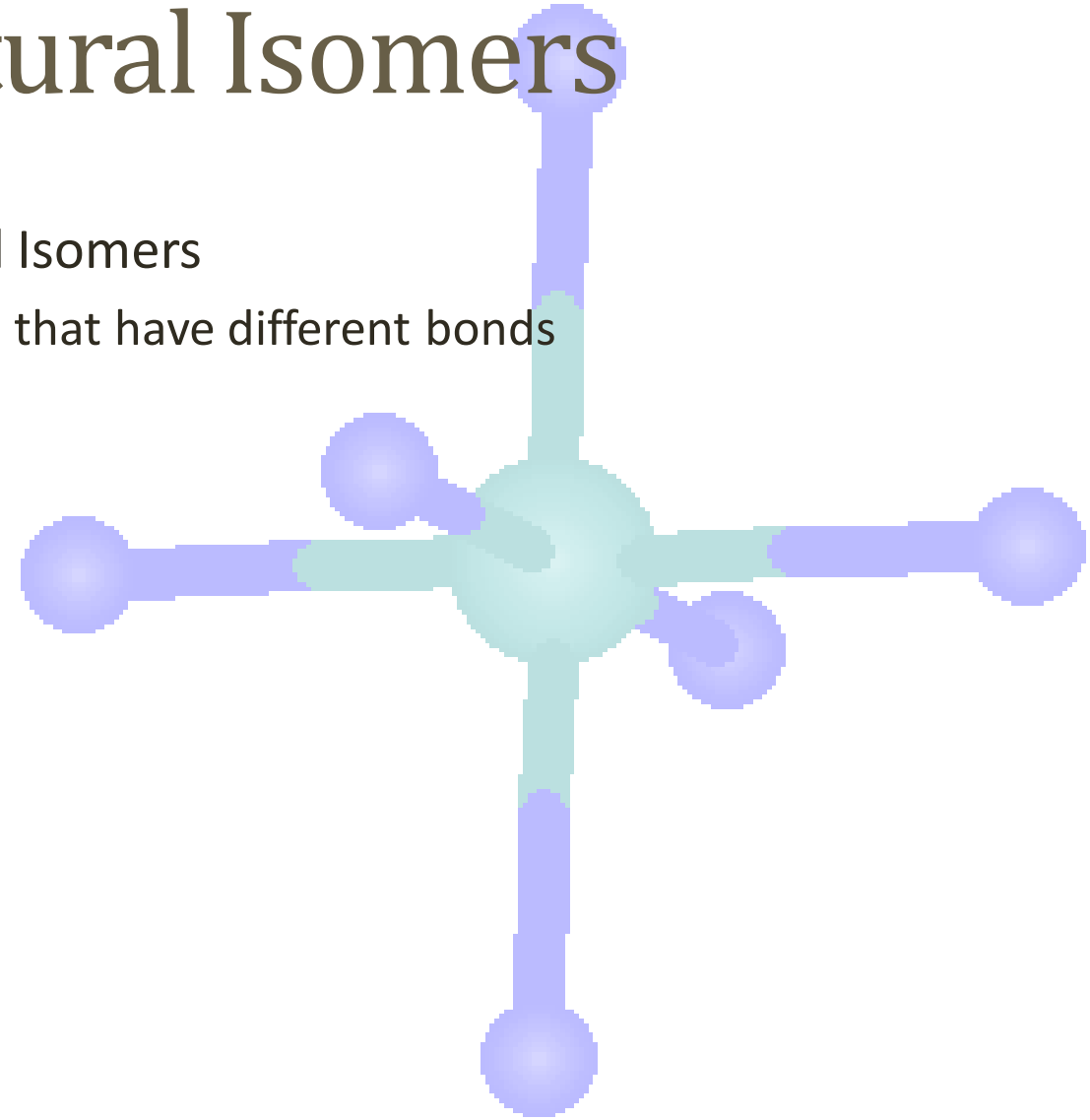
Isomerism

- Isomers
  - compounds that have the same composition but a different arrangement of atoms
- Major Types
  - structural isomers
  - stereoisomers



