

# Transition Metals and Complex Ion Chemistry

## Definitions

**Complex ion** - a metal ion with Lewis bases attached to it through coordinate covalent bonds.

A **Complex** (or **Coordination compound**) is a compound consisting either of complex ions with other ions of opposite charge or a neutral complex species.

**Ligand** - the Lewis bases attached to the metal ion in a complex. Lewis bases are electron pair donors. They can be ions or neutral molecules. Anions are the most common ionic Lewis bases. Cations only very rarely form ligands with metal ions because the electron pair is usually held in place by the positive charge.

**Coordination number** - the total number of bonds a metal forms with ligands. The most common coordination number is 6, although 4 is somewhat common also. Complex ions with coordination number of 2 through 8 are known.

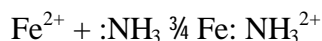
**Monodentate** - ligand that bonds through one of its atoms to the metal ion. (e.g. H<sub>2</sub>O, NH<sub>3</sub>, CO, CN<sup>-</sup>)

**Bidentate** - ligand that bonds through two of its atoms with the metal ion. (e.g., C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, ethylenediamine (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>) represented as "en")

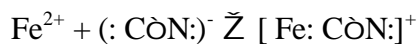
**Polydentate** - ligand that bonds through two or more of its atoms to the metal ion. (e.g. EDTA)

**Chelate** - a complex formed from polydentate ligands.

Bonding in complex ions.



Or



Note that the charge on the complex is the sum of the charges of the ions from which it is formed.

## Nomenclature of Complex ions

The name of the complex ion tells everything there is to know about the ion.

1. When you are naming a salt the name of the cation goes first. (No change from anything here.)
2. The name of the complex - anion, cation, or neutral - consists of 2 parts. The first part identifies the ligand and the second part identifies the metal.

3. The complete name consists of a Greek prefix indicating the number of ligands followed by the name of the ligand. If there is more than one ligand they are named in alphabetical order (ignoring the prefix).

a. anion ligands end in "-o."

ANION NAME	LIGAND NAME
bromide	bromo
cyanide	cyano
oxalate	oxalato,

b. neutral ligands are given the name of the molecule except:

ammonia	ammine
carbon dioxide	carbonyl
water	aqua (older form is "aquo")

c. the prefixes are

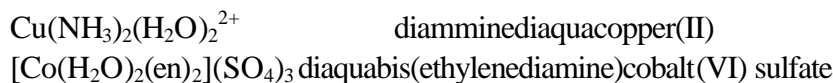
1	mono
2	di
3	tri
4	tetra
5	penta
6	hexa
et cetera	

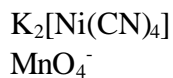
d. when the prefix is part of the name of the compound the number of ligands is denoted by "bis" (2), "tris" (3), "tetrakis" (4). The name of the ligand follows in parenthesis.

4. The complete metal name consists of the name of the metal followed by "-ate" if it is an anion followed by the oxidation state of the metal in Roman numerals in parenthesis. When there is a Latin name of the metal it is used to identify the metal in the anions (Except Hg).

Copper	cuprum	cuprate
Gold	aurum	aurate
Iron	ferrum	ferrate
Lead	plumbum	plumbate
Silver	argentum	argentate
Tin	stannum	stannate.

Name the following





potassium tetracyanonickelate(II)  
tetraoxomanganate(VII)

What data do we use to determine the geometry and bonding of the complex ions?

1. **Isomerism** - these are compounds with the same chemical formula but different arrangements of atoms. Because the atoms are arranged differently, the compounds have different chemical formulas.
2. **Paramagnetism** - indicates the number of unpaired electrons in the compound. This gives information about the bonding in the compound.
3. **Color** - the color absorbed gives information about the electronic structure of the compound.

## Isomerism

**Structural isomerism** - isomers that differ in how the atoms are connected.

**Stereoisomers** - isomers in which the atoms are connected in the same order but have a different arrangement in space.

### Structural isomers

**Ionization isomers** - differ in the anion which is bonded to the metal



**Hydrate isomers** - differ in the placement of water molecules



**Coordination isomers** - differ in the distribution of ligands between metal ions in complex compounds



**Linkage isomers** - differ in the atom of the ligand that is bonded to the metal



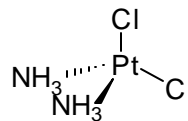
### Stereoisomers

**Geometric isomers** - isomers where the atoms are bonded in the same way but differ because some atoms occupy different relative positions in space.

