

COURSE CODE: *CHM 411*

COURSE TITLE: *Coordinaton Chemistry*

NUMBER OF UNITS: *2 Units*

COURSE DURATION: *Two hours per week*

COURSE DETAILS:

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Other Lecturer(s) Dr. (Mrs) C.A Akinremi and Dr. Amolegbe Saliu Alao

COURSE CONTENT:

Isomerism of complexes. Theories of bonding; Valence bond, crystal field and Ligand field theories. Stereochemistry of complexes and John-Teller distortions. Stability of complex and chelate effect. Physical methods of structural investigation (Spectroscopic, magnetic and thermal properties). Preparations and reactions of complexes. Application of complexes.

COURSE REQUIREMENTS:

This is a compulsory course for all 400 LEVEL Chemistry students only. In view of this students are expected to participate in all the course activities and have minimum of 75% attendance to able to write the final examination.

READING LIST:

1. . Basola, F. and Johnson R. Coordination Chemistry , 2nd ed. W. A. Benjamin, Inc. New York. 1964.
2. Lee, J. D. A new Concise Inorganic Chemistry, 3rd Ed., Van Nostrand Reinhold (UK) Co. Ltd, England, 1977.
3. Cotton,F.A.; and Wilkinson,G. Advanced Inorganic Chemistry, a Comprehensive Text , 4th Ed., New York, 1988.
4. Wilkinson,G., Gillard,R.D.,and McCleverty, J.A.Comprehensive Coordination,Voll, Pergamon Press, Elmsford, New York, 1987.
5. David. N. Complexes and 1st row Transition elements 1st ed. Macmillian Press Ltd, London, 1974.

LECTURE NOTES

ISOMERISM OF COMPLEXES:

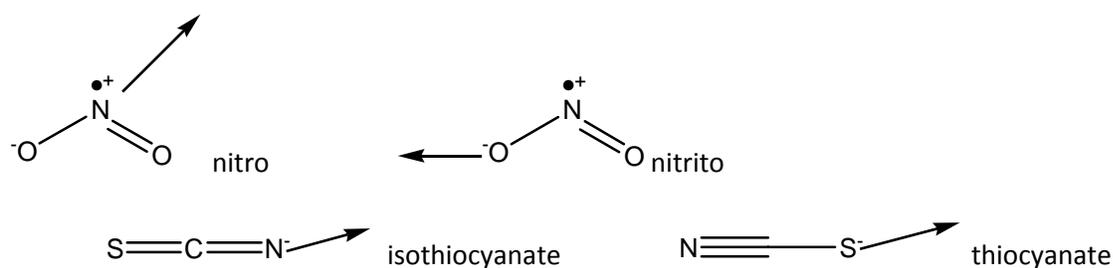
What is Isomerism? Isomerism occurs in four and six coordinate complexes, due to the stereochemical position of the ligands. Isomers are compounds with same molecular formula but different arrangement of their constituent atoms (i.e. different structural formula).

Isomerism can be divided into two classes: Constitutional isomerism and Stereoisomerism. These can be further subdivided as follows:

Constitutional isomerism

Compounds with the same empirical formulae but differ in atom connectivity. This includes linkage, coordination, polymerization, hydrate, ligand and ionization isomerism.

Linkage isomerism: applies to ambidentate ligands eg $-\text{NO}_2$ —nitro and $-\text{ONO}$ —nitrito



Ionisation isomerism: This occurs when isomers produce different ions in solution. Often there is an exchange of an anionic ligand with a counterion examples: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ (give a white precipitate with BaSO_4 and no precipitate with AgNO_3) and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ (give a white precipitate with AgNO_3 and no precipitate with BaSO_4).

Hydrate isomerism: This is a type of ionization isomerism. Example, $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$, $[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ {With AgNO_3 , 1, 2, 3 Cl^- ions are precipitated respectively}. $[\text{CrCl}_3(\text{H}_2\text{O})_6]$ has three differently coloured isomers with different conductivities in aqueous solution, since they produce different number of ions.

