1. **Substantiation for the subject**. Coordination compounds (complexes) are widely present in the minerals, plants and animals and play many important functions. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The common examples are: hemoglobin which is coordination compound of iron, chlorophyll which is coordination compound of magnesium, etc.

2. **The purpose of the subject**:

- general: to explain the well-known physical and chemical properties of Lewis bases(Ligands), Lewis acids(transition elements and their cations) and the relationship in the structure of complexes.

a) **to know:** the role of transition elements and their metal complexes in the industry, pharmaceutical drugs and other applications.

b) **to be able to**: determine the type of the complex compound; name the complex compound; write the equation of the complex ion dissociation; write the equation of the constant of instability of the complex ion; determine oxidation state of the complexing agent (central ion), the charge of complex ion, coordination number.

3. **Tasks for self-work**:

- List of questions to be studied:

1. Complexes: general aspects, fundamentals of the Alfred Werner's coordination theory.
2. Structure of complex compounds.
3. Bonding in Coordination Compounds.
4. Spatial Structure and Isomerism in Coordination Compounds.
5. Nomenclature of Coordination Compounds (given by IUPAC).

Complexes: general aspects, fundamentals

Complexes (coordination compounds, complex compounds) are a special class of compounds in which the central metal atom or ion is surrounded by oppositely charged ions or neutral molecules more than its normal valence. These compounds are widely present in the minerals, plants and animals and play many important functions. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The common examples are: hemoglobin which is coordination compound of iron, vitamin B_{12} which is coordination compound of cobalt, chlorophyll which is coordination compound of magnesium, etc.

The properties and structure of complex compounds are explained most successfully by the ***coordination theory*** proposed by Alfred Werner (1866–1919), a Swiss chemist, Nobel Prize winner, in 1893. According to the coordination theory, one of the ions in a molecule of any complex compound, generally a positively charged one occupies a central position and is called a ***complexing agent*** or ***central ion.*** Around it in direct proximity are arranged, or as we say, coordinated, a certain number of oppositely charged ions or electrically neutral molecules called ***ligands***. They form the ***inner coordination sphere*** of the compound. The remaining ions not accommodated in the inner sphere are farther from the central ion and form the ***outer coordination sphere***. The number of ligands surrounding the central ion is called the ***coordination number***.

The inner sphere of a complex retains its stability when dissolved. Its boundaries are shown in formulas by brackets. The ions in the outer sphere are readily detached in solutions. For this reason, the ions in the inner sphere are said to have a ***non-ionizable*** bond, and those in the outer sphere, an ***ionizable*** one. Let's consider the structure of complex compound in detail.

Transition Elements

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electro negativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

Physical Properties

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block) such as Calcium.

Transition elements:

Transition metals, are located in groups 3 through 11. They are called transition metals because they transition between the highly reactive s block metals and the much less reactive metals of group 12 and the p block. Horizontal trends in key atomic properties of the Period 4 elements Coordination Chemistry of Transition Metals and their main physical properties are below:

1-have large charge/radius ratio;

2-are hard and have high densities;

3-have high melting and boiling points;

4-form compounds which are often paramagnetic;like complexes of Mn^{2+} and Ni^{2+}

5-show variable oxidation states like Cr(III),Cr(VI),Cr(V) and Fe(II),Fe(III),Fe(VI).

6-form coloured ions and compounds;

7-form compounds with profound catalytic activity;

8-form stable complexes like metal chelates :$[Co(bipy)_3]^{3+}$ and $K_3[Fe(C_2O_4)_3]$.

Some notes about increasing and decreasing the periodic properties of T.E:

1-Atomic size decreases overall across a period. The d electrons fill inner orbitals , so they shield outer electrons from the increasing nuclear charge very efficiently and the outer 4s electrons are not pulled closer.

2-Electronegativity usually increases across a period but the transition metals exhibit a relatively small change in electro negativity.

3-IE1 increase relatively little because the inner 3d electrons shield efficiently and the outer 4s electron experiences only a slightly higher effective nuclear charge.

4-Ionic bonding is more prevalent for the lower oxidation states and covalent bonding is more prevalent for the higher oxidation states. At room temperature TiCl2 is an ionic solid and TiCl4 is a molecular liquid

5-In high oxidation states atoms have higher charge densities ⇒ polarize electron clouds of non-metals ⇒ covalent bonding

6-The oxides become less basic as the oxidation state increases Cr_2O_3 is a weak base in water and CrO2 is a more acidic.

7-Most main group ionic compounds are colorless because the metal ion has a filled outer level; On the contrary,

8-Electrons in particular filled d-sublevels can absorb visible wavelengths and move to slightly higher energy d-orbitals. Therefore, many transition metal compounds have striking colors. Exceptions occur when d orbitals are empty or filled. Zn+2: [Ar] 3d10 and Sc+3 or Ti+4 [Ar] 3d0.

The following table shows some of the physical properties of transition elements:

Element	roup	**density /g cm^{-3}**	**. p.** **/ °C**	**.p.** **/ °C**	**adius** **/ pm**	free atom configuration	**ionization energy** **/ kJ mol^{-1}**	Uses
Sc		2.99	541	831	64	[Ar] $3d^{1}4s^{2}$	631	
Ti		4.50	660	287	47	[Ar]$3d^{2}4s^{2}$	658	-engines/aircraft industry-density is 60% of iron
V		5.96	890	380	35	[Ar]$3d^{3}4s^{2}$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr		7.20	857	670	29	[Ar]$3d^{5}4s^{1}$	653	-alloys eg with C steel, the most significant use
Mn		7.20	244	962	37	[Ar]$3d^{5}4s^{2}$	717	-alloys eg with Cu
Fe		7.86	535	750	26	[Ar]$3d^{6}4s^{2}$	759	-alloys eg with C steel, the most significant use
Co		8.90	495	870	25	[Ar]$3d^{7}4s^{2}$	758	-alloys eg with Cr and W for hardened drill bits
Ni	0	8.90	455	730	25	[Ar]$3d^{8}4s^{2}$	737	-alloys Fe/Ni armour plating, resists corrosion
Cu	1	8.92	083	567	28	[Ar]$3d^{10}4s^{1}$	746	-high electrical conductivity (2nd to Ag), wiring

Zn	2	7 .14	20	07	37	[Ar]3d^{10}4s^{2}	906	

Densities and metallic radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.

Melting and boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.

Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by about 580 kJ mol^{-1}.

Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration [Ar] $3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes $[Ar]3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	°/V
$Mn^{2+}(aq.)/Mn(s)$	-1.18
$H^+(aq.)/H_2(g)$	.00

This shows that elemental Mn is a stronger reductant than dihydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

Structure of complex compounds

Complex ion

As it was mentioned above a coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules. For example, $[Co(NH_3)_3Cl_3]$ is a coordination compound in which the cobalt (+3) ion is surrounded by three ammonia molecules and three negatively charged chloride ions. Other examples are $[Ni(NH_3)_6]Cl_2$, $K[Ag(CN)_2]$, $[Cu(NH_3)_4]SO_4$, etc. As you can see, a coordination compound contains a complex ion. For example, $[Ni(NH_3)_6]Cl_2$ contains complex ion $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]SO_4$ contains complex ion $[Cu(NH_3)_4]^{2+}$, $K[Ag(CN)_2]$ contains complex ion $[Ag(CN)_2]^-$ and so on. ***A complex ion*** may be defined as an electrically charged species which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules. For example, $[Ni(NH_3)_6]^{2+}$ is a complex ion in which the central nickel ion, Ni^{2+}, is surrounded by six ammonia molecules. It may be noted that the complex ion may be positively charged or negatively charged or a neutral species.

Cationic complex is a complex ion which has a net positive charge. For example, $[Co(H_2O)_6]^{2+}$, $[Cr(en)_3]^{2+}$

Anionic complex is a complex ion which has a net negative charge. For example, $[Ag(CN)_2]^-$, $[Fe(CN)_6]^{4-}$.

Neutral complex is a complex ion which has no net charge. For example, $[Co(NH_3)_3Cl_3]$, $[Ni(CO)_4]$, $[Pt(NH_3)_2Cl_2]$.

Central ion and Ligands

The cation to which on or more neutral molecules or anions are attached is called ***central ion*** while the neutral molecules or ions are called ***ligands.*** In the complex ion $[Ni(NH_3)_6]^{2+}$, Ni^{2+} ion is the central ion and the molecules of ammonia are the ligands. Similarly, in the complex ion $[Co(NH_3)_5Cl]^{2+}$, Co^{2+} ion is the central ion while the ammonia molecules and the chloride ion are the ligands. The ligands are attached to the central metal atom or ion through ***coordinate bonds***. It means that while central ion should have vacant orbitals, the ligands should have lone pairs of electrons in the outermost orbitals which can be donated to the central ion. The atom in the ligand which can donate the electron pairs is called ***donor atom***. For example, in ammonia nitrogen is the donor atom and in water oxygen is the donor atom.