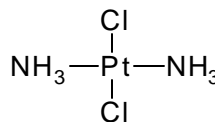
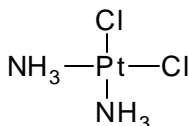
Cisplatin (diamminedichloroplatinum(II)) two compounds are known with this composition. One is orange yellow and is somewhat soluble in water and acts as a cancer-fighting drug. The other is yellow and is much less soluble and doesn't have the cancer fighting ability.

With four ligands there are two possibilities for the structure; tetrahedral and square planar. Which is this compound?

If it were tetrahedral there would be no geometric isomers.

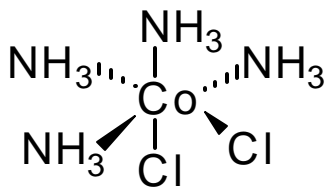
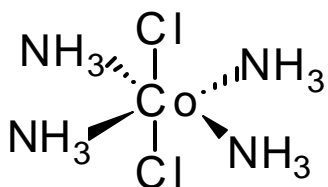


With a square planar geometry there are two geometric isomers:



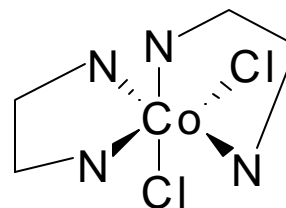
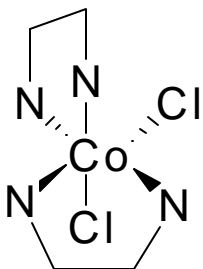
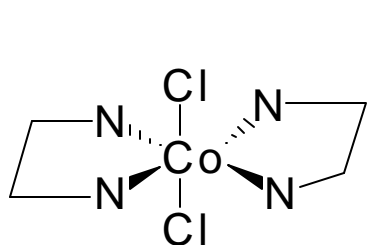
One of these isomers is denoted trans (the one that has the same ligand on opposite sides of the complex). The other is denoted cis. One is soluble. The complex that is polar is soluble.

Six coordinate compounds (with octahedral geometry) are also capable of geometric isomers.



The cis isomer is purple and the trans isomer is green.

Also



The trans isomer is green and the 2 cis isomers are violet.

The 2 cis isomers are known as optical isomers or enantiomers. Enantiomers are isomers that are non-superimposable mirror images of each other. In a symmetrical environment the two isomers have the same physical properties (solubilities, melting points, colors). They can be distinguished by how they rotate plane polarized light. Because of this they are also known as optically active compounds. Is the compound rotates light to the right it is called dextrorotary and is labeled “d”. A compound that rotates light to the left is called levorotary and is labeled “l”. A chemical reaction usually produces a mixture of these two compounds (an exception is biochemical reaction, which produce only one form). The mixture is called racemic. A racemic mixture can be separated or resolved by making a salt with an optically active ion of the opposite charge.

## Valence Bond Theory of Complexes

### Octahedral complexes



all complexes of this ion have six ligands (octahedral geometry) and are paramagnetic indicating 3 unpaired electrons. The electron configuration of this ion is



Let's look at the hexaquaacobalt(III) ion. If all of the water molecules bond to the  $\text{Cr}^{3+}$  ion we will need 6 hybrid orbitals. We can use the 4s and 4p orbitals and either two of the 3d orbitals or 2 of the 4d orbitals. Because the 3d orbitals are lower in energy than the 4d we use those orbitals. This gives a hybridization of  $d^2sp^3$  (the d first indicates that the d orbitals come from the energy level 1 lower than the s and p orbitals).

Now look at the hexammineiron(II) ion. The iron ion has an electron configuration of:



Using the same argument as above we would have a hybridization of  $sp^3d^2$ . But what about a complex like the hexacyanoferrate(II) ion? This is a diamagnetic ion so all of the electrons are paired up. In this case we use the excited state of the iron(II) ion which has the orbital diagram of  $\uparrow \uparrow \uparrow \downarrow \downarrow$ . Now 2 of the 3d orbitals are empty so the hybridization here would be the same as the chromium complex,  $d^2sp^3$ . This indicates that there are two kinds of complexes possible. One in which there is a minimum of pairing of electrons, which is known as a high-spin complex. The other is a low-spin complex, which has more pairing of electrons than in a high-spin complex.

High-spin	weakly bonding ligands.
Low-spin	strongly bonding ligands.

