Nomenclature of Coordination Compounds

Coordination compounds are named according to the rules suggested by International Union of Pure and Applied Chemistry, IUPAC (1976). These rules are given blow:

1- The positive ion (cation) comes first, followed by the negative ion (anion). This is also the common order for simple salts.

diamminesilver(I)chloride,$[Ag(NH_3)_2]Cl$
potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$

2- The inner coordination sphere is enclosed in square brackets in the formula. Within the coordination sphere, the ligands are named before the metal, but in formulas the metal ion is written first.

tetraamminecopper(II)sulfate,$[Cu(NH_3)_4]SO_4$

hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$

3- The number of ligands of one kind is given by the following prefixes. If the ligand name includes these prefixes or is complicated, it is set of in parentheses and the second set of prefixes is used.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	hiptakis
8	octa	octakis
9	nona	nonakis
10	deca	decakis

dichlorobis(ethylenediamie)cobalt(III), $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$
tris(bipyridine)iron(II), $[Fe(NH_4C_5\text{-}C_5NH_4)_3]^{2+}$

4- Ligands are named in alphabetical order (according to the name of the ligand, not the prefix).
tetraamminedichlorocobalt(III), $[Co(NH_3)_4Cl_2]^+$
amminebromochloromethylamineplatinum(II), $[Pt(NH_3)BrCl(CH_3NH_2)]$

5- Anionic ligands are given an o suffix.
chloro, Cl^-
bromo, Br^-
sulfato, SO_4^{2-}

Neutral ligands retain their usual name. Coordinated water is called *aqua* and coordinated ammonia is called *ammine* (the double m distingishes NH_3 from alkyl amines). Methylamine, CH_3NH_2

6- To name the central metal atom, the following two cases arise:

a- If the coordination sphere of the complex compound has **negative charge,** the name of the central metal atom ends in **ate** and the oxidation state of the metal (whether positive, negative or zero) is written in roman numerals (0, I, II, III…. -I, -II, -III etc) in brackets at the end of the name of the metal atom.

Cr……chromate Pd……palladate
Co……cobaltate Re……rhenate
Cu……cuperate Pt …….platinate

$Na_2[CrOF_4]$, sodium tetrafluorooxochromate(IV)
$K_4[Ni(CN)_4]$, potassium tetracyanonickelate(0)
$[Co(CO)_4]^-$, tetracarbonylcobaltate(-I)

For some metals, their Latin names are used :

Fe……ferrate Pb……plumbate

Ag……argentate Au……aurate

Sn……stannate

$K_4[Fe(CN)_6]$ potassium hexacyanoferrate(II)

$Na_3[AgF_4]$ sodium tetrafluoroargentate(I)

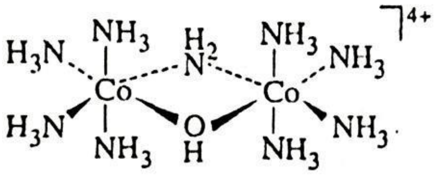
b- If the coordination sphere of the complex compound has positive charge or is neutral (non-ionic), the name of the central metal atom remains as such and the oxidation state of the metal is written in Roman numerals in bracket at the end of the name of the metal.
$[Ag(NH_3)_2]^+$ diamminesilver(I)
$[Ni(CO)_4]^0$ tetracarbonylnickel(0)

7- For complex compounds which are composed of complex cation and complex anion, the cation is named first then followed by the anion name.
$[Cr(NH_3)_6]^{3+}$ $[CoF_6]^{3-}$ hexaamminechromium(III)-hexafluorocobaltate(III) $[Pd(NH_3)_4]^{2+}$ $[PdCl_4]^{2-}$ tetraamminepalladium(II)-tetrachloropalladate(II)

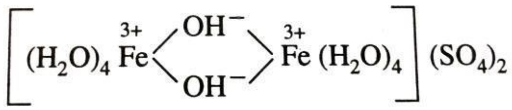
8- There are many ligands which have two or more different donor atoms in their structure. Such ligands can coordinate to the metal atom through any of their donor atoms and hence are given different names corresponding to the nature of donor atoms linked to the metal atom. Such compounds are called linkage isomers.
$[Co(NH_3)_5(NO_2)]Cl_2$ pentaamminenitrocobalt(III) chloride
$[(Co(NH_3)_5(ONO)]Cl_2$ pentaamminenitritocobalt(III) chloride

