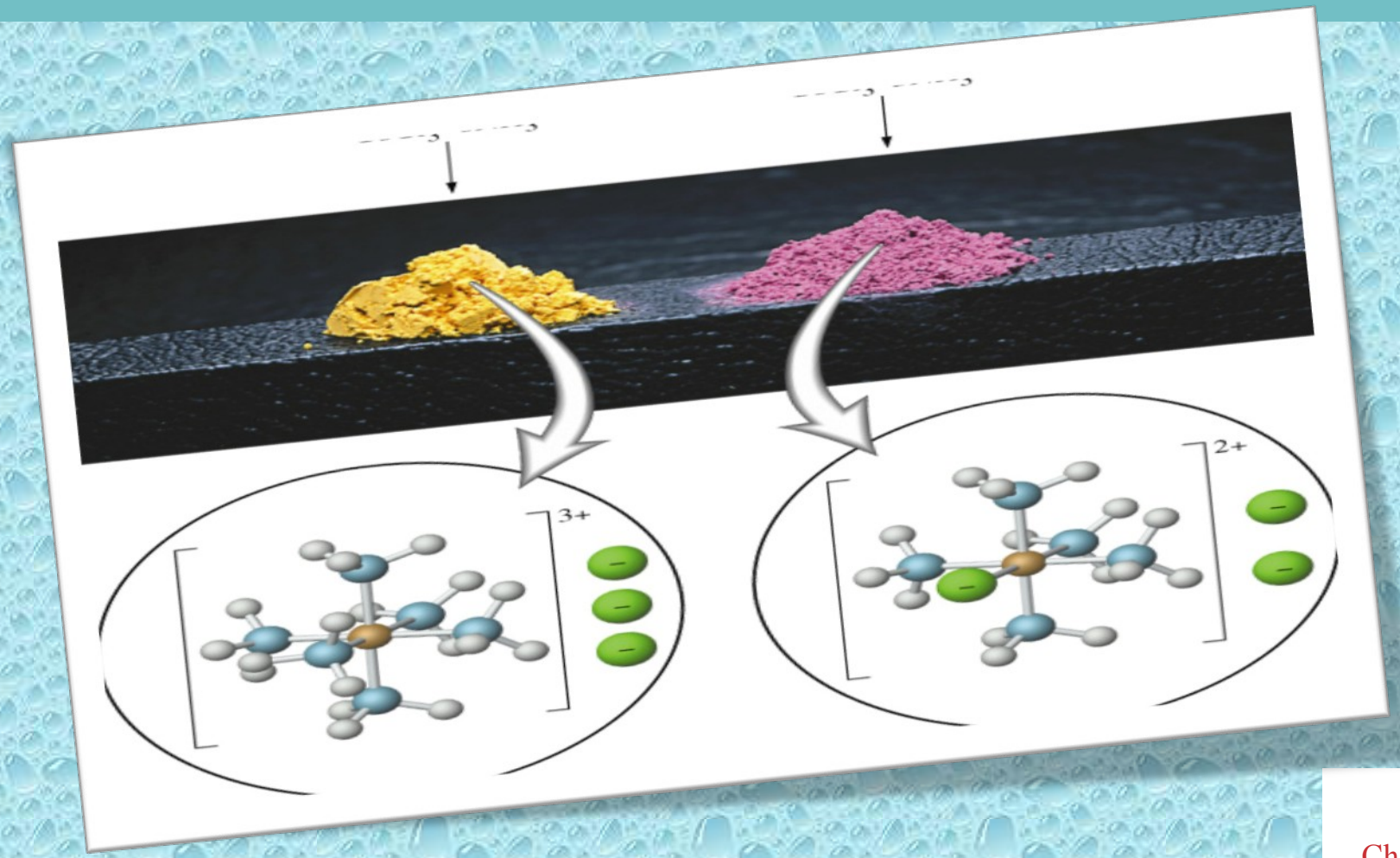
COORDINATION COMPOUNDS



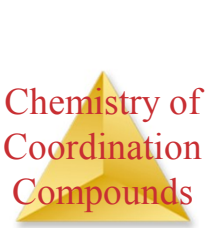
Chemistry of Coordination Compounds

Coordination Compounds

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\ NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\ NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\ NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\ NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

- Many coordination compounds are brightly colored.
- Different coordination compounds from the same metal and ligands can give quite different numbers of ions when they dissolve.