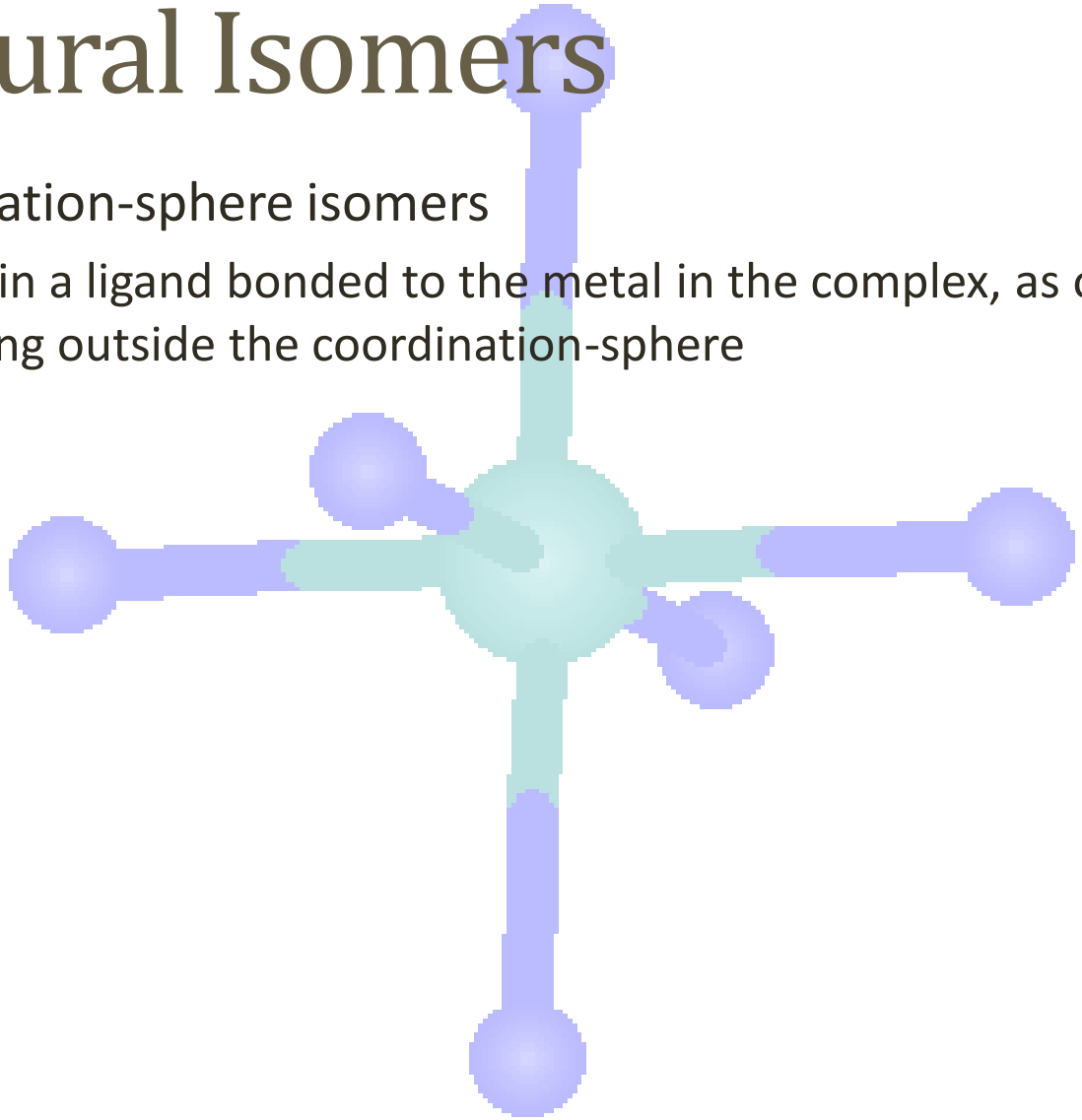
Structural Isomers

- Structural Isomers
  - isomers that have different bonds



Structural Isomers

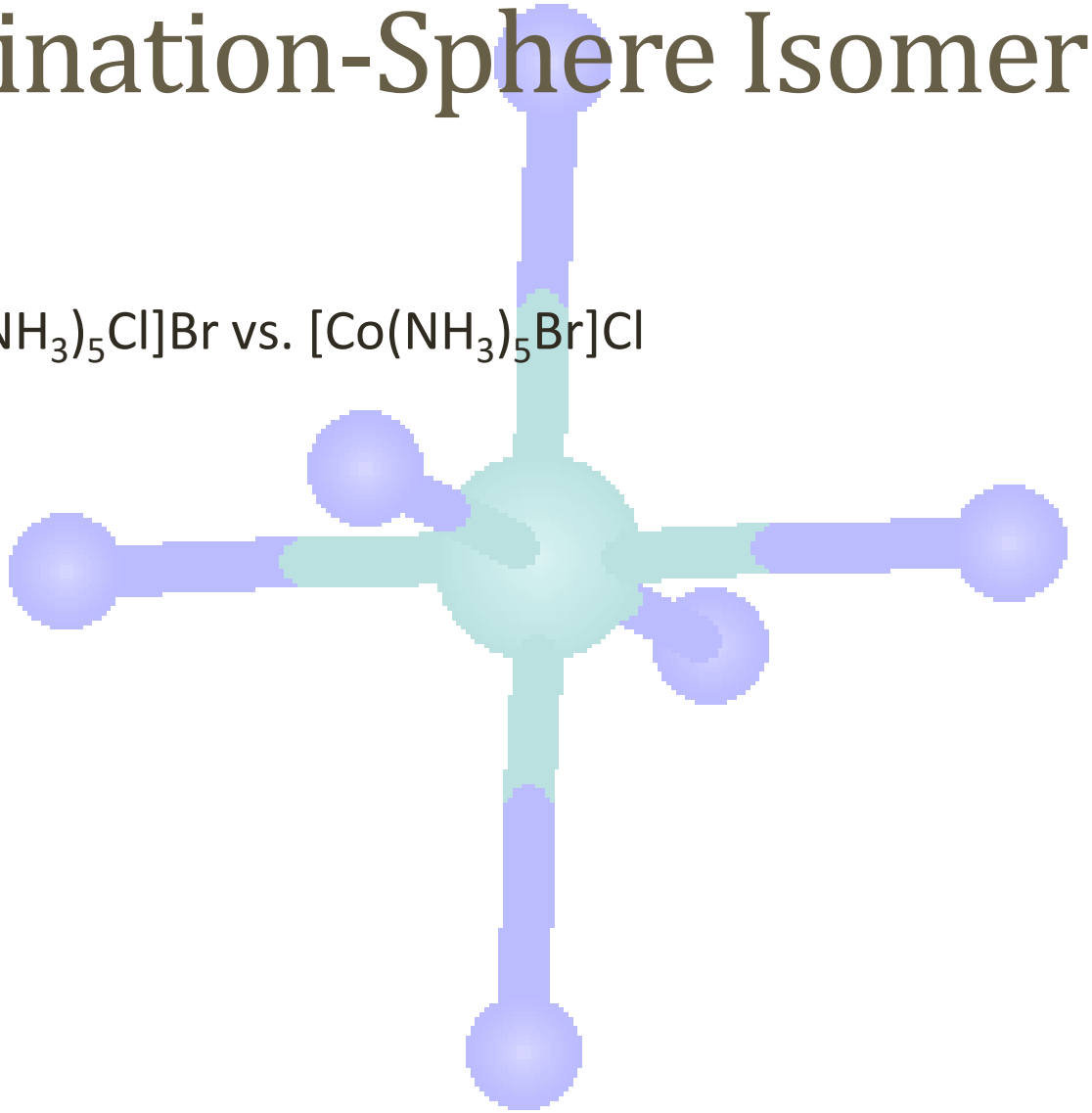
- Coordination-sphere isomers
  - differ in a ligand bonded to the metal in the complex, as opposed to being outside the coordination-sphere