NO_2^- ion coordinated to the metal atom through the lone pair of electrons on negativelycharged N atom, while ONO^- through the lone pair of electrons on negatively-charged on O atom.
SCN^- ion thiocyanato (through S)
^-NCS ion isothiocyanato (through N)

9- To name bridging ligands between two metal ions, the prefix µ is used before the name of each of the ligands.
$[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]^{4+}$
Octaammine-µ-amido-µ-hydroxodicobalt(III)



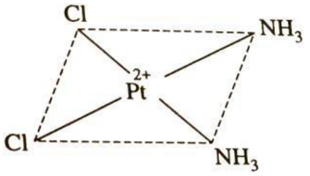
If a complex has two similar bridging ligands, μ-di is used for its name.



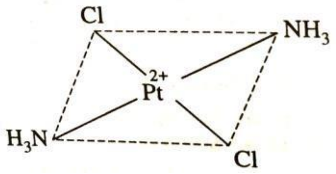
octaaqua-μ-di-hydroxodi-iron(III) sulphate

10- The prefixes cis- and trans- designate adjacent and opposite geometric locations in square planar complexes type $[MA_2B_2]$.

$[PtCl_2(NH_3)_2]$ cis-and trans-diamminedichloroplatinum(II)



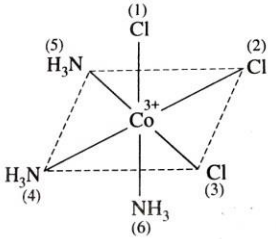
cis



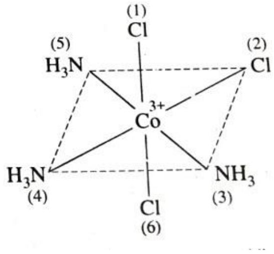
trans

For octahedral complexes of $[MA_3B_3]$ type the prefixes fac (facial) and mer (meridional) are used.

$[Co(NH_3)_3Cl_3]$ fac. And mer. triamminetrichlorocobalt(III)



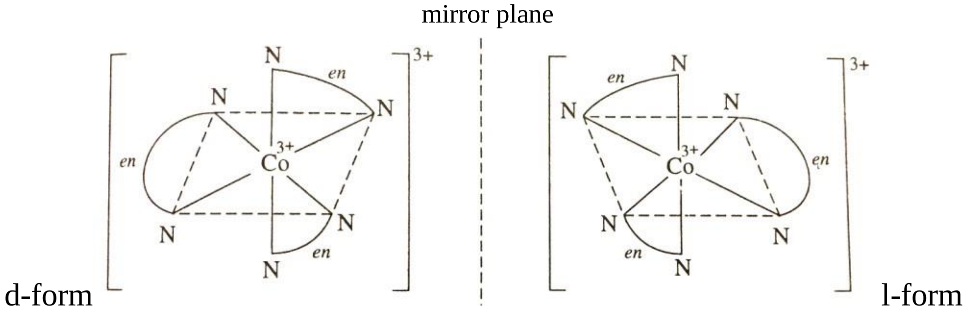
(fac) isomer



(mer) isomer

11- For optical isomers, octahedral complexes of $[M(AA)_3]$ type, the prefixes d (dextro) and l (levo) are used.

$[Co(en)_3]^{3+}$ d and l tris(ethylenediamine)cobalt(III)



Coordination Numbers

Coordination number can be defined as the number of the lone pairs of electrons which are bonded directly with the metal ion.

The overall shape of a coordination compound is the product of several interacting factors. Some factors involved in determining the structures of coordination complexes include the following:

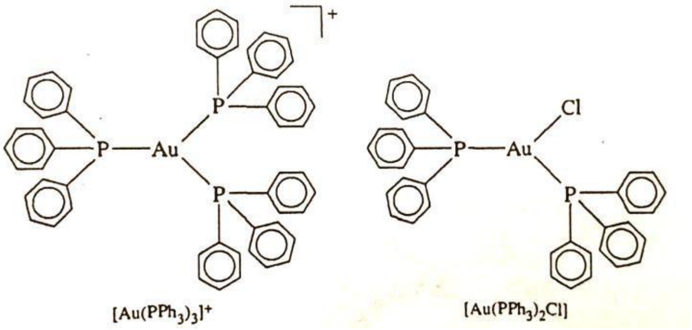
1- The number of bonds. Because bond formation is usually considered exothermic, more bonds should make for a more stable molecule.
2- VSEPR arguments, as used in the simpler cases of the main group elements.
3- Occupancy of d orbitals. Example of how the number of d electrons may affect the geometry (square-planar versus tetrahedral).
4- Steric interference by large ligands crowding each other around the central metal.
5- Crystal packing effects. These include the effects resulting from the sizes of ions and the overall shape of coordination complexes.