Werner's Theory

Werner proposed putting all molecules and ions within the sphere in brackets and those "free" anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

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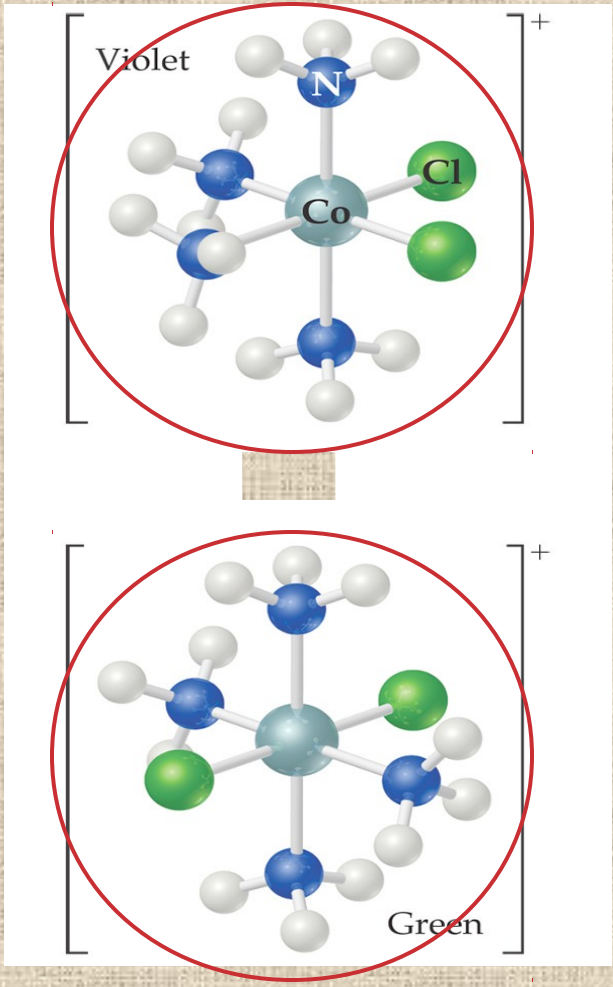
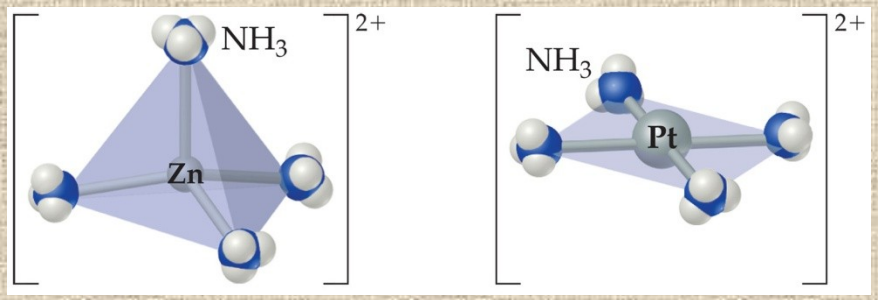
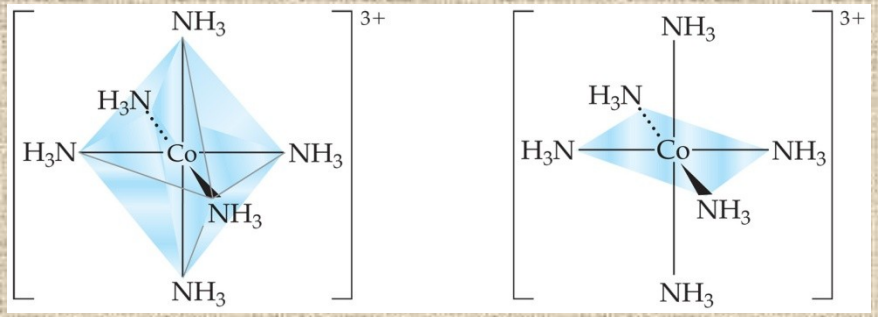
Werner's Theory



- This approach correctly predicts there would be two forms of $CoCl_3 \cdot 4\ NH_3$.
  - The formula would be written $[Co(NH_3)_4Cl_2]Cl$.
  - One of the two forms has the two chlorines next to each other.
  - The other has the chlorines opposite each other.