Coordination-Sphere Isomers

- Example

  $[Co(NH_3)_5Cl]Br$ vs. $[Co(NH_3)_5Br]Cl$



Coordination-Sphere Isomers

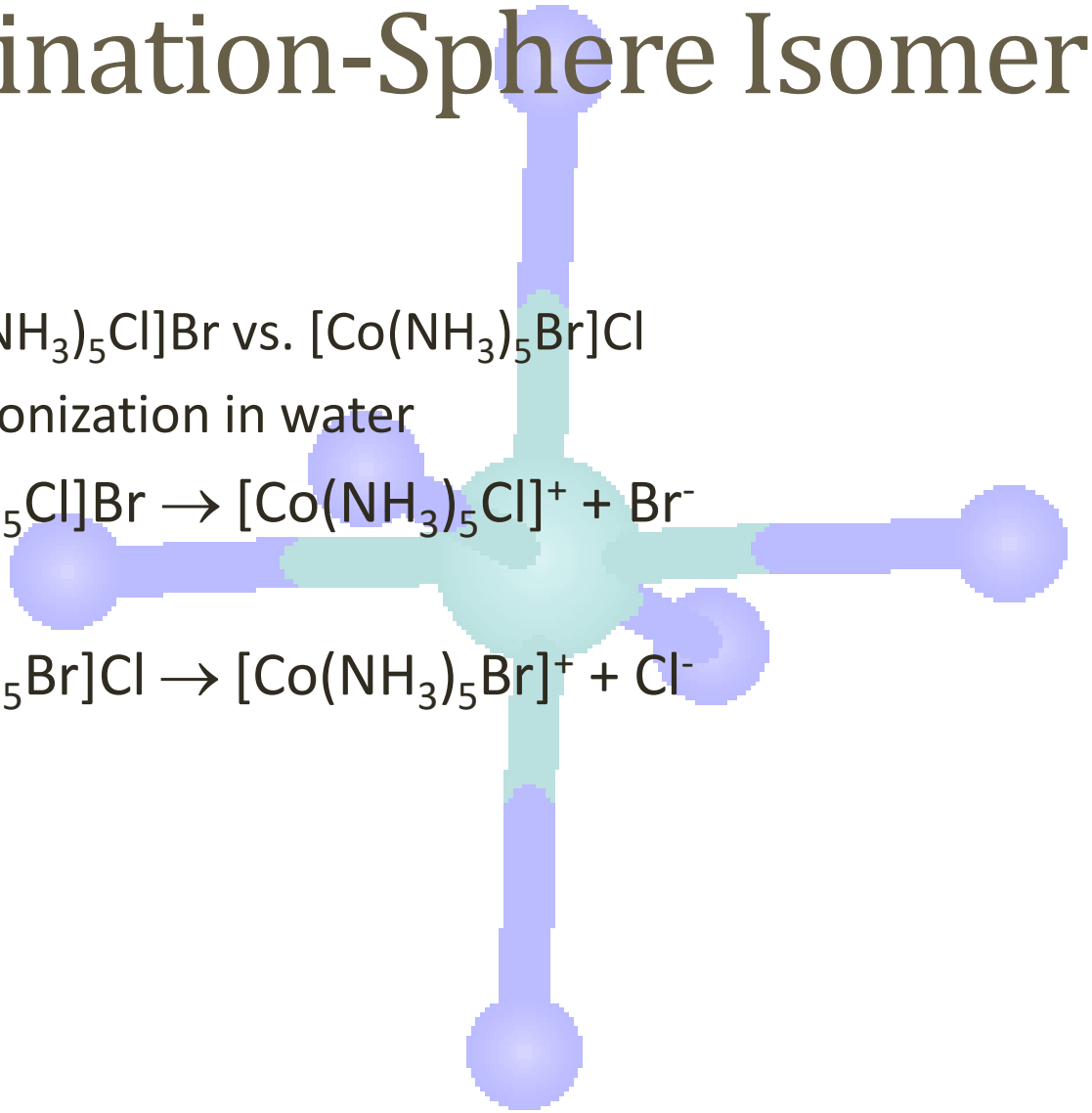
- Example

  $[Co(NH_3)_5Cl]Br$ vs. $[Co(NH_3)_5Br]Cl$

- Consider ionization in water