Coordination Number 2

Coordination number 2 is rare The best known example is $[Ag(NH_3)_2]^+$, the diamminesilver(I) ion. The silver 1+ ion is d^{10} (a filled, spherical subshell), so the only electrons to be considered in the VSEPR treatment are those forming the bonds with the ammonia ligands, and the structure is linear as expected for two bonding positions. Other examples are also d^{10} and linear $[CuCl_2]^-$, $[Hg(CN)_2]$ and $[Au(CN)_2]^-$.

Coordination Number 3

Coordination number 3 also is more likely with d^{10} ions, with a trigonal-planar structure being the most common. Three-coordinate Au(I) and Cu(I) complexes that are known include $[Au(PPh_3)_3]^+$ and $[Au(PPh_3)_2Cl]$. Most three coordinate complexes seem to have a low coordination number because of ligand crowding.



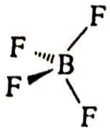
Coordination Number 4

Tetrahedral and square-planar structures are two common structures with four ligands. Crowding around small ions of high positive charge prevents higher coordination numbers for ions such as Mn(VII) and Cr(VI), and large ligands can prevent higher coordination for other ions.

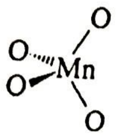
Many d^0 or d^{10} complexes have tetrahedral structures, such as MnO_4^- , CrO_4^{2-}, $[Ni(CO)_4]$, and $[Cu(py)_4]^+$, with a few d^5 , such as $MnCl_4^{2-}$.

Square-planar geometry is also possible for four-coordinate species, with the same geometric requirements imposed by octahedral geometry (both require 90^0 angles between ligands).

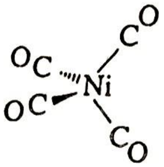
Pd(II) and Pt(II) complexes are square-planer, as are the d^8 complexes $[AgF_4]^-$, $[RhCl(PPh_3)_3]$, $[Ni(CN)_4]^{2-}$ and $[NiCl_2(PMe_3)_2]$.



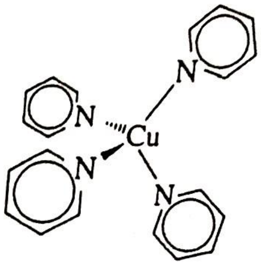
BF_4^-



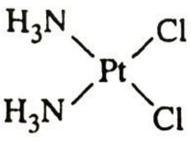
MnO_4^-

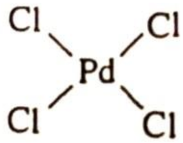


$Ni(CO)_4$



$[Cu(py)_4]^+$

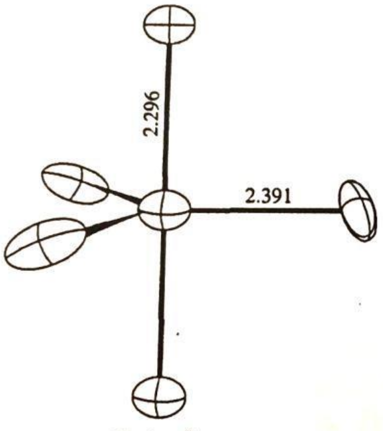




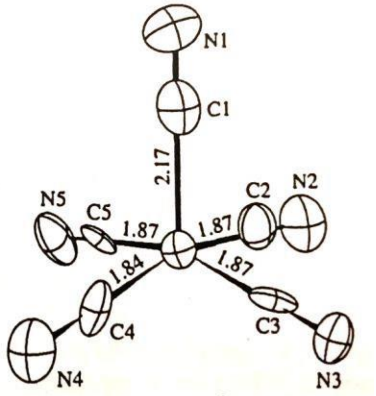
Coordination Number 5

The structures possible for coordination number 5 are the trigonal bipyramid, and the square pyramid. The energy difference between the trigonal bipyramid and the square pyramid is very small, In fact, many molecules with five ligands either have structures between these two or can switch easily from one to the other in fluxional behavior. For example, $Fe(CO)_5$ and PF_5.