Types of Ligands

The ligands may contain one or more than one donor atoms for coordination with the central atom. Accordingly, the ligands are classified as follows:

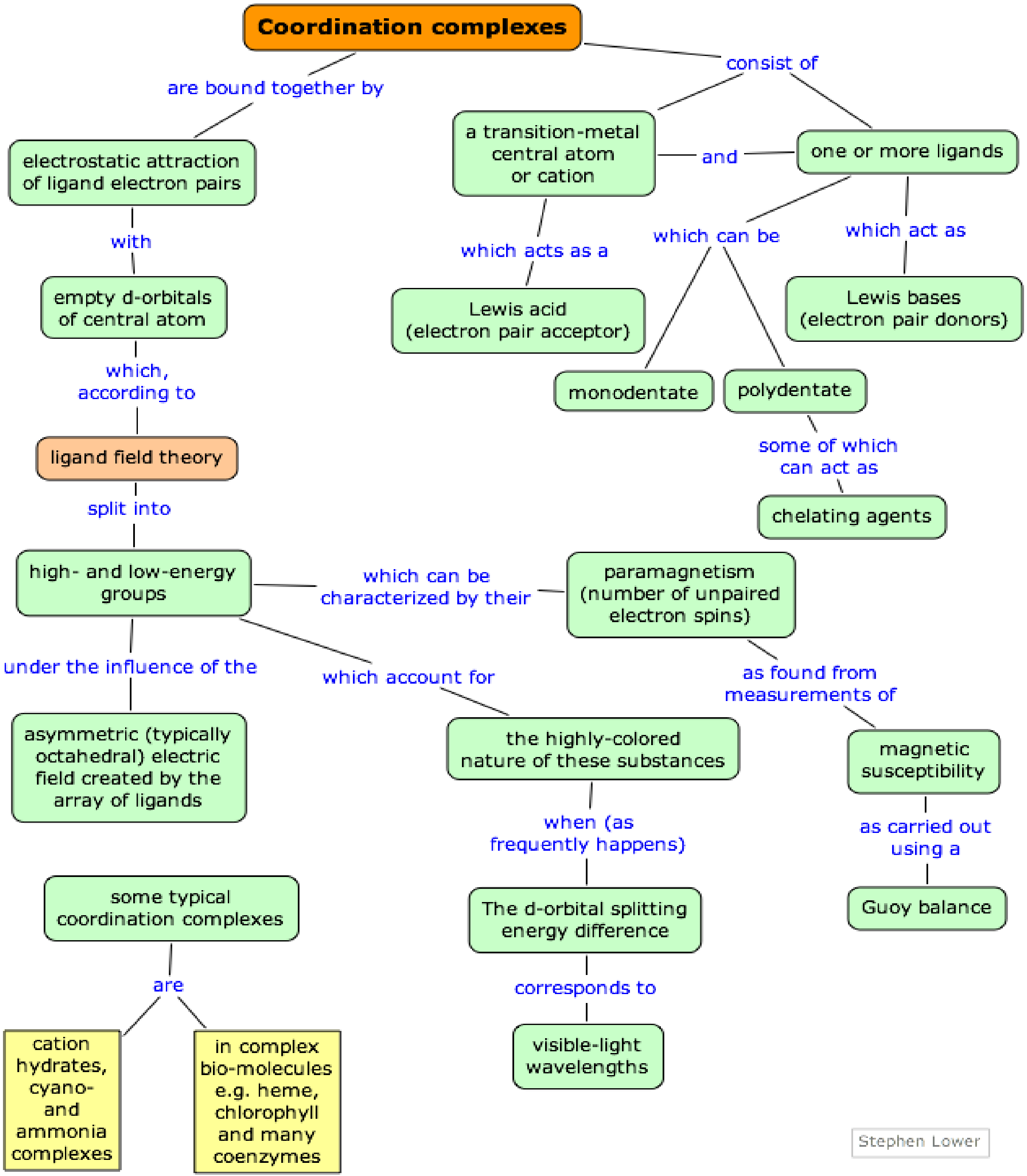
1. ***Unidentate or monodentate ligands*** are ligands which can coordinate to the central ion through only one donor atom. For example, Ammine(NH_3), Aqua(H_2O),Chlorido(Cl^-), Cyanido(CN^-), Pyridine(Py-C_5H_5N), Hydroxo(OH^-), Thiocyanato(-SCN), Nitro(NO2-), Carbonyl(CO),etc.

2. ***Bidentate ligands*** are ligands which have two donor atoms and therefore, can coordinate to the central ion at two positions. For example, oxalate ion $C_2O_4^{2-}$, Ethylenediamine $H_2N–CH_2–CH_2–NH_2$, bipyridine, diphosphine, phenanthroline and dithiocarbamate R_2-N-CS_2^{-1} etc.

3. ***Polydentate ligands*** are those having more than two donor atoms present in the molecule. Theses may be called ***tridentate, tetradentate*** ligands etc**.** depending upon the number of donor atoms present in their molecules. The doubly charged anion of ethylenediaminetetraacetic acid is a tetradentate ligand: EDTA

Coordination Sphere

Central metal atom and the ligands (molecules or ions) directly bonded to it is collectively known as ***coordination sphere.*** This part of the complex behaves as one unit and is non-ionizable. It is generally written in a square bracket. For example, $[Pt(NH_3)_4]^{2+}$ represents coordination sphere in the compound $[Pt(NH_3)_4]Cl_2$. The portion outside the square bracket (coordination sphere) is ionizable. Thus, the coordination compound $[Pt(NH_3)_4]Cl_2$ ionizes as: $[Pt(NH_3)_4]Cl_2 \quad [Pt(NH_3)_4]^{2+} + 2Cl^-$. $[Co(NH_3)_3Cl_3]$ does not ionize because there is no group outside the square bracket.



Coordination Number

The ligands in a coordination compound are attached to the central metal ion through coordination bonds. The total number of ligands attached to a central metal ion is called the ***coordination number*** (C.N.) of that ion. In other words, coordination number is the number of ligands in the coordination sphere of the complex compound. For example, the coordination number of central metal ion in different complexes is:

$[Ag(CN)_2]^{-}$	C.N. of Ag^{+} = 2
$[Cu(NH_3)_4]^{2+}$	C.N. of Cu^{2+}= 4
$[Co(NH_3)_3Cl_3]$	C.N. of Co^{3+}= 6
$[Fe(C_2O_4)_3]^{3-}$	C.N. of Fe^{3+} = 6

Oxalate ion $C_2O_4^{2-}$ is a bidentate ligand so one bidentate ligand should be counted as two ligands. Therefore, three bidentate ligands make C.N. = 6. It may be noted that the ions or molecules present outside the square bracket are not counted in the coordination number because these are not bonded through coordinate bonds to the metal ion. For example, $Ni(NH_3)_6]Cl_2$ C.N. of Ni^{2+} = 6.

Charge of a Complex ion

The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it. For example, $[Ni(NH_3)_6]^{2+}$ carries a charge of +2 because Ni^{2+} ion carries a charge of +2 and ammonia molecule is neutral.

$[Ni(NH_3)_6]^{2+}$: Charge = +2 +6(0) = +2.

Similarly, the complex ion $[Co(NH_3)_5Cl]^{2+}$, carries a net charge of +2 because it is formed by the coordination of one Co^{3+} ion with five neutral molecules of ammonia and one Cl^{-} ion.

$[Co(NH_3)_5Cl]^{2+}$: Charge = +3 +5(0)–1 = +2.

A coordination compound sometimes may not have any charge. For example, $[Co(NH_3)_3Cl_3]$ carries no charge because Co^{3+} ion carries a charge of +3, three ammonia molecule are neutral and three Cl^{-} ions carry together a charge of -3.

$[Co(NH_3)_3Cl_3]$: Charge = +3 +3(0)–3 =0.

Oxidation number or oxidation state of the central metal atom

It is the number which represents the charge which an atom actually has when combined with the other ions or molecules. For example, the oxidation number (O.N.) of Co in the complex $[Co(NH_3)_6]^{3+}$ is +3. Oxidation number of the central atom is the main factor affecting the coordination number. A comparison of the most characteristic coordination numbers in solutions and the charge of the central ion is given below:

Charge of the central ion	+1	+2	+3	+4
Coordination number	2	4,6	6,4	8

The coordination numbers encountered more often when two different kinds of coordination are possible are set here in boldface type. The coordination number 6 is encountered in the complex compounds of Pt^{4+}, Cr^{3+}, Co^{3+}, and Fe^{3+}, the coordination number 4 – in the complexes of Cu^{2+}, Zn^{2+}, Pd^{2+}, and Pt^{2+}, the coordination number 2 – in the complexes of Ag^{+} and Cu^{+}.

Knowing the charge of the complex ion, we can calculate the oxidation number of the central metal atom. For this, the oxidation number of the central metal atom is assumed to be x and the oxidation number of all other species are substituted. The sum of the oxidation numbers is equated to the total charge of the complex and the value of x is calculated.

$[Ni(NH_3)_6]^{2+}$: $x+6(0)= +2$ or $x = +2$
O.N. of Ni = +2
$[Co(NH_3)_5Cl]^{2+}$: $x+5(0)–1= +2$ or $x = +3$
O.N. of Co = +3
$[Fe(C_2O_4)_3]^{3-}$: $+3(–2) = –3$ or $x = +3$
O.N. of Fe = +3
$K_4[Fe(CN)_6]$: $4(+1)+x+6(–1) = 0$ or $x = +2$
O.N. of Fe = +2
$[Ni(CO)_4]$: $x+4(0) = 0$ or $x = 0$
O.N. of Ni = 0

These calculations will be used while writing the names of compounds. The different terms in a complex $[Co(NH_3)_4Cl_2]Cl$ are illustrated below:

Bonding in Coordination Compounds

The main assumptions of **Valence Bond Theory** for bonding in coordination compounds are listed below:

1. The central metal ion in the complex makes available a number of empty orbitals for the formation of coordinate bonds with suitable ligands. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion. For example, if coordination number is 6, six empty orbitals are made available in the central metal ion.