Coordination Number





- The most commonly encountered numbers are 4 and 6.
- Some metals, such as chromium(III) and cobalt(III), consistently have the same coordination number (6 in the case of these two metals).

Geometries

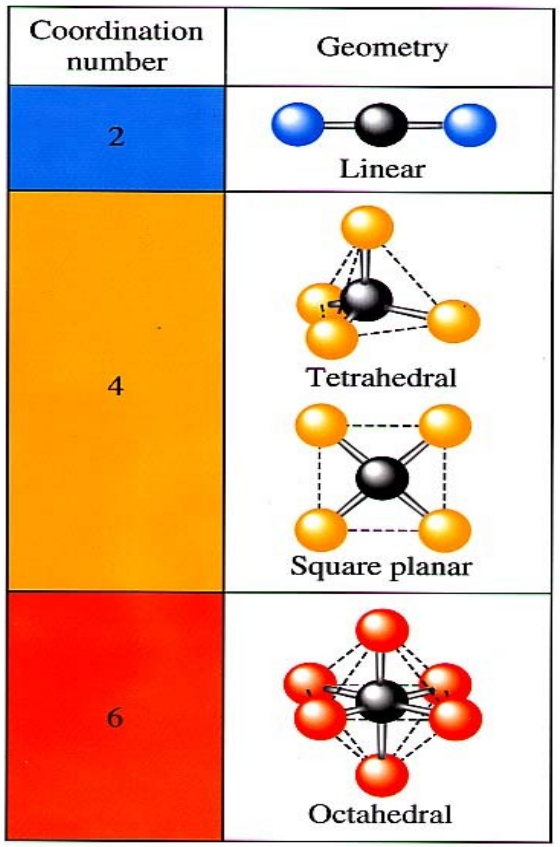


Figure 20.6
Various coordination geometries

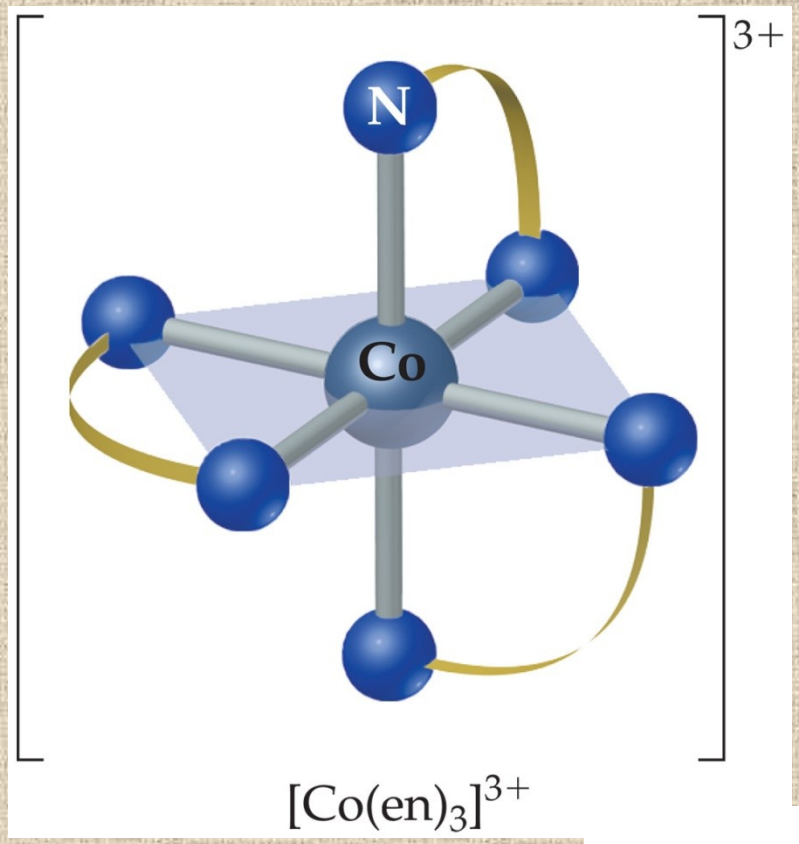
Steven S. Zumdahl, *Chemistry*, Third Edition, © 1993 by D. C. Heath and Company

- Shape of various coordination compounds depends upon the number of ligands around central atom.