Ions with  $d^1$ ,  $d^2$ , or  $d^3$  configurations form only one spin type of octahedral complex ( $d^2sp^3$ ). Ions with configurations of  $d^8$  and  $d^9$  are similar ( $sp^3d^2$ ).

### Tetrahedral and square planar complexes

The coordination number 4 is almost as common as 6 (octahedral complexes). Here the geometries are either tetrahedral or square planar.

Tetrahedral	$sp^3$
Square planar	$dsp^2$

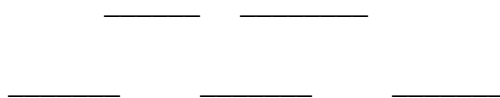
$Ni(CN)_4^-$  is square planar (evidence is from the fact that it is diamagnetic).  $Ni^{2+}$  has an electron configuration of  $[Ar] 3d^8$  and its orbital diagram is (in this case it is the excited state of  $Ni^{2+}$ )  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$  so the 3d, 4s, and 3-4p orbitals are available for hybridization, which results in the hybridization  $dsp^2$ .

## CRYSTAL FIELD THEORY

VB theory explains the bonding and magnetism but it doesn't explain why the complexes are largely colored. Crystal field theory takes care of this. The theory looks at the effect of the ligands on the d orbitals of the ion. (Review d orbitals).

Octahedral field on the orbitals

The ligands approach the metal ion along the +/- x, y, and z axes. The ligands are represented by negative point charges if they are anions and partial negative point charges if they are neutral. The electrons in the d orbitals are going to be repelled by the negative charges, which alter the energy levels of the orbital. However, the amount by which it is altered depends on whether the charge approaches the orbital head on (more repulsion) or at an angle (less repulsion). The  $d_{z^2}$  and the  $d_{x^2-y^2}$  orbitals point along the Cartesian axes. The others ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) do not point along the Cartesian axes. The first two are repelled more, which raises their energy level. The last three are also repelled but less which raises their energy level also but not as much.



The separation between the two levels is given the symbol,  $\Delta$ , and is called the crystal field splitting.

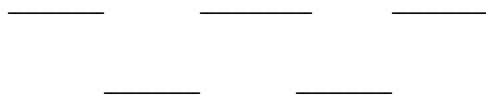
Back to high-spin and low-spin complexes. The difference between the two is related to  $\Delta$  and another energy, the pairing energy, P. If the pairing energy is greater than  $\Delta$ , the electrons are not going to pair up. This leads to a high-spin complex. If  $P < \Delta$ , we have a situation where it is more likely for electrons to pair up than to go into higher energy levels and we have a low-spin complex.

Which ligands lead to which spin type?? Those that bond strongly will give a larger  $\Delta$  and lead to a low-spin complex. Those that bond weakly will give a smaller  $\Delta$  and a high-spin complex. The spectrochemical series orders the ligands according to the  $\Delta$  they generate.

weakly bonding	strongly bonding
$I < Br < Cl < F < OH^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$	
increasing $\Delta$	$\uparrow$

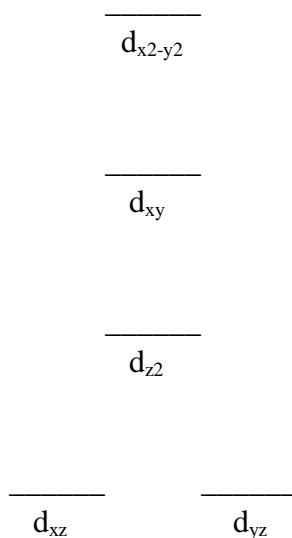
Tetrahedral complexes.

In a tetrahedral complex we have an energy level diagram inverted from that of the octahedral complexes.



However,  $\Delta$  is smaller here than in the octahedral complexes. This means that only high-spin complexes are observed ( $P > A$ ).

The square planar energy level diagram is



Since the  $\Delta$  here is much larger overall, we have only low-spin complexes ( $P < \Delta$ ).

Visible spectra of complexes

Related to  $\Delta$ :  $\Delta = h\nu = hc/\lambda$

Unlike atomic spectra the complex ions absorb in broader bands. This is due to the changes in the nuclear motion that result from the changes in the electron occupation of the energy levels.

If  $\Delta$  is a large value, the wavelengths that are absorbed are the shorter wavelength (blues and violets). This means that we would see the complimentary color (reds, yellows, and oranges).

If  $\Delta$  is a small value, the reds and yellows are absorbed. We would see the blues and violets.