2. The appropriate atomic orbitals (*s*, *p* and *d*) of the metal hybridize to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral, octahedral and so on. The following types of hybridization are involved for different geometries of the complexes.

Coordination number	Hybridisation	Geometry
4	sp^3	Tetrahedral
4	dsp^2	Square planar
6	sp^3d^2 or d^2sp^3	Octahedral

3. The *d*-orbitals involved in the hybridization may be either inner *d*-orbitals i.e. (*n*–1)d or outer *d*-orbitals i.e., nd. For example, in case of octahedral

hybridization, the orbitals may be two 3*d*, one 4*s* and three 4*p* (d^2sp^3) or one 4*s*, three 4*p* and two 4*d* (sp^3d^2 hybridization).

4. Each ligand has at least one orbital (of donor atom) containing a lone pair of electrons.

5. The empty hybrid orbitals of metal ion overlap with filled orbitals of the ligand to form metal-ligand coordinate covalent bonds.

Be^{2+} + 4:F →$[BeF_4]^{2-}$
acceptor donor tetrahedral geometry (sp^3 hybridization)

Cr^{3+} + 6:H_2O → $[Cr(H_2O)_6]^{3+}$
acceptor donor octahedral geometry (d^2sp^3 hybridization)

$$As well as the coordination number CN=5.0 is known for the square pyramid d^4s hybridization like $[VO(acac)_2]$ complex or sP^3d or dsp^3 like Trigonal bipyramid geometry of $[Mn(CO)_5]$ or $CuCl_5^{3-}$ complexes.

Spatial Structure and Isomerism in Coordination Compounds

Identical ligands are symmetrically arranged in the space around the central atom. The even coordination numbers 2, 4 and 6 are encountered more often. The following geometrical configurations correspond to them:

For the coordination number 4 and tetrahedral configuration, all the positions of the ligands relative to the central atom are equivalent. Consequently, tetrahedral complexes of the $[MA_2B_2]$ type (where M is the central atom and A and B are ligands) have no isomers. For square-planar configuration two isomers are possible.

For example, the complex $[Pt(NH_3)_2Cl_2]$ have two isomeric forms differing in colour, solubility, reactivity, and the way of preparation. In one of the isomers, the chlorine atoms are diagonally opposite (trans-isomer), and in the other one they adjacent to each other (cis-isomer).

Compound $[Pt(NH_3)_2Cl_4]$ (where the coordination number of the platinum is 6) exists in two isomeric forms differing from each other in their colour and in other properties. In one case, the NH_3 molecules are at diagonally opposite corners of the octahedron (trans-isomer), and in the other at adjacent corners (cis-isomer). However, the others coordination numbers C.N=6.0 in octahedral geometry have been taken regular or distorted on *z*-out or *z*-in axis like copper(II) and Cr(II) complexes.

Classification of Complex Compounds

The basic types of complex compounds include the following.

Ammines – complexes in which ammonia molecules are the ligands, for instance $[Cu(NH_3)_4]SO_4$, $[Co(NH_3)_6]Cl_3$. Complexes similar to the ammines are known in which the role of the ligands is played by amine molecules: CH_3NH_2

(methylamine), $C_2H_5NH_2$ (ethylamine), $H_2NCH_2CH_2NH_2$ (ethylenediamine), etc. Such complexes are known as ***aminates***.

Aquacomplexes contain water as the ligand: $[Rh(H_2O)_6]Cl_3$, $[Mo(H_2O)_6]Cl_2$, etc.

Acidocomplexes. In these complexes, anions are the ligands. For example, $Na_2[PdCl_4]$, $Cs_4[Fe(CN)_6]$, $Na_2[Mn(OH)_4]$, $KFe[Ru(SCN)_6]$.

Transition series exist between these classes, which include complexes with different ligands. Below is given the transition series between the ammines and Acidocomplexes of platinum (II): $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_3Cl]Cl$, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)Cl_3]$, and $K_2[PtCl_4]$.

Cyclic or ***chelate*** (from the Greek word «chele» – claw) complex compounds contain a bi- or poly dentate ligand that grips the central atom, as it were, like the claws of a crab. Chelating ligand is attached by two or more donor atoms to the same central metal ion forming a ring structure. For example, when a bidentate ligand such as ethylenediamine attaches to Cu^{2+} ion through amino groups and forms a ring structure, it is called chelating ligand. The resulting complex ion $[Cu(en)_2]^{2+}$ is called a chelate.

Similarly, $[Fe(C_2O_4)_3]^{3-}$ is a chelate in which oxalate ion acts as chelating ligand. The group of chelates also includes ***intra complex compounds*** in which the central atom is part of a ring, forming covalent bonds with ligands in various ways – donor-acceptor bonds and bonds at the expense of unpaired atomic electrons. Complexes of this kind are very characteristic of the aminocarboxylic acids. Their simplest representative is amino acetic acid (glycine) NH_2CH_2COOH – it forms chelates with Cu^{2+}, Pt^{2+} ions, for example:

Complexes are also known with more complicated amino carboxylic acids and their analogues. Such ligands are known as ***complexons.*** The doubly charged anion of ethylenediaminetetraacetic acid in the form of its bisodium salt is called ***complexon III*** or ***B trilon***; it produces a complex of the following type with a bivalent metal:

Chelate compounds are extremely stable because their central atom is “blocked”, as it were, by the cyclic ligand. Complexons bond metal cations very strongly. That’s why they are used for softening water, in medicine as antidotes in poisonings with metals. Chelate compounds play a great role in nature. For instance, hemoglobin consists of a complex – heme – bonded to a protein – globin. The central ion in heme is the Fe^{2+} ion around which four nitrogen atoms are coordinated that belong to a complex ligand with cyclic groups. Hemoglobin reversibly attaches oxygen and carries it from lungs via the blood vessels to all the tissues. Chlorophyll, which participates in photosynthesis processes in plants, has a similar structure, but its central ion is Mg^{2+}.

All the classes of complex compounds listed above contain one central atom, i.e. they are ***mononuclear***. Complexes are also encountered with a more complicated structure that contain two or more central atoms of the same or different elements. These complexes are known as ***polynuclear*** ones.

Nomenclature of Coordination Compounds (given by IUPAC)

1. Order of naming ions. In ionic complexes, the cation is named first and then the anion (as in NaCl: sodium chloride). Non-ionic complexes are given a one word name.

2. Naming the coordination sphere. In naming the coordination sphere, the ligands are named first and then the central metal ion.

3. Names of ligands. The names of negative ligands end in ***–o*** and names of positive ligands end in ***–ium.*** The neutral ligands are named as such. For example:

a) negative ligands end in *–o*:

b) positive ligands end in –ium:

NO^+ – nitrosonium

c) neutral ligands are named as such

$NH_2CH_2CH_2NH_2$ – ethylenediamine, C_6H_5N pyridine, NO nitrosyl,etc…

However, there are a few exceptions in naming neutral ligands, for example: H_2O aquo (aqua), PH_3 Phosphine ,, NH_3 ammine, CO carbonyl.

4. Order of naming ligands. When more than one type of ligands are present, they are named in **alphabetical order** of preference without separation by hyphen. For example, in the complex $[Co(NH_3)_4Cl(NO_2)]^+$, the ligands are named in the order: ammine, chloro and nitro.

5. Numerical prefixes to indicate number of ligands. When more than one ligands of a particular kind are present in the complex, the prefixes di-, tri-, tetra, penta-, hexa-, etc. are used to indicate their number: two, three, four, five and six respectively like $[Rh(en)_2Br_2]SO_4$ Bis(ethylenediamine)dibromido Rohdium(II) sulphate.

6. Ending of names. When the complex is anionic, the name of the central metal atom ends in **–ate**. For cationic and neutral complexes, the name of the metal is written without any characteristic ending.

$[Co(NH_3)_6]Cl_3$ Hexaammine cobalt (III) chloride (cationic complex – no characteristic ending).

$K[Pt(NH_3)Cl_5]$ Potassium ammine pentachloro platinate (IV) (anionic complex is named with ending of the name of the metal as –ate).

$Ca_2[Fe(CN)_6]$ Calcium hexacyanido ferrate (II), It may be noted that for anionic complexes the Latin names of certain metals are commonly used. For example, ferrate for Fe, cuperate for Cu, argentate for Ag, aurate for Au, stannate for Sn, etc. However, if the complex is cationic the name of the metal ia given as such, e.g. iron for Fe, silver for Ag, gold for Au, copper for Cu, etc. For example: $K_3[Fe(CN)_6]$ – Potassium hexacyanoferrate (III), $[Fe(CO)_5]$ – Pentacarbonyl iron (0).

7. Oxidation state of central metal ion is designated by a Roman numeral in the brackets at the end of the name of the complex without a gap between the two. It may be noted that the gap should be only between cation and anion. The complex part should be written as one word.