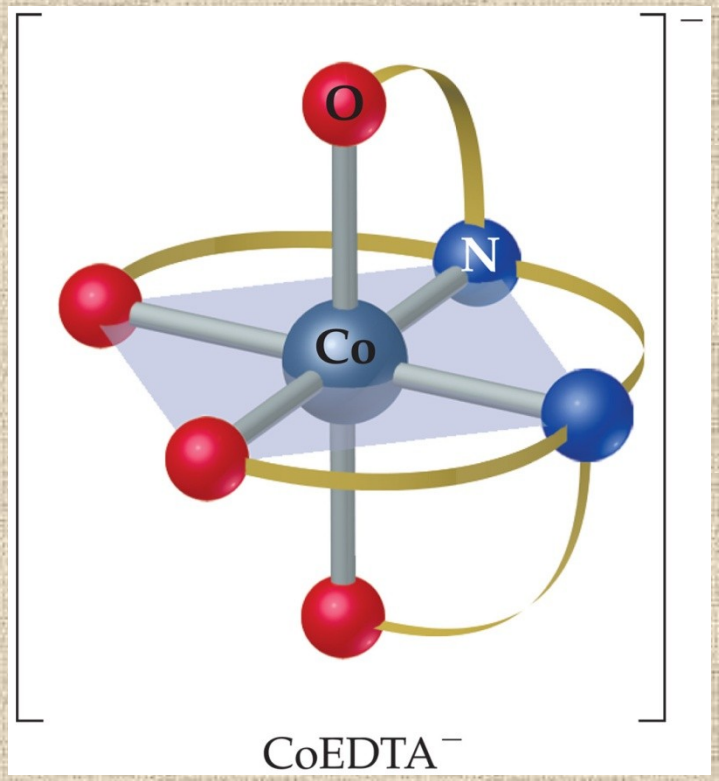
Chemistry of Coordination Compounds

Denticity of Ligands

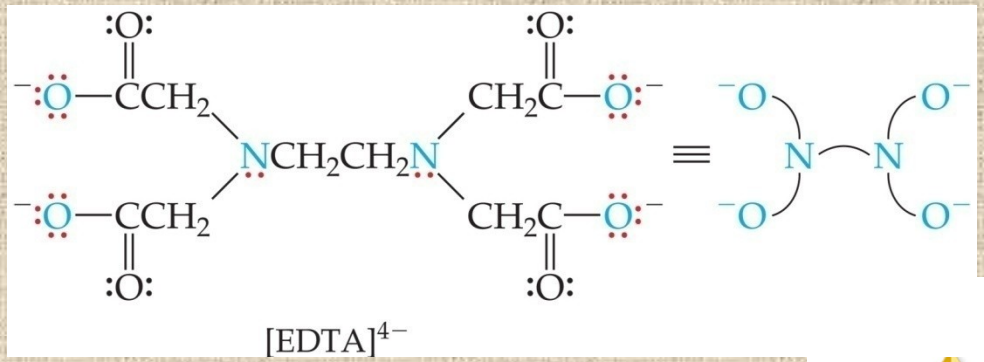
- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylene diamine , ($NH_2CH_2CH_2NH_2$) represented here as en, each N is a donor atom.
- Therefore, en is called bidentate.



Polydentate Ligands



Ethylene diamine tetra acetate, shortly abbreviated as EDTA, has six donor atoms.