Molecular Formula	Moles of ion deduced from conductivity	Number of Chloride ion deduced from AgCl ppt	Structural Formula	Colour
$\text{CrCl}_3(\text{H}_2\text{O})_6$	4	3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} \cdot 3\text{Cl}^-$	Violet
$\text{CrCl}_3(\text{H}_2\text{O})_6$	3	2	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{+2} \cdot 2\text{Cl}^- \cdot \text{H}_2\text{O}$	Light green
$\text{CrCl}_3(\text{H}_2\text{O})_6$	2	1	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+ \cdot \text{Cl}^- \cdot 2\text{H}_2\text{O}$	Dark green

They precipitate different amount of AgCl with AgNO_3 solution because they contain different number of free chloride ions (Cl^-).

Coordination isomerism: This occurs when ligands are distributed differently between the two metal centres, for example $[\text{Co}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CoCl}_4]$, $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{IV}}\text{Cl}_6]$ and $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2][\text{Pt}^{\text{II}}\text{Cl}_4]$

Polymerisation isomerism: Here the isomers have the same empirical formula with different values of n . For example, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ -----both polymers have the empirical formula $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_n$.

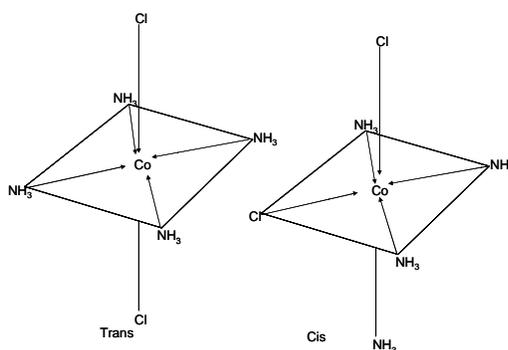
Ligand Isomerism: Here, the ligands have different isomeric forms, example, $[\text{CoCl}(\text{en})_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me})\text{Cl}_2]$ - $\text{NH}_2\text{C}_6\text{H}_4\text{Me}$ -toluidine could be o-, m- or p-form.

Stereoisomerism

Same connectivities but individual atoms are arranged differently in space. This includes geometrical and optical isomerism.

Geometrical isomerism: This is based on how the ligands are arranged around the metal. This occurs especially around 6-coordinates-octahedral and 4-coordinates-square planar.

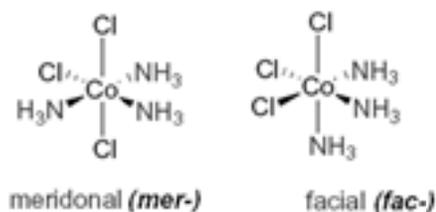
6-coordinate complexes of the type MA_2B_4 exhibit cis/trans (geometric) isomerism.



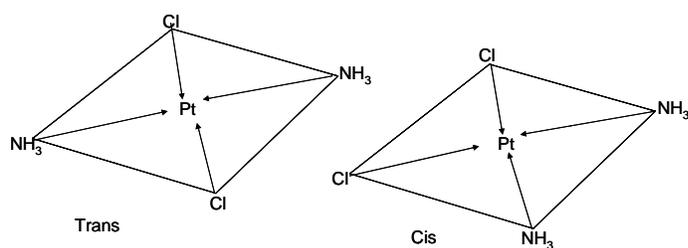
Example: $[Co(NH_3)_4Cl_2]^+ Cl^-$

The cis form is blue-violet coloured crystals while the trans form is green coloured crystals. The structures of these isomers differ in the orientation of the two chloride ions around the Co^{3+} ion. In the trans isomer, the chlorides occupy positions across from one another in the octahedron. In the cis isomer, they occupy adjacent positions.

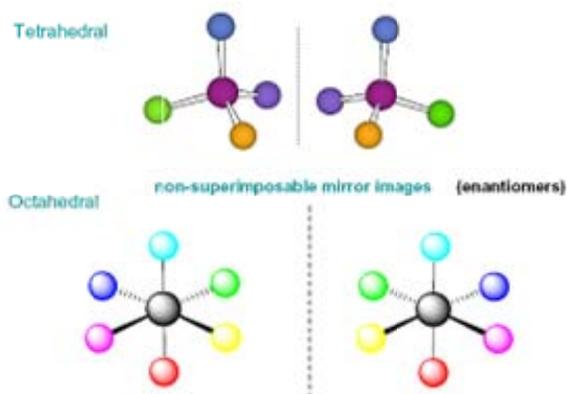
The type MA_3B_3 exhibit meridional(*mer-*)/facial(*fac-*).