$K^{+1}{}_4[Ni^0(CN)^{-1}{}_4]^{4-}$ – Potassium tetracyanonickelate (0)

$Cu^{+2}{}_2[Fe^{+2}(CN)^{-1}{}_6]^{4-}$ – Copper hexacyanoferrate (II)

$[Pt^{+4}(NH_3)^0{}_4Cl^{-1}(NO_2)^{-1}]^{2+}SO_4{}^{2-}$ – Tetraamminechlorido nitro platinum (IV)
sulfate

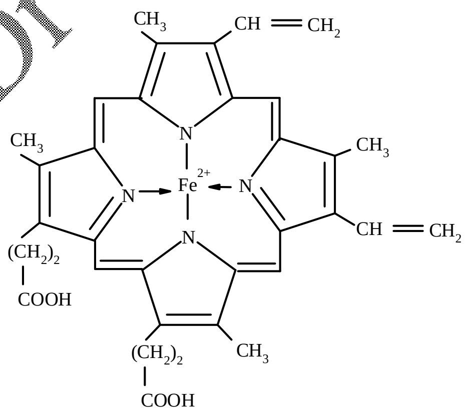
$K^{+1}[Ag^{+1}(CN)^{-1}{}_2]^{1-}$ – Potassium dicyanido Argentate (I)

$[Ni^0(CO)^0{}_4]^0$ – Tetracarbonyl Nickel (0).

Biologicaly important complexes. Chelation

Cations of d-block metals in the organism are tightly bonded with polydentate ligands, as a rule, with polypeptides or cyclic polydentate ligands – derivatives of porphyrins (e.g. in hemoglobin). In the free state these cations exist only in the blood plasma in negligible amounts.

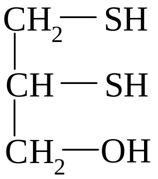
In the biological systems the amino acids, proteins and acids of Tricarboxylic acid cycle (Krebs cycle) are the main ligands and the metals involved are iron, magnesium, manganese, copper, cobalt, and zinc. Iron enters the composition of hemoglobin, myoglobin, oxidases, peroxidases, cytochromes. More than 60 biologically active substances contain zinc, e.g. enzymes carbonic anhydrase and carboxypeptidase. Cobalt is in composition of vitamin B_{12} (cyanocobalamin).



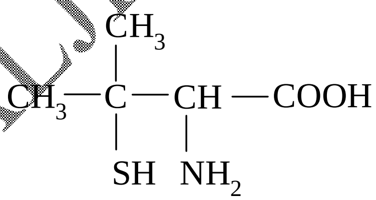
Formation and destruction of biological complexes occur constantly in the organism and metal-ligand homeostasis is maintained on the definite level. Metal-ligand homeostasis can be disturbed due to deficiency or excess of biometals cations, entering of toxic metals cations, entering or formation of alien ligands. For example, entering into the organism of such toxic ligand as carbon monoxide leads to the disturbance of hemoglobin function and hemoglobin loses its ability to transport oxygen. Toxicity of d-metals in many cases is explained by the stability of biological complexes formed by them.

Toxic metals and toxic ligands pollute the environment, enter into the human organisms and disturb metal-ligand homeostasis in the result of anthropogenous activity. Complexing agents are used for removal of metal poisoning. Antidote therapy of poisonings caused by heavy metals cations is based on the formation of stable complexes (chelation) between these metals and special ligands.

Dimercaprol is an effective antidote for the organic arsenical like lewisite, but can be used for poisoning due to antimony, gold and mercury.



2,3-dimercaptopropan-1-ol
(BAL, dimercaprol)



Penicillamine (dimethylcystein)

Penicillamine is an effective antidote for the treatment of poisonings by copper, mercury and lead. Trilon B (bisodium salt of EDTA) is used for treatment of hypercalcemia, poisoning by calcium compounds.

In general, chelation can be used for sequestration of metal ions, stabilization of drugs, elimination of toxic metals from intact organisms and also for the improvement of metal absorption. Recently, platinum complex cis $[Pt(NH_3)_2Cl_2]$ known as cisplatin has found use in cancer chemotherapy.

Crystal Field Theory

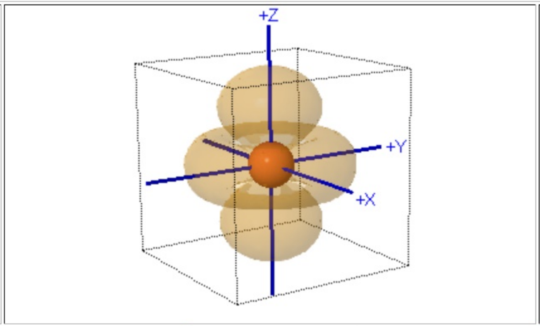
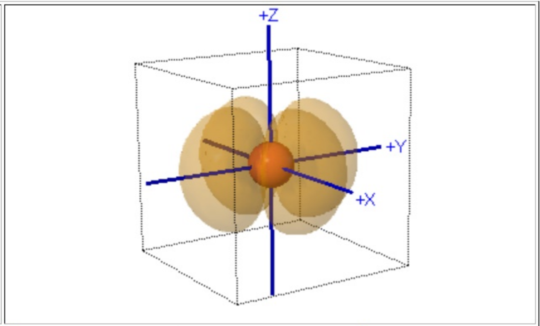
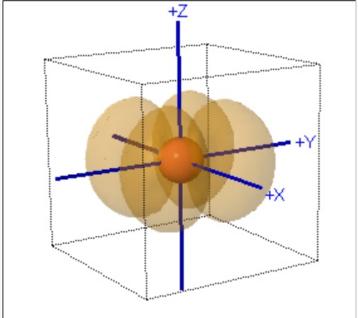
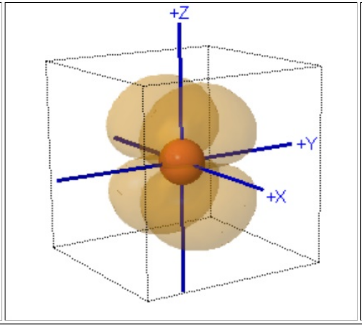
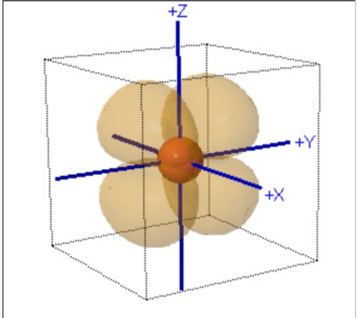
In the ionic CFT, it is assumed that the ions are **simple point charges**. When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

The bond energy between the charges is proportional to $q_1 * q_2/r$

where q_1 and q_2 are the charges of the interacting ions and r is the distance separating them. This leads to the correct prediction that large cations of low charge, such as K^+ and Na^+, should form few coordination compounds.

For transition metal cations that contain varying numbers of d electrons in orbitals that are NOT spherically symmetric, however, the situation is quite different. The shape and occupation of these d-orbitals then becomes important in an accurate description of the bond energy and properties of the transition metal compound.

To be able to understand and use CFT then, it is essential to have a clear picture of the shapes (angular dependence functions) of the d-orbitals.

<table>
<tr><td>d_{z^2}, $d_{x^2-y^2}$</td><td colspan="3">
</td><td colspan="3">
</td></tr>
<tr><td>d_{xy}, d_{xz}, d_{yz}</td><td colspan="2">
</td><td colspan="2">
</td><td colspan="2">
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JSmol is an Open Source application for the display of molecular graphics that is capable of displaying atomic orbitals so it is possible to see the relationship between their orientation and ligands in different stereochemistries. See the cases for octahedral, tetrahedral and square planar complexes.

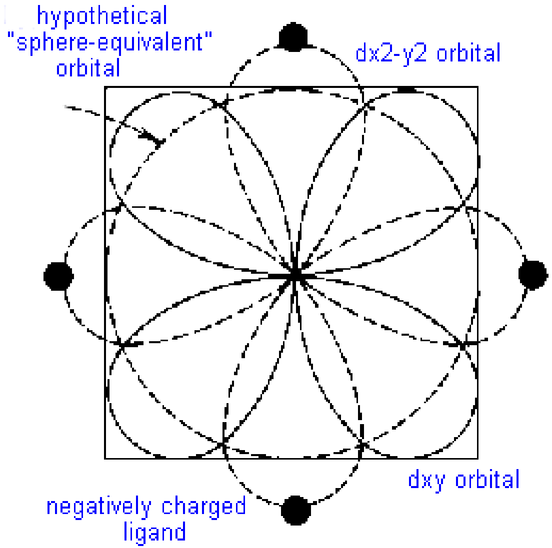
A cube provides a convenient reference for displaying the coordination centre of complexes since octahedral compounds have cubic symmetry i.e. the six anions sit at the centres of the faces of the cube and for tetrahedral complexes the 4 ligands sit at opposite diagonal edges.

You should be able to see that two of the d-orbitals, the dz^2 and $dx^2\text{-}y^2$ meet the faces of the cube, but the remaining three (dxy, dyz and dxz) point towards the edges of the cube and actually have a node meeting the centres of the faces.

What happens then to the energy of the d-electrons if negatively charged ligands are brought in towards the metal centre to give an octahedral complex - where the ligands sit at the centre of the faces of the cube i.e. on the X, Y and Z axes? Since the d electrons are themselves negatively charged they would experience repulsion and their energies would be raised. For 's' and 'p' electrons this is of little consequence but for 'd' electrons there will be an energy difference involved depending on the orbital distribution and occupation.