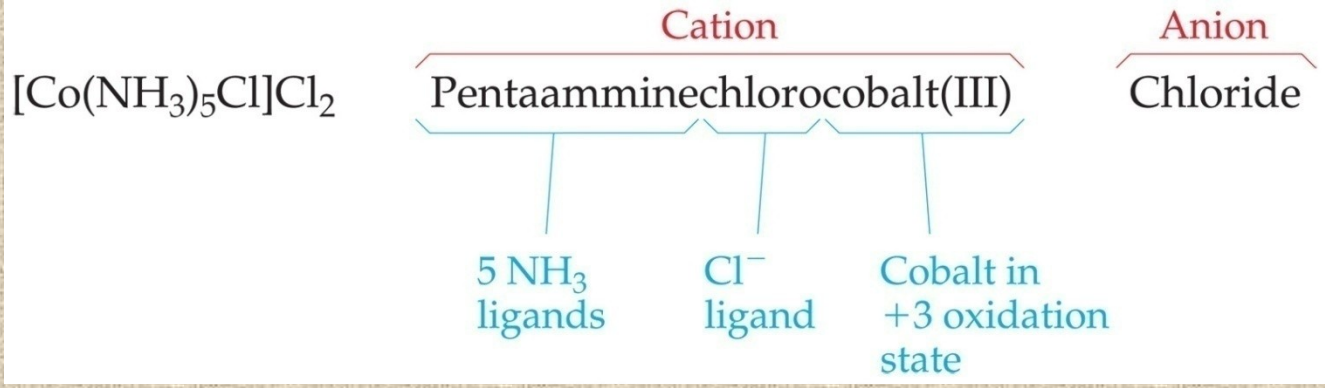
Nomenclature of Coordination Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxo	Pyridine, C_5H_5N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

- The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.
- Some common ligands and their names are listed above.

Nomenclature of Coordination Compounds

- As is the case with ionic compounds, the name of the cation appears first; the anion is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.



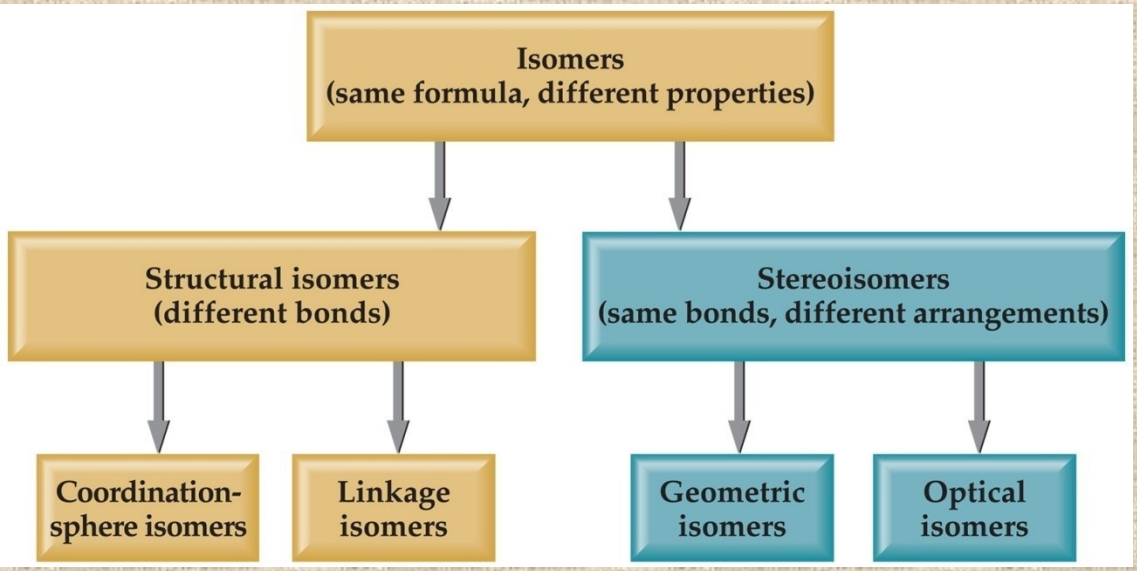
Nomenclature of Coordination Compounds

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like *bis*-, *tris*-, etc., are used.for eg.