$[VO(acac)_2]$ is a square pyramid, with the doubly bonded oxygen in the apical site. There is also evidence that $[Cu(NH_3)_5]^{2+}$ exists as a square pyramidal structure in liquid ammonia.



$[CuCl_5]^{3-}$

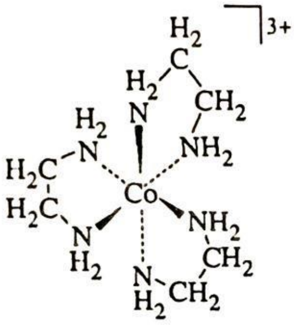


$[Ni(CN)_5]^{3-}$

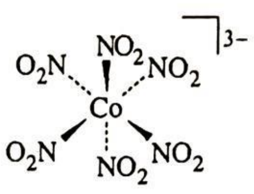
Coordination Number 6

Six is the most common coordination number. The most common structure is octahedral. If a metal ion is large enough to allow six ligands to fit around it and the d electrons are ignored, an octahedral shape results from VSEPR arguments. Such compounds exist for all the transition metals with d^0 to d^{10} configurations.

Examples of octahedral complexes include tris(ethylenediamine)cobalt(III), $[Co(en)_3]^{3+}$ and hexanitritocobaltate(III) $[Co(NO_2)_6]^{3-}$.



$[Co(en)_3]^{3+}$



$[Co(NO_2)_6]^{3-}$

For complexes that are not regular octahedral, several types of distortion are possible. The first is elongation, leaving four short bonds in a square-planar arrangement together with two longer bonds above and below the plane. Second is the reverse , a compression with two short bonds at the top and bottom and four longer bonds in the plane.

Elongated Compressed

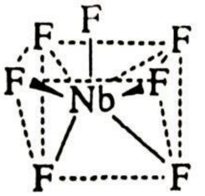
Coordination Number 7

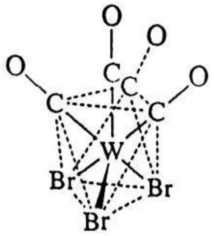
Three structures are possible for seven-coordinate complexes, the pentagonal bipyramid, capped trigonal prism and capped octahedron.

Although seven-coordination is not common, all three shapes are found experimentally, with the differences apparently resulting from different counterions and the steric requirements of the ligands (especially chelating ligands).

Examples include the following:

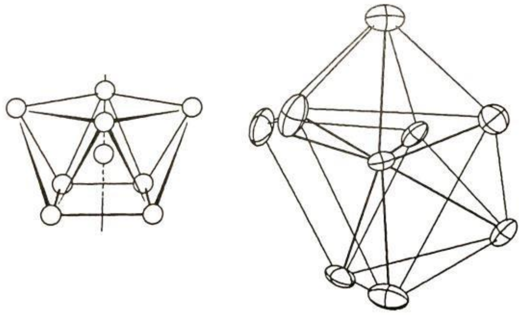
Pentagonal bipyramids; $[NiF_7]^{2-}$ and $[NbF_7]^{2-}$, in both of which the seventh fluoride caps a rectangular face of a trigonal prism; and $[W(CO)_4Br_3]^-$, a mono capped octahedron.





Coordination Number 8

Although the cube has eight-coordinated geometry, it exists only in simple ionic lattices such as CsCl. The square antiprism and dodecahedron are common in transition metal complexes, and there are many eight-coordinate complexes. Because the central ion must be large in order to accommodate eight ligands, eight-coordination is rare among the first row transition metals. Solid state examples include $Na_7Zr_6F_{31}$, which has square antiprisms of ZrF_8 units, and $[Zr(acac)_4]$, a regular dodecahedron. $[AmCl_2(H_2O)_6]^+$ is a trigonal prism of water ligands with chloride caps on the trigonal faces.



ZrF_8

Higher Coordination Numbers

There are few structures known with coordination numbers larger than 8. Discrete ninecoordinate structures are known for complexes such as $[Ln(H_2O)_9]^{3+}$ and for the hydride complexes $[MH_9]^{2-}$ (where M = Tc or Re). These structures (capped square-antiprism) are formed by adding a ligand to each of the rectangular faces of a trigonal prism.