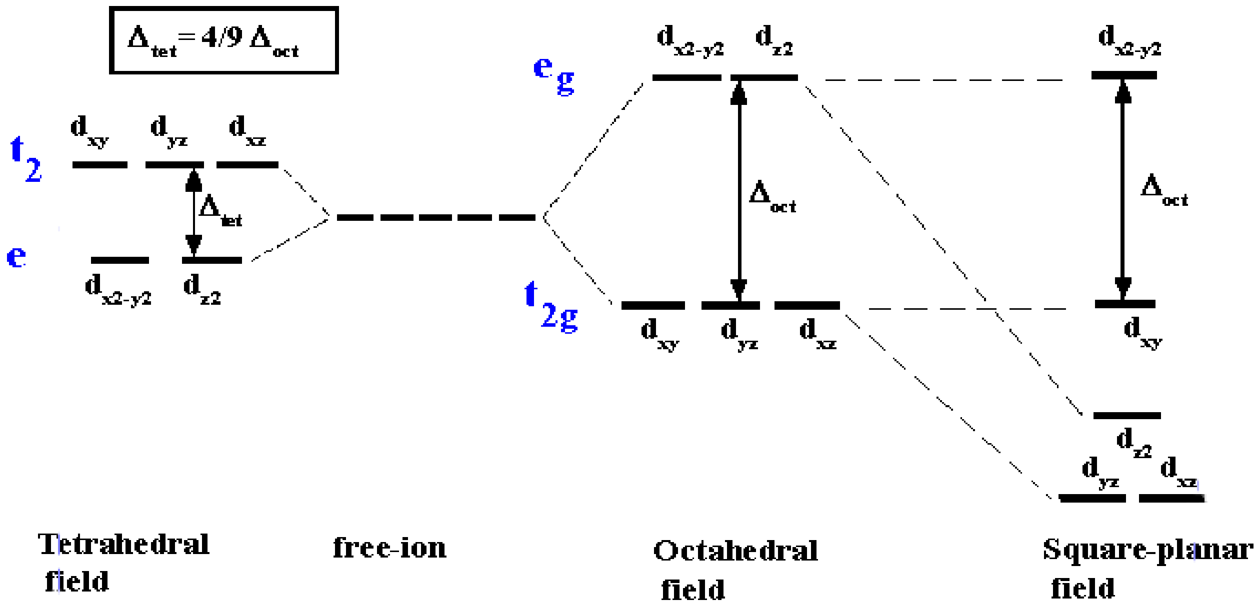
Consider the the example of $TiCl_6^{3-}$ in which six chloride ions octahedrally surround the Ti^{3+} cation. There is only one d-electron to be allocated to one of the five d- orbitals. If it were to occupy the dz^2or dx^2-y^2 orbital, both of which meet the face of the cube and thus point directly towards the chloride ligands, it would be strongly repelled. The geometry of these orbitals and their nodes would require the electron to stay near the negatively charged ligands causing even more repulsion than a spherically distributed electron would experience. On the other hand, if the electron were to occupy the dxy, dyz or dxz orbital, it would spend less time near the ligands than would a spherically distributed electron and would be repelled less.

This difference between for example the dx^2-y^2 orbital, the dxy orbital and a spherical distribution can be graphically represented by



The result of these differences for the d-orbitals is an energy difference between the dz^2 and dx^2-y^2 orbitals compared to the dxy, dyz and dxz orbitals.

Energy levels of the d-orbitals in common stereochemistries



The CFT approach can be easily extended to other geometries and the next most important case is the **tetrahedron**. To predict the splitting pattern of the energy of the d-orbitals under a tetrahedal crystal field you may once again find it convenient to consider how the ligands can fit into a cube to give a tetrahedron.

The next step is to consider how the d-orbitals interact with these incoming ligands. For tetrahedral complexes, the energy of those orbitals which point towards the edges should now be raised higher than those which point towards the faces. That is, the exact opposite of the situation we just dealt with for the octahedral crystal field. The end result is a splitting pattern which is represented in the splitting diagram above.

The square planar case can be considered as an extension of the octahedral, where we remove the two ligands from the Z axis. Consequently, repulsion of an electron in the dz^2 orbital will no longer be equivalent to that experienced by an electron in the dx^2-y^2 orbital, and the end result is shown above. For the first year course, the only square planar complexes will be for d^8 complexes, i.e all four coordinate complexes are tetrahedral except for d^8 which may be **tetrahedral or square planar**.

Once we accept that the energy of the 5 'd' orbitals are no longer degenerate in a coordination compound we can begin to explore some of the implications. **Note that a different CFT energy splitting diagram has to be applied for each stereochemistry. In this course we will only be concerned with diagrams for octahedral, tetrahedral and square planar complexes.**

One of the important aspects of CFT is that not all ligands are identical when it comes to causing a separation of the energy of the d-orbitals. For transition metal compounds, there is clear evidence for this from the multitude of colours available for a given metal ion when the ligands or stereochemistry are varied. For octahedral complexes this is a reflection of the energy difference between the higher dz^2, dx^2-y^2 (eg subset) and the dxy, dyz, dxz (t2g subset).

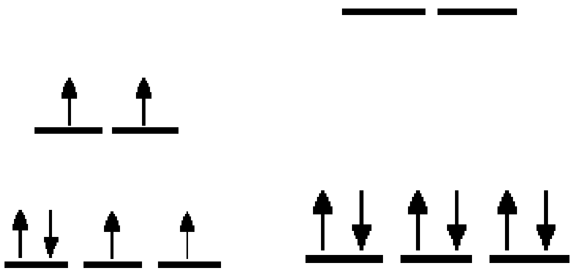
It has been established that the ability of ligands to cause a large splitting of the energy between the orbitals is essentially independent of the metal ion and the Spectrochemical series is a list of ligands ranked in order of their ability to cause large orbital separations.

A shortened list includes:

I- < Br- < SCN- ~Cl- < F- < OH- ~ ONO- < $C_2O_4^{2-}$ < H_2O < NCS- < $EDTA^{4-}$ < NH_3 ~ pyr ~ en < bipy < phen < CN- ~ CO

When metal ions that have between 4 and 7 electrons in the d orbitals form octahedral compounds, two possible electron distributions can occur. These are referred to as either weak field - strong field or high spin - low spin configurations.

Take for example, Fe^{2+}- d^6.



The diagram on the left represents the case for the aqua ion (small Δ, $t_{2g}^4e_g^2$) and on the right that of the hexacyano ion (large Δ, t_{2g}^6).

What this means is that if we use a technique that can detect the presence of unpaired electrons in each compound, then for the first we should find 4, while in the latter none. This accounts for the names high spin compared to low spin. The terms weak field, strong field give an indication of the splitting abilities of the ligand. Water always give rise to small splittings of the enregy of the d orbitals for first row transition metal ions and hence is referred to as a weak field ligand. Conversely, CN- is a strong field ligand, since it causes large splittings of the energy of the d-orbitals.

Complexes such as $Cu(NH_3)_6^{2+}$ have been known and studied since the mid-nineteenth century. and their structures had been mostly worked out by 1900. Although the hybrid orbital model was able to explain how neutral molecules such as water or ammonia could bond to a transition metal ion, it failed to explain many of the special properties of these complexes. Finally, in 1940-60, a model known as *ligand field theory* was developed that is able to organize and explain most of the observed properties of these compounds. Since that time, coordination complexes have played major roles in cellular biochemistry and inorganic catalysis.

The present lesson will introduce you to this very important class of compounds.

1 What is a coordination complex?

If you have taken a lab course in chemistry, you have very likely admired the deep blue color of **copper sulfate** crystals, $CuSO_4{\cdot}5H_2O$. The proper name of this substance is copper(II) sulfate pentahydrate, and it is typical of many salts that incorporate ***waters of hydration*** into their crystal structures. It is also a ***complex***, a term used by chemists to describe a substance composed of two other substances (in this case, $CuSO_4$ and H_2O) each of which is capable of an independent existence. The binding between the components of a complex is usually weaker than a regular chemical bond; thus most solid hydrates can be decomposed by heating, driving off the water and yielding the ***anhydrous*** salt:

$$CuSO_4{\cdot}5\,H_2O \rightarrow CuSO_4(s) + 5\,H_2O$$

Driving off the water in this way also destroys the color, turning it from a beautiful deep blue to a nondescript pale yellow. If the anhydrous salt is now dissolved in water, the blue color now pervades the entire solution. It is apparent that the presence of water is somehow necessary for the copper(II) ion to take on a blue color, but why should this be?