$[Co(NH_2CH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as :

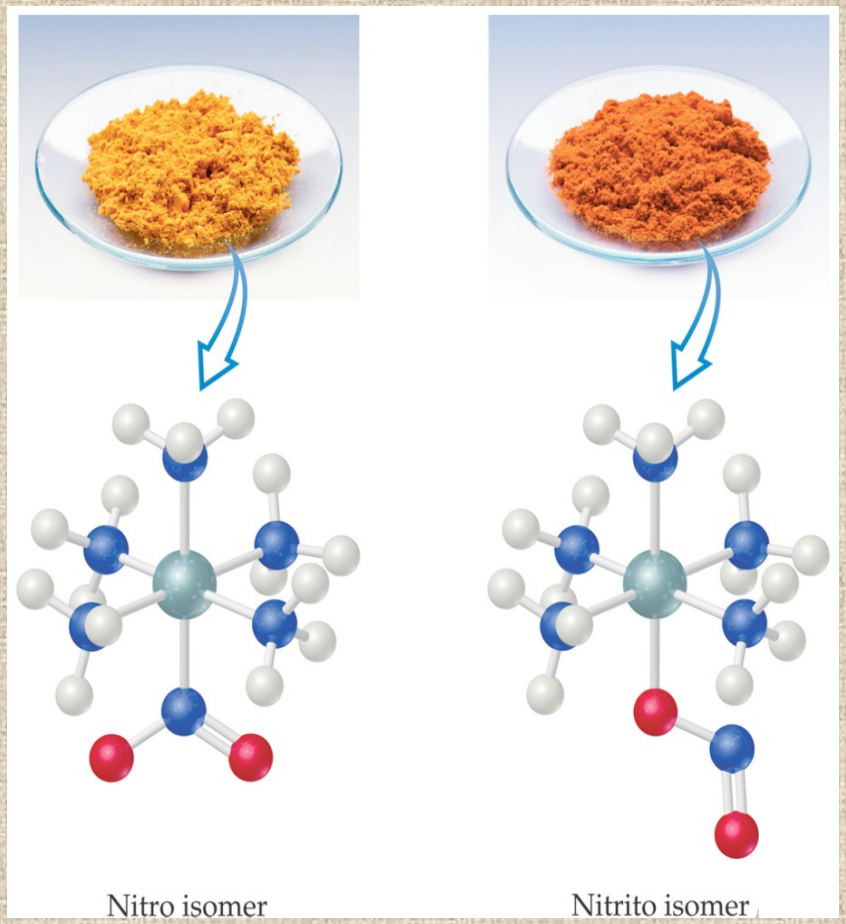
Tris(ethane-1,2-diammine)cobalt(III)sulphate

Isomers



Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

Structural Isomers

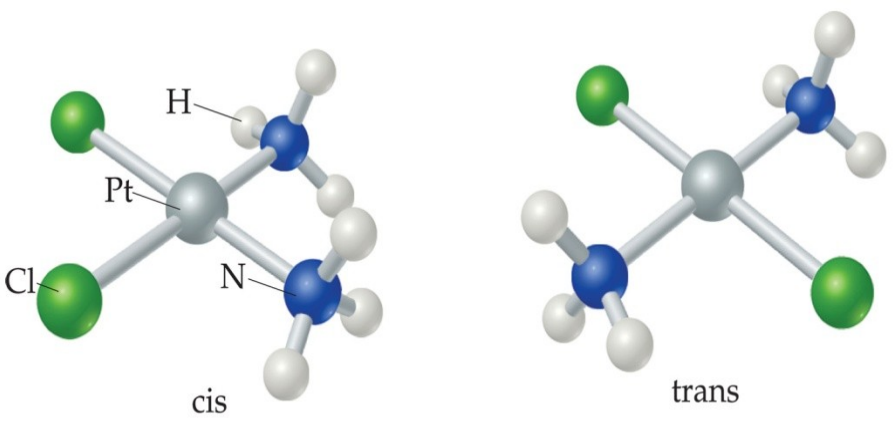


If a ligand (like the NO_2 group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.

Structural Isomers

- Some isomers differ in what ligands are bonded to the metal and what is outside the coordination sphere; these are coordination-sphere isomers.
- Three isomers of $CrCl_3(H_2O)_6$ are
  - The violet $[Cr(H_2O)_6]Cl_3$,
  - The green $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and
  - The (also) green $[Cr(H_2O)_4Cl_2]Cl \cdot 2\ H_2O$.