$[Co(NH_3)_5Cl]Br \rightarrow [Co(NH_3)_5Cl]^+ + Br^-$

$[Co(NH_3)_5Br]Cl \rightarrow [Co(NH_3)_5Br]^+ + Cl^-$

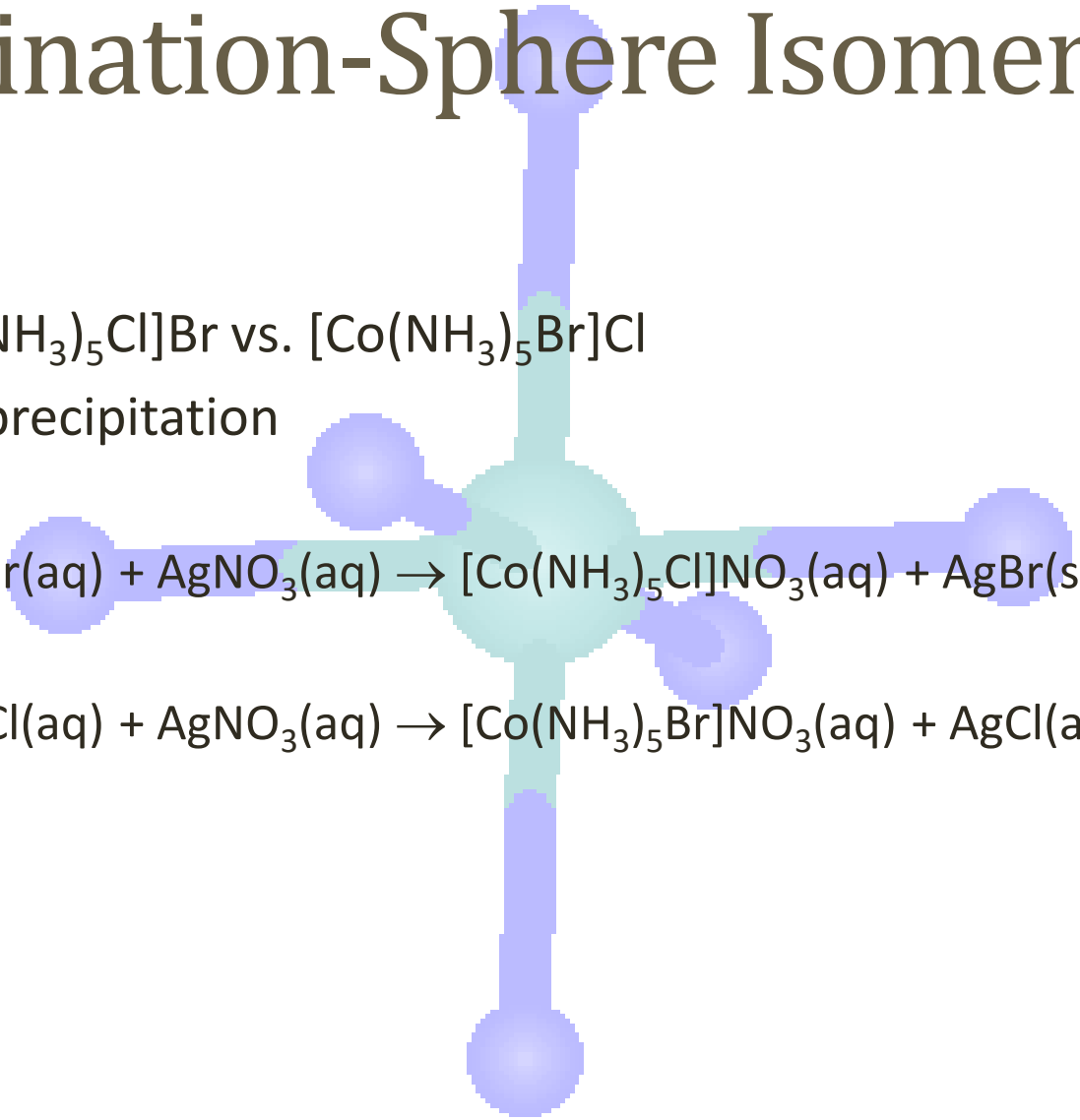


Coordination-Sphere Isomers

- Example

  $[Co(NH_3)_5Cl]Br$ vs. $[Co(NH_3)_5Br]Cl$