A very common lab experiment that most students carry out is to add some dilute ammonia to a copper sulfate solution. At first, the solution turns milky as the alkaline ammonia causes the precipitation of copper hydroxide:

$$Cu^{2+} + 2\,OH^{-} \rightarrow Cu(OH)_2(s).$$

But if more ammonia is added, the cloudiness disappears and the solution assumes an intense deep blue color that makes the original solution seem pale by comparison. The equation for this reaction is usually given as

$$Cu^{2+} + 6\,NH_3 \rightarrow Cu(NH_3)_6^{\;2+}$$

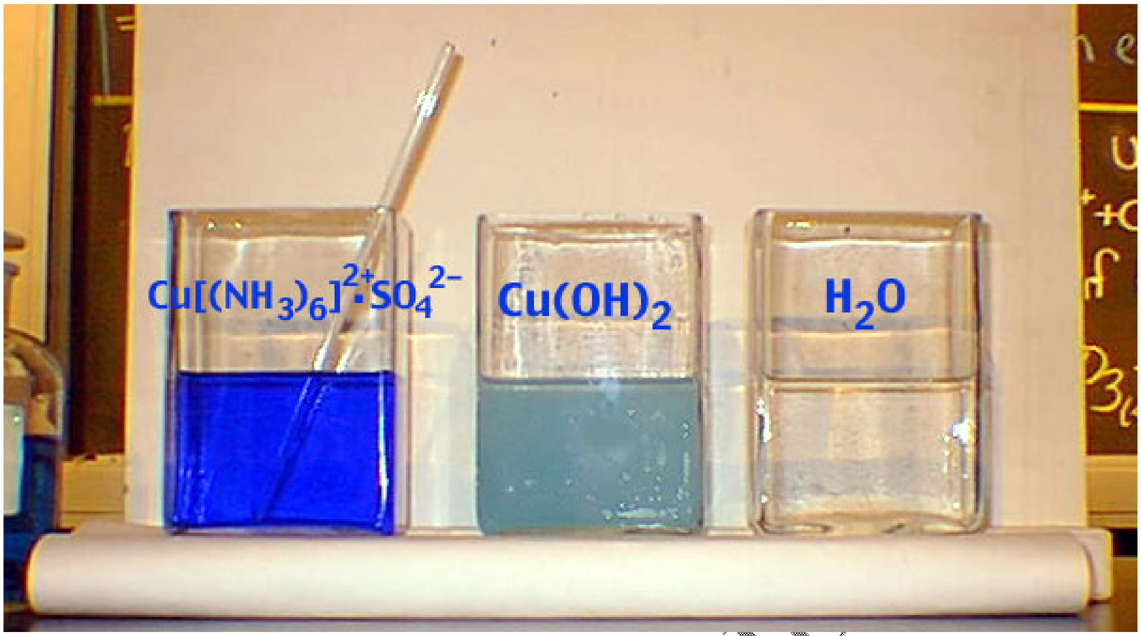


image from UC Berkeley Chemistry site

The new product is commonly known as the ***copper-ammonia complex ion***, or more officially, hexamminecopper(II). This equation is somewhat misleading, however, in that it implies the formation of a new complex where none existed before. In fact, since about 1895 it has been known that the ions of most transition metals dissolve in water to form complexes with water itself, so a better representation of the reaction of dissolved copper with ammonia would be

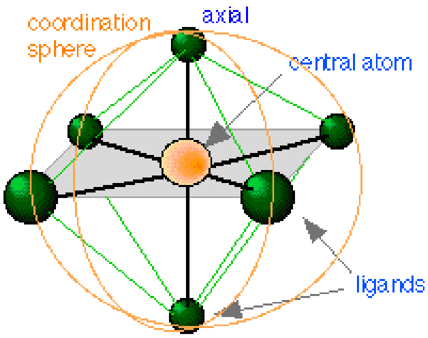
$$Cu(H_2O)_6^{2+} + 6\ NH_3 \rightarrow Cu(NH_3)_6^{2+} + 6\ H_2O$$

In effect, the ammonia binds more tightly to the copper ion than does water, and it thus displaces the latter when it comes into contact with the *hexaaquocopper(II) ion*, as the dissolved form of Cu^{2+} is properly known.

2 The basics of coordination complexes

Although our primary focus in this unit is on bonding, the topic of coordination complexes is so important in chemistry and biochemistry that some of their basic features are worth knowing about, even if their detailed chemistry is beyond the scope of this course. These complexes play an especially crucial role in physiology and biochemistry. Thus heme, the oxygen-carrying component of red blood cells (and the source of the red color) is basically a complex of iron, and the part of chlorophyll that converts sunlight into chemical energy within green plants is a magnesium complex.

Terms used to describe complexes



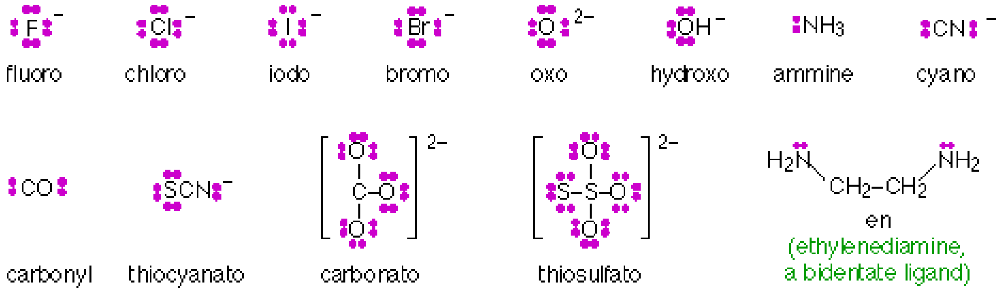
We have already defined a ***complex*** as a substance composed of two or more components capable of an independent existence. A ***coordination complex*** is one in which a ***central atom*** or ion is joined to one or more ***ligands*** (Latin *ligare*, to tie) through what is called a **coordinate covalent bond** in which both of the bonding elecrons are supplied by the ligand. In such a complex the central atom acts as an electron-pair acceptor (**Lewis acid** — think of H^+ which has no electrons at all, but can accept a pair from something like Cl^-) and the ligand as an electron-pair donor (**Lewis base**). The central atom and the ligands coordinated to it constitute the **coordination sphere**. Thus the salt $[Co(NH_3)_5Cl]Cl_2$ is composed of the complex ion $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- ions; components within the square brackets are inside the coordination sphere, whereas the two chloride ions are situated outside the coordination sphere. These latter two ions could be replaced by other ions such as NO_3^- without otherwise materially changing the nature of the salt.

The central atoms of coordination complexes are most often **cations** (positive ions), but may in some cases be neutral atoms, as in nickel carbonyl $Ni(CO)_4$.

Ligands composed of ions such as F^- or small molecules such as H_2O or CN^- possess more than one set of lone pair electrons, but only one of these pairs can coordinate with a central ion. Such ligands are said to be **monodentate**("one tooth".) Larger ligands may contain more than one atom capable of coordinating with a single central ion, and are described as **polydentate**. Thus ethylenediamine (shown below) is a **bidentate** ligand. Polydentate ligands whose geometery enables them to occupy more than one coordinating position of a central ion act as **chelating agents** (Greek χελος *chelos*, claw) and tend to form extremely stable complexes known as **chelates**.

Chelation is widely employed in medicine, water-treatment, analytical chemistry and industry for binding and removing metal ions of particular kinds.

Some of the more common ligands (chelating agents) are shown here:



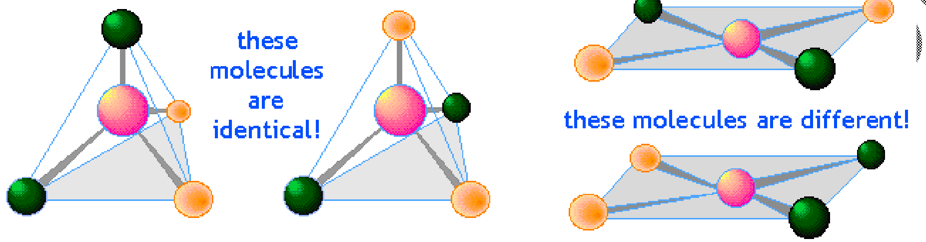
(ethylenediamine, a bidentate ligand)

Structure and bonding in transition metal complexes

Complexes such as $Cu(NH_3)_6^{2+}$ have been known and studied since the mid-nineteenth century. Why they should form, or what their structures might be, were complete mysteries. At that time all inorganic compounds were thought to be held together by ionic charges, but ligands such as water or ammonia are of course electrically neutral. A variety of theories such as the existence of "secondary valences" were concocted, and various chain-like structures such as $CuNH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3$ were proposed. Finally, in the mid-1890s, after a series of painstaking experiments, the chemist ALFRED WERNER (Swiss, 1866-1919) presented the first workable theory of complex ion structures.

Werner claimed that his theory first came to him in a flash after a night of fitful sleep; by the end of the next day he had written his landmark paper that eventually won him the 1913 Nobel Prize in Chemistry.

Werner was able to show, in spite of considerable opposition, that transition metal complexes consist of a central ion surrounded by ligands in a square-planar, tetrahedral, or octahedral arrangement. This was an especially impressive accomplishment at a time long before X-ray diffraction and other methods had become available to observe structures directly. His basic method was to make inferences of the structures from a careful examination of the chemistry of these complexes and particularly the existence of structural isomers. For example, the existence of two different compounds AX_4 having the same composition shows that its structure must be square-planar rather than tetrahedral.



What holds them together?

An understanding of the nature of the bond between the central ion and its ligands would have to await the development of Lewis' ***shared-electron pair theory*** and Pauling's ***valence-bond*** picture. We have already shown how ***hybridization*** of the *d* orbitals of the central ion creates vacancies able to accommodate one or more pairs of unshared electrons on the ligands. Although these models correctly predict the structures of many transition metal complexes, they are by themseves unable to account for several of their special properties:

The metal-to-ligand bonds are generally much weaker than ordinary covalent bonds;

Some complexes utilize "inner" *d* orbitals of the central ion, while others are "outer-orbital" complexes;

Transition metal ions tend to be intensely colored.