Stereoisomers



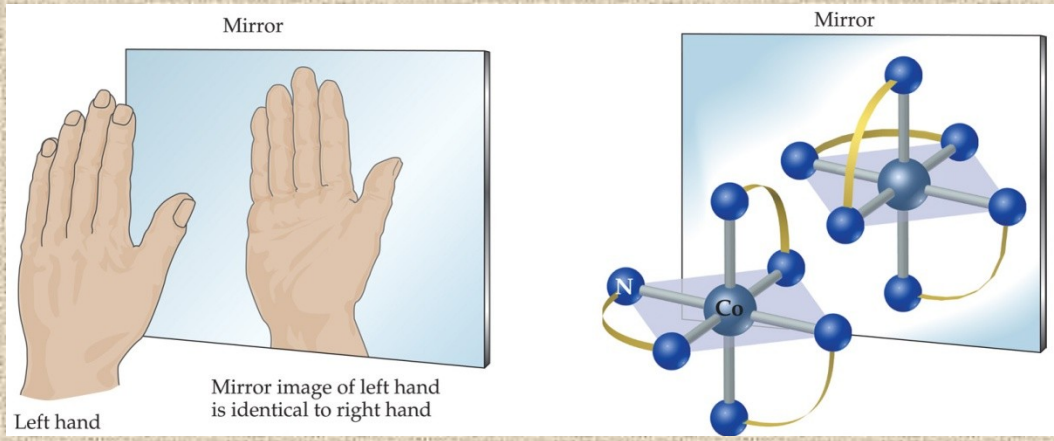
GEOMETRIC ISOMERS

- With these geometric isomers, two chlorines and two NH_3 groups are bonded to the platinum metal, but are clearly different.

➢ *cis*-Isomers have like groups on the same side.

➢ *trans*-Isomers have like groups on opposite sides.

Stereoisomers



- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

Valence bond theory

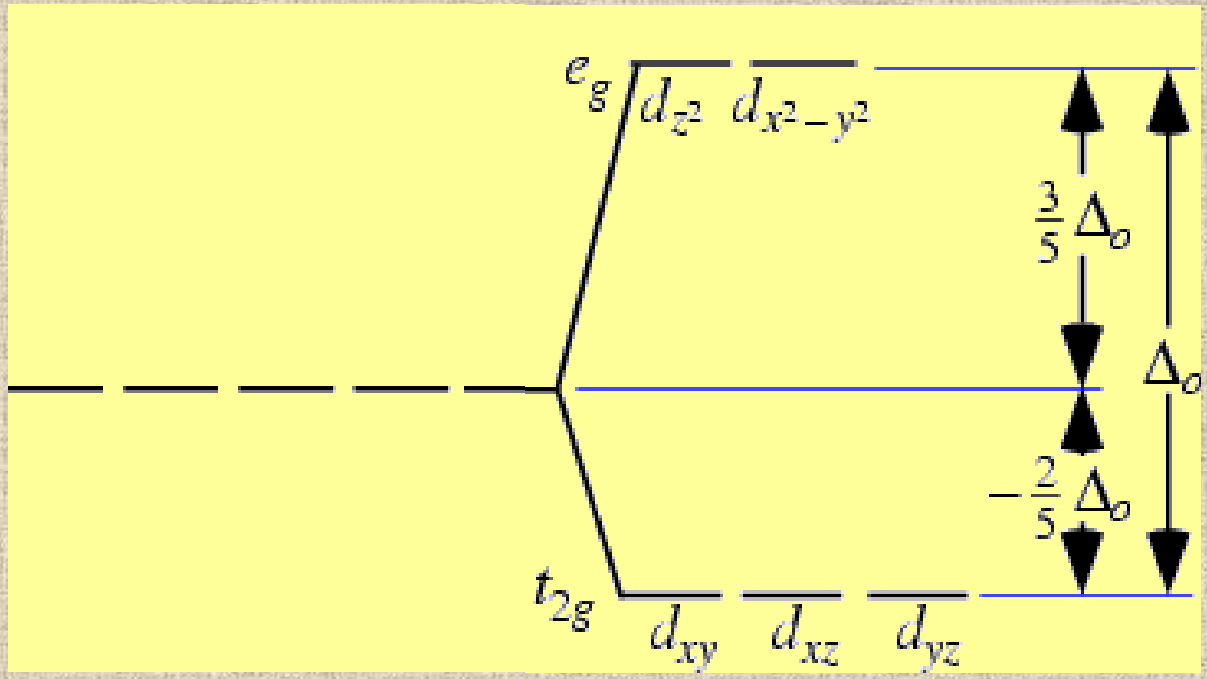
Coordination number	Type of hybridisation	Structure
4	sp^3	tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	$sp^3 d^2$ (nd orbitals are involved – outer orbitals complex)	Octahedral
6	d^2sp^3((n-1) d orbitals are involved –inner orbital)	octahedral