- Consider precipitation

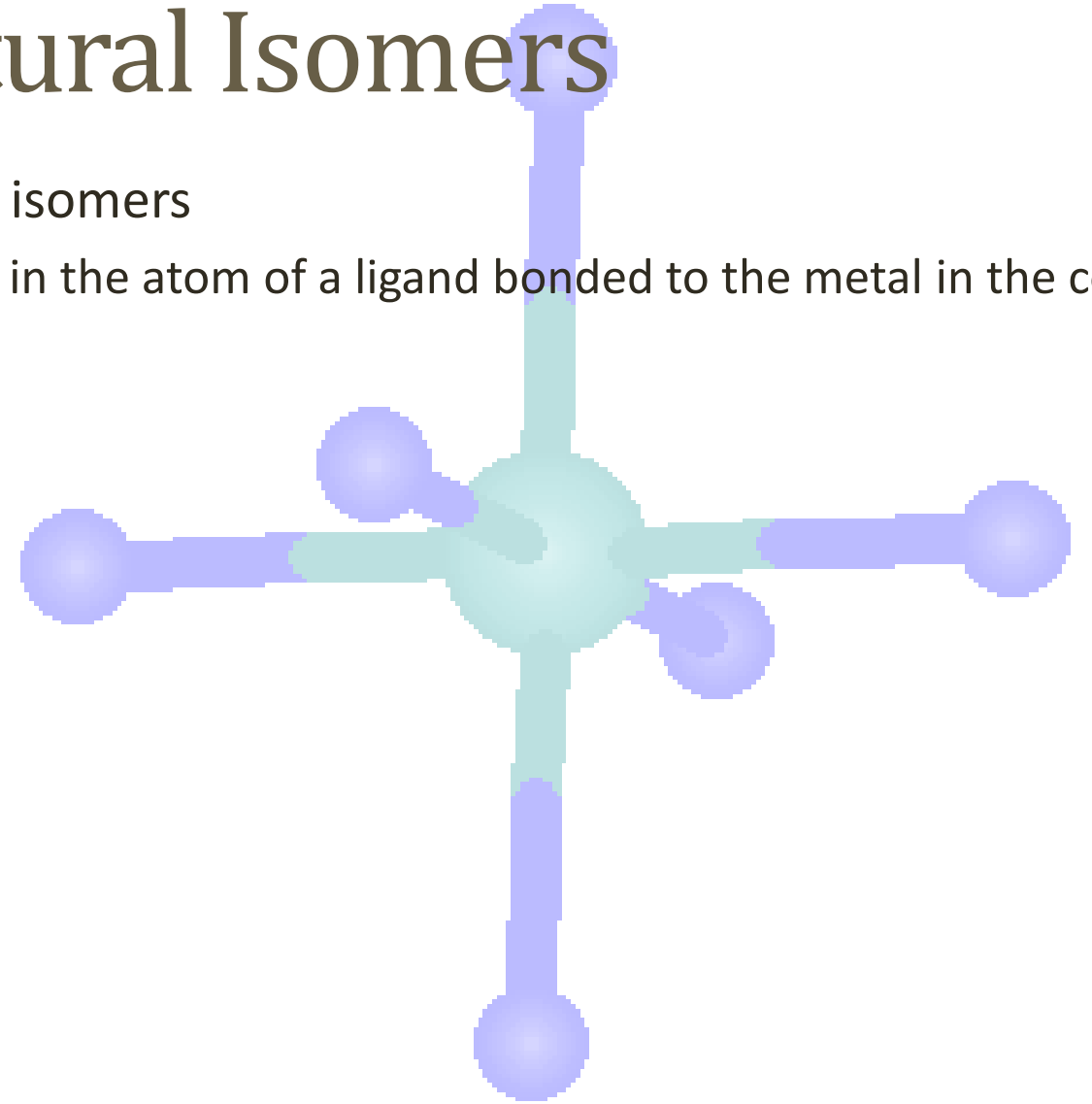


$$[Co(NH_3)_5Cl]Br(aq) + AgNO_3(aq) \rightarrow [Co(NH_3)_5Cl]NO_3(aq) + AgBr(s)$$

$$[Co(NH_3)_5Br]Cl(aq) + AgNO_3(aq) \rightarrow [Co(NH_3)_5Br]NO_3(aq) + AgCl(aq)$$