Magnetic properties of coordination comples

Unpaired electrons act as tiny magnets; if a substance that contains unpaired electrons is placed near an external magnet, it will undergo an attraction that tends to draw it into the field. Such substances are said to be *paramagnetic*, and the degree of paramagnetism is directly proportional to the number of unpaired electrons in the molecule. Magnetic studies have played an especially prominent role in determining how electrons are distributed among the various orbitals in transition metal complexes.

Studies of this kind are carried out by placing a sample consisting of a solution of the complex between the poles of an electromagnet. The sample is suspended from the arm of a sensitive balance, and the change in apparent weight is measured with the magnet turned on and off.

An increase in the weight when the magnet is turned on indicates that the sample is attracted to the magnet (***paramagnetism***) and must therefore possess one or more unpaired electrons. The precise number can be determined by calibrating the system with a substance whose electron configuration is known.

3 Crystal field theory

The current model of bonding in coordination complexes developed gradually between 1930-1950. In its initial stages, the model was a purely electrostatic one known as ***crystal field theory*** which treats the ligand ions as simple point charges that interact with the five atomic *d* orbitals of the central ion. It is this theory which we describe below.

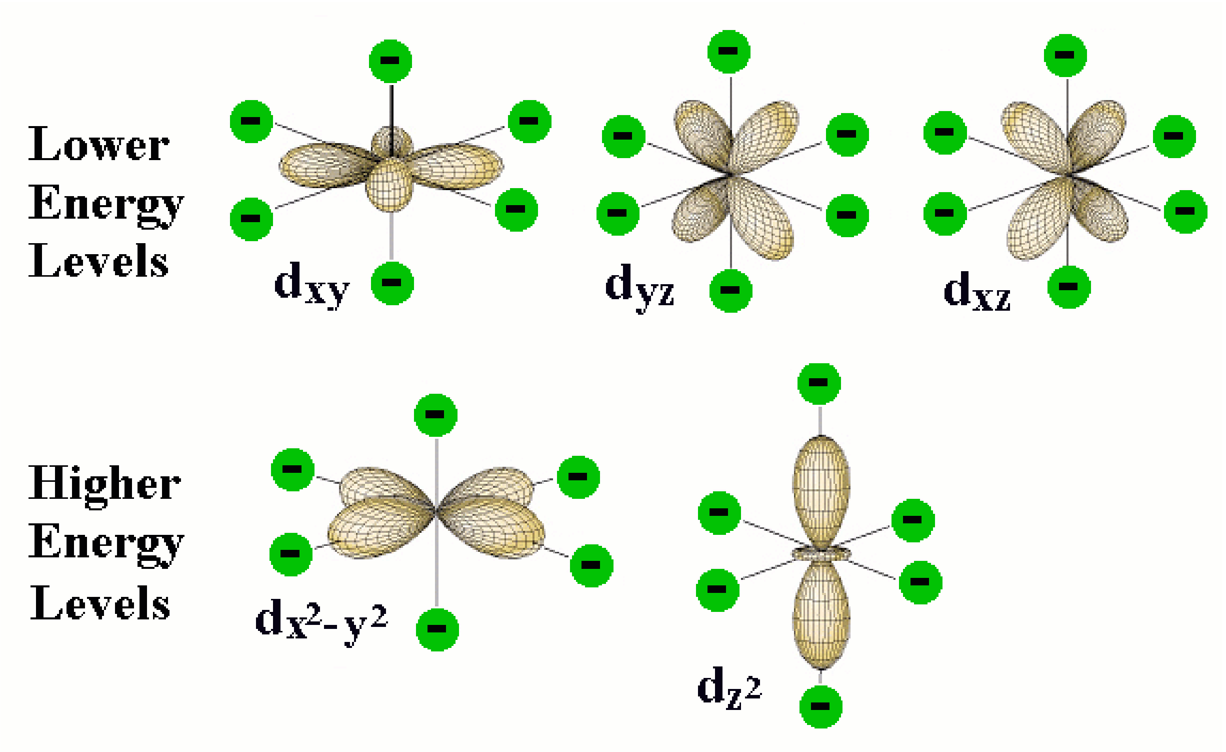
It is remarkable that this rather primitive model, quite innocent of quantum mechanics, has worked so well. However, an improved and more complete model that incorporates molecular orbital theory is known as *ligand field theory*.

In an isolated transition metal atom the five outermost *d* orbitals all have the same energy which depends solely on the spherically symmetric electric field due to the nuclear charge and the other electrons of the atom. Suppose now that this atom is made into a ***cation*** and is placed in solution, where it forms a hydrated species in which six H_2O molecules are coordinated to the central ion in an ***octahedral*** arrangement. An example of such an ion might be **hexaaquotitanium(III), $Ti(H_2O)_6^{3+}$**.

The ligands (H_2O in this example) are bound to the central ion by electron pairs contributed by each ligand. Because the six ligands are located at the corners of an octahedron centered around the metal ion, these electron pairs are equivalent to clouds of negative charge that are directed from near the central ion out toward the corners of the octahedron. We will call this an octahedral electric field, or the ***ligand field***.

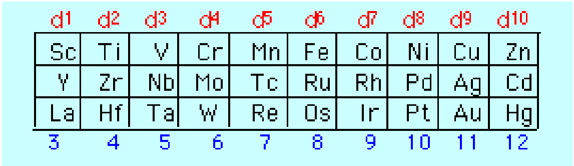
d-orbital splitting

The differing shapes of the five kinds of d orbitals cause them to interact differently with the electric fields created by the coördinated ligands. This diagram (from a Purdue U. chemistry site) shows outlines of five kinds of d orbitals.



The green circles represent the coordinating electron-pairs of the ligands located at the six corners of the octahedron areound the central atom. The two d orbitals at the bottom have regions of high electron density pointing directly toward the ligand orbitals; the resulting electron-electron repulsion raises the energy of these *d* orbitals.

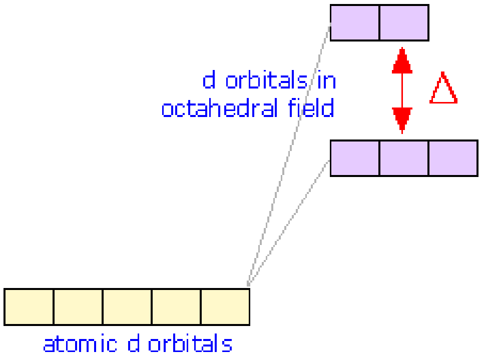
Although the five *d* orbitals of the central atom all have the same energy in a spherically symmetric field, their energies will not all be the same in the octahedral field imposed by the presence of the ligands. The reason for this is apparent when we consider the different geometrical properties of the five d orbitals. Two of the *d* orbitals, designated d_{x2} and $d_{x2\text{-}y2}$, have their electron clouds pointing directly toward ligand atoms. We would expect that any electrons that occupy these orbitals would be subject to repulsion by the electron pairs that bind the ligands that are situated at corresponding corners of the octahedron. As a consequence, the energies of these two *d* orbitals will be raised in relation to the three other *d* orbitals whose lobes are not directed toward the octahedral positions.



d1	d2	d3	d4	d5	d6	d7	d8	d9	d10
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
3	4	5	6	7	8	9	10	11	12

The number of electrons in the *d* orbital of the central atom is easily determined from the location of the element in the periodic table, taking in account, of course, of the number of electrons removed in order to form the positive ion.

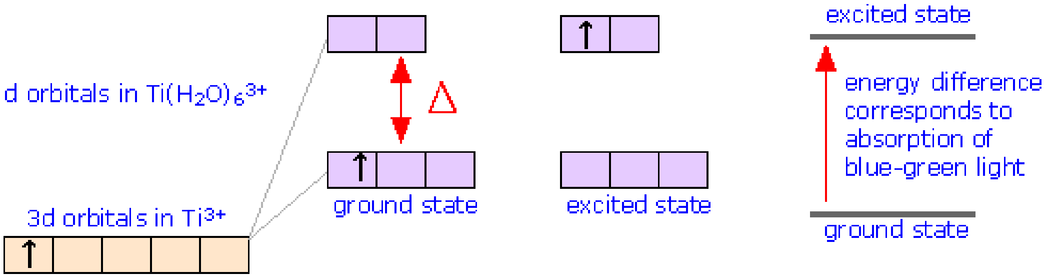
The effect of the octahedral ligand field due to the ligand electron pairs is to split the *d* orbitals into two sets whose energies differ by a quantity denoted by ***Δ*** ("delta") which is known as the ***d* orbital splitting energy**. Note that both sets of central-ion *d* orbtials are repelled by the ligands and are both raised in energy; the upper set is simply raised by a



greater amount. Both the total energy shift and Δ are strongly dependent on the particular ligands.

Why are transition metal complexes often highly colored?

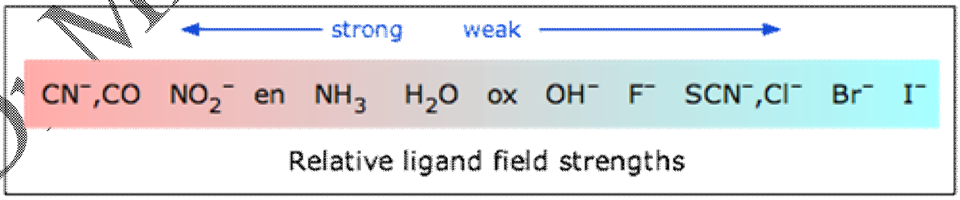
Returning to our example of $Ti(H_2O)_6^{3+}$, we note that Ti has an outer configuration of $4s^23d^2$, so that Ti^{3+} will be a d^1 ion. This means that in its ground state, one electron will occupy the lower group of *d* orbitals, and the upper group will be empty. The *d*-orbital splitting in this case is 240 kJ per mole which corresponds to light of blue-green color; absorption of this light promotes the electron to the upper set of *d* orbitals, which represents the *exited state* of the complex. If we illuminate a solution of $Ti(H_2O)_6^{3+}$ with white light, the blue-green light is absorbed and the solution appears violet in color.