- According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, and square planar. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding

Crystal Field Theory

- Created to explain why transition metal ions in complexes (having unfilled d-shells) are not necessarily *paramagnetic*.

- With coordination bonding, valence d-orbitals are not truly degenerate. Instead, they "split".
  - Some are lower in energy (more stable) and some higher.

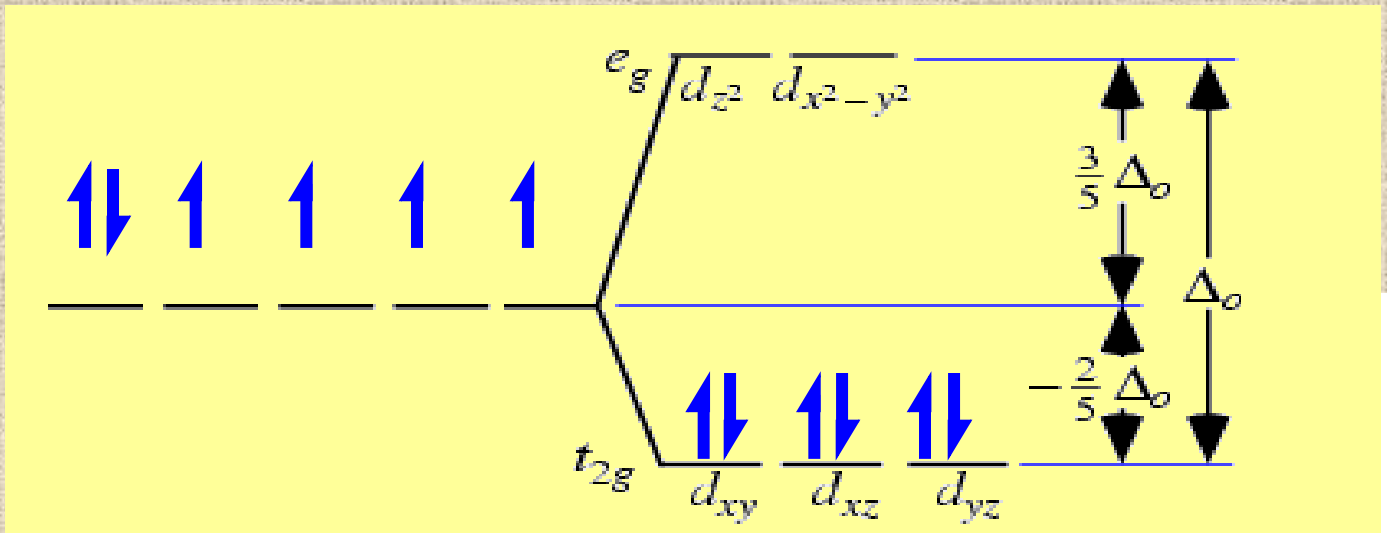


Chemistry of Coordination Compounds

Crystal field theory

- The gap between the higher and lower energy levels is called the crystal-field splitting energy, which varies with each ligand, yielding different E, (different λ, different colors).
- e- in an "unfilled" d-shell can actually be all paired (i.e., diamagnetic).

  Ex: Co^{3+} (has 6 d e-)



Chemistry of Coordination Compounds

Applications of coordination compounds

Coordination compounds are used for many applications :

- Extraction processes of gold and silver.
- Used as catalysts in many industrial processes.
- Hardness of water (EDTA).
- Purifications of metals.
- Chelate therapy (removal of toxic proportion of metals in the body).
- EDTA is used in treatment of lead poisoning.
- Platinum compounds inhibits the growth of tumors.

THANK YOU....