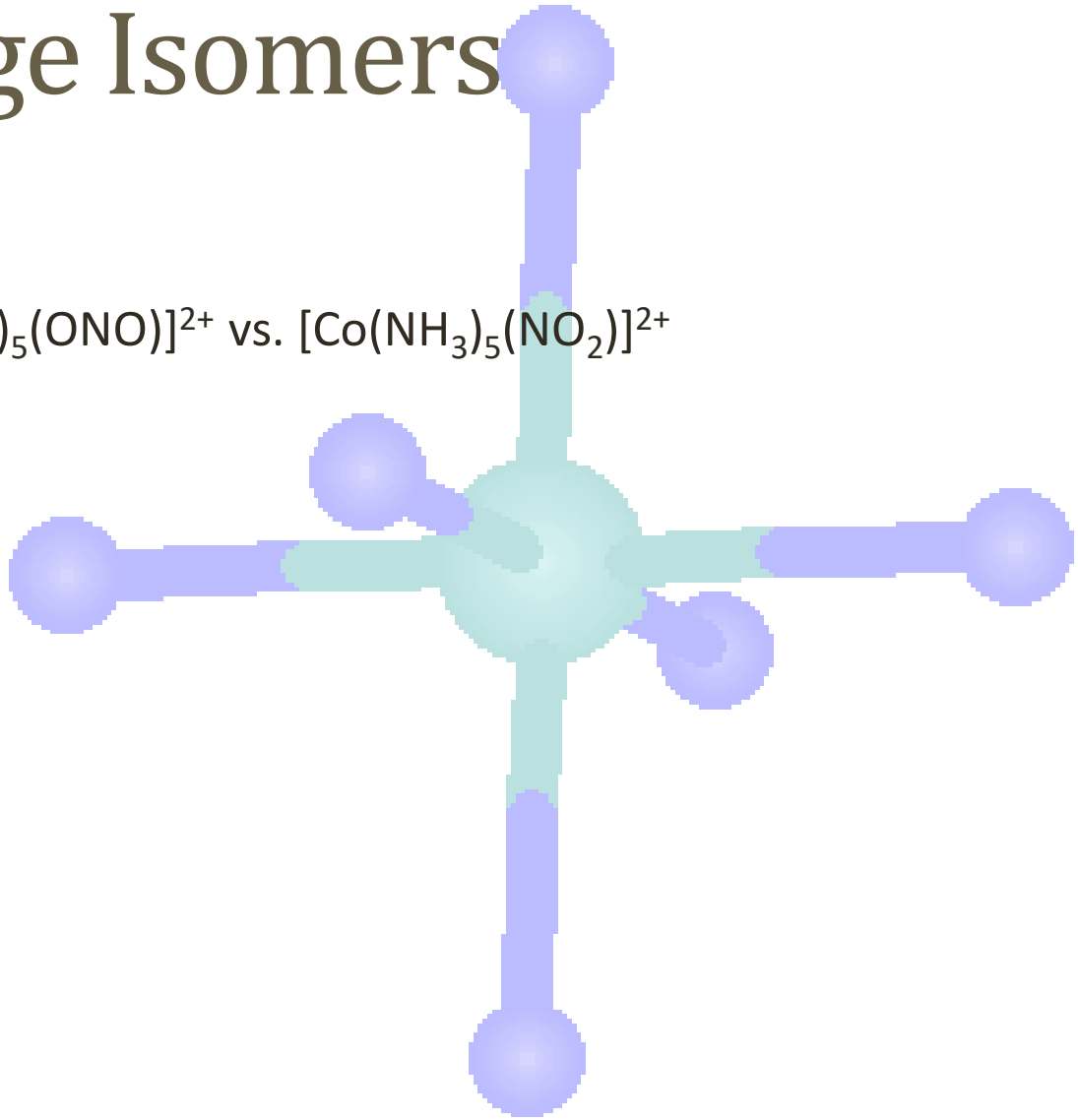
Structural Isomers

- Linkage isomers
  - differ in the atom of a ligand bonded to the metal in the complex

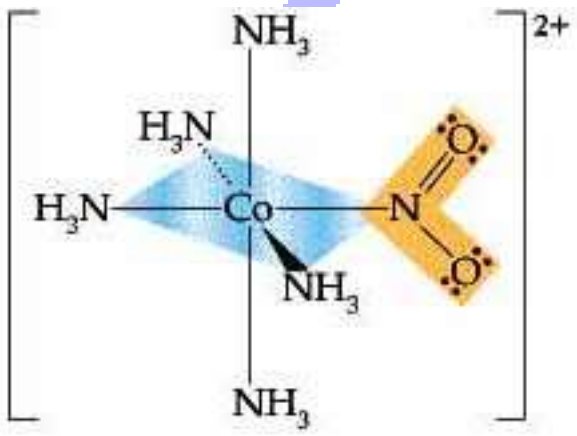


Linkage Isomers

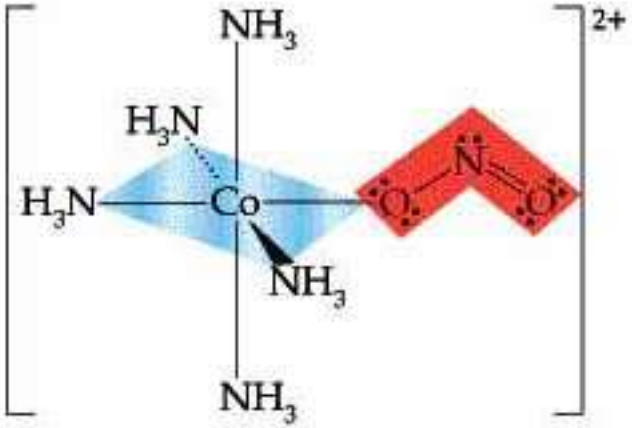
- Example
  - $[Co(NH_3)_5(ONO)]^{2+}$ vs. $[Co(NH_3)_5(NO_2)]^{2+}$



Linkage Isomers



(a)



(b)

Linkage Isomers

- Example
  - $[Co(NH_3)_5(SCN)]^{2+}$ vs. $[Co(NH_3)_5(NCS)]^{2+}$
    - Co-SCN vs. Co-NCS