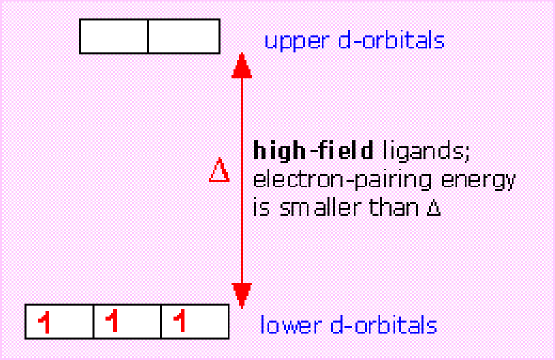
This illustration, taken from the description of a student lab experiment, shows how the colors of hexaaquacobalt II and III complexes are affected by a variety of different ligands including NH_3*(c)*, H_2O *(g)*, and CO_3^{2-} *(i)*.

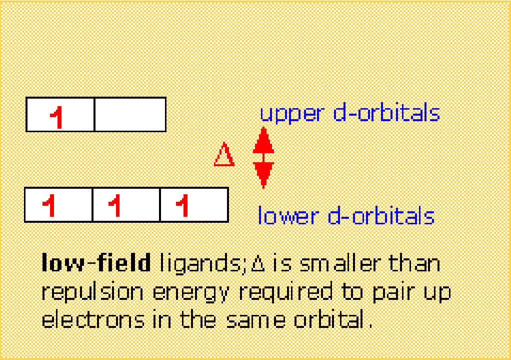
Hign- and low spin complexes

The magnitude of the *d* orbital splitting depends strongly on the nature of the ligand and in particular on how strong an electrostatic field is produced by its electron pair bond to the central ion.



If Δ is not too large then the electrons that occupy the *d* orbitals do so with their spins unpaired until a d^5 configuration is reached, just as occurs in the normal *Aufbau* sequence for atomic electron configurations. Thus a weak-field ligand such as H_2O leads to a "high spin" complex with Fe(II).





In contrast to this, the cyanide ion acts as a strong-field ligand; the *d* orbital splitting is so great that it is energetically more favorable for the electrons to pair up in the lower group of *d* orbitals rather than to enter the upper group with unpaired spins. Thus hexacyanoiron(II) is a “low spin” complex— actually zero spin, in this particular case.

Different *d* orbital splitting patterns occur in square planar and tetrahedral coordination geometries, so a very large number of arrangements are possible. In most complexes the value of Δ corresponds to the absorption of visible light, accounting for the colored nature of many such compounds in solution and in solids such as $CuSO_4 \cdot 5H_2O$.

One method of determining the number of Magnetic Properteis of Transition Elements

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes.
A common laboratory procedure for the determination of the magnetic moment for a complex is the Gouy method which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight. A template is provided for the calculations involved.
For first row transition metal ions in the free ion state, i.e. isolated ions in a vacuum, all 5 of the 3d orbitals are degenerate.

A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the energy of the d orbitals are no longer degenerate but are split such that two orbitals, the d_{x2-y2} and the d_{z2} (e_g subset) are at higher energy than the d_{xy}, d_{xz}, d_{yz} orbitals (the t_{2g} subset).

For octahedral ions with between 4 and 7 d electrons, this gives rise to 2 possible arrangements called either high spin/weak field or low spin/strong field respectively. The energy gap is dependent on the position of the coordinated ligands in the SPECTROCHEMICAL SERIES.

Note:, we assume that all Co(III), d^6 complexes are octahedral and LOW spin, i.e. t_{2g}^6.

In tetrahedral complexes, the energy levels of the orbitals are again split, such that the energy of two orbitals, the d_{x2-y2} and the d_{z2} (e subset) are now at lower energy (more favoured) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t2 subset) which are destabilised.

Tetrahedral complexes are ALL high spin since the difference between the 2 subsets of energies of the orbitals is much smaller than is found in octahedral complexes.

The usual relationship quoted between them is: $\Delta_{tet} \approx 4/9 \Delta_{oct}$.

Square planar complexes are less commmon than tetrahedral and **we will assume that the only ions forming square planar complexes are d^8 e.g. Ni(II), Pd(II), Pt(II), etc.** *d^8 can therefore be either square planar or tetrahedral.* As with octahedral complexes, the energy gap between the dxy and dx^2-y^2 is Δoct and these d^8 systems are all considered strong field / low spin complexes hence they are all diamagnetic, $\mu=0$ Bohr Magneton (B.M.).

The formula used to calculate the spin-only magnetic moment can be written in two forms; the first based on the number of **unpaired** electrons, n, and the second based on the **total** electron spin quantum number, S. Since for each unpaired electron, n=1 and S=1/2 then the two formulae are clearly related and the answer obtained must be identical.

$$\mu_{so} = \sqrt{n(n+2)} \text{ B.M.}$$

$\mu_{so} = \sqrt{4S(S+1)}$ B.M. - a variation of this will be introduced in the second year Inorganic course: $\mu_{S+L} = \sqrt{\{4S(S+1) + L(L+1)\}}$ B.M.

Comparison of calculated spin-only magnetic moments with experimentally observed data for some octahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	$\sqrt{3} = 1.73$	1.6-1.7
V(III)	d^2 (t_{2g}^2)	$\sqrt{8} = 2.83$	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	$\sqrt{1}$	3.7

		5 = 3.88	-3.9
Cr(II)	d^4 high spin (t_{2g}^3 e_g^1)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II) / Fe(III)	d^5 high spin (t_{2g}^3 e_g^2)	√35 = 5.92	5.6-6.1
Mn(II) / Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1
Fe(II)	d^6 high spin (t_{2g}^4 e_g^2)	√24 = 4.90	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin (t_{2g}^5 e_g^2)	√15 = 3.88	4.3-5.2
Co(II)	d^7 low spin (t_{2g}^6 e_g^1)	√3 = 1.73	1.8
Ni(II)	d^8 (t_{2g}^6 e_g^2)	√8 = 2.83	2.9-3.3
Cu(II)	d^9 (t_{2g}^6 e_g^3)	√3 = 1.73	1.7-2.2

Comparison of calculated spin-only magnetic moments with experimental data for some tetahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Cr(V)	d^1 (e^1)	√3 = 1.73	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	√8 = 2.83	2.6 - 2.8
Fe(V)	d^3 (e^2 t_2^1)	√15 = 3.88	3.6-3.7
-	d^4 (e^2 t_2^2)	√24 = 4.90	-
Mn(II)	d^5 (e^2 t_2^3)	√35 = 5.92	5.9-6.2
Fe(II)	d^6 (e^3 t	√24	5.3-

	$_{2}^{3}$)	= 4.90	5.5
Co(II)	d^7 (e^4 t_2^3)	√15 = 3.88	4.2-4.8
Ni(II)	d^8 (e^4 t_2^4)	√8 = 2.83	3.7-4.0
Cu(II)	d^9 (e^4 t_2^5)	√3 = 1.73	-

unpaired electrons is by looking at the magnetic properties of the compounds. A simple technique to determine a magnetic moment (measured in Bohr magneton units BM) involves weighing the sample in the presence and absence of a strong magnetic field. By careful calibration using a known standard, such as $Hg[Co(SCN)_4]$ the number of unpaired electrons can be determined.

To predict the magnetic moment, we can use the simple spin-only formula:

$$\mu = \sqrt{[4S(S+l)]} \quad \text{Bohr Magneton} \quad (BM)$$

where S is the spin quantum number (1/2 for each unpaired electron). An alternative representation is:

$$\mu = \sqrt{[n(n+2)]} \quad \text{Bohr Magneton} \quad (BM)$$

where n is the number of unpaired electrons. These simple formulae give good results for most first row transition metal compounds and can be refined to include orbital contributions (COVERED IN MORE

It is expected that all students will be able to calculate the spin-only magnetic moment of any coordination compound. To do this, you must know the number of d-electrons in the central metal ion, the stereochemistry and whether weak field-strong field considerations are necessary.

	$K_3[Fe(oxalate)_3]$ $3H_2O$	$K_2[CuCl_4]$
metal ion	Fe^{3+}	Cu^{2+}
number of d electrons	5 - t_{2g}^3 e_g^2	9 - e^4 t_2^5
stereochemistry	octahedral	tetrahedral
High Spin/Low Spin	High Spin	Not relevant (all High spin)
# of unpaired electrons	5	1
magnetic moment	√(35) B.M	√(3) B.M

Note that if there are 1-3 or 8-9 d electrons in an **octahedral** complex, the spin-only magnetic moment will have the same value irrespective of whether the ligands present are considered weak field or strong field. For octahedral Co(III) complexes, we will make the simplification that all are low-spin, so regardless of the types of ligands present the magnetic moment will be μ=0 B.M., that is, diamagnetic.