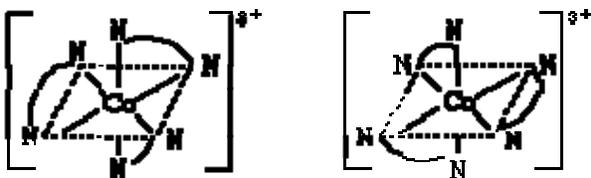
4-coordinates-Cis/trans isomers are also possible in four-coordinate complexes that have a square-planar geometry. The figure ($PtCl_2(NH_3)_2$) shows the structures of the *cis* and *trans* isomers of dichlorodiammineplatinum(II). The *cis* isomer is used as a drug to treat brain tumors, under the trade name *cisplatin*.



Optical isomerism: Optical isomers have the ability to rotate plane-polarized light in opposite directions. Optical isomers exist when the molecules of the substances are mirror images but are not superimposable upon one other.



For example [Co(en)₃], an octahedral compound



VALENCE BOND THEORY:

This theory considers which atomic orbital on the metal is used for bonding. Ligands must have a lone pair of electrons and the metal must have an empty orbital of suitable energy available for bonding. It involves promotion of electrons to another orbital giving rise to hybrid orbitals (that is different hybridization).

Limitations

1. Provides no explanation for their electronic spectra or their kinetic inertness which is characteristic of low spin d^6 .
2. Doesnot explain why the magnetic properties vary with temperature

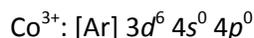
Application of VBT to Coordination Compounds

the sp , sp^2 , sp^3 , dsp^3 , and d^2sp^3 orbitals. It is easy to apply the valence-bond theory to some coordination complexes:

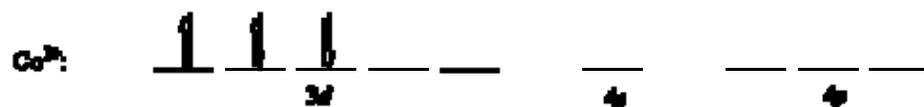
1. $\text{Co}(\text{NH}_3)_6^{3+}$ ion. We start with the electron configuration of the transition- metal ion.



We then look at the valence-shell orbitals and note that the $4s$ and $4p$ orbitals are empty.



Concentrating the $3d$ electrons in the d_{xy} , d_{xz} , and d_{yz} orbitals in this subshell gives the following electron configuration.



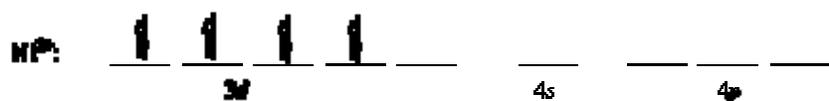
The $3d_{x^2-y^2}$, $3d_z^2$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals are then mixed to form a set of empty d^2sp^3 orbitals that point toward the corners of an octahedron. Each of these orbitals can accept a pair of nonbonding electrons from a neutral NH_3 molecule to form a complex in which the cobalt atom has a filled shell of valence electrons.



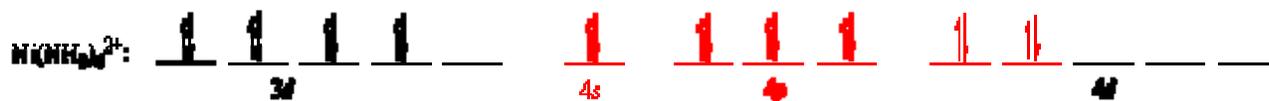
2. At first glance, complexes such as the $\text{Ni}(\text{NH}_3)_6^{2+}$ ion seem hard to explain with the valence-bond theory. We start, as always, by writing the configuration of the transition-metal ion.



This configuration creates a problem, because there are eight electrons in the $3d$ orbitals. Even if we invest the energy necessary to pair the $3d$ electrons, we can't find two empty $3d$ orbitals to use to form a set of d^2sp^3 hybrids.



There is a way around this problem. The five $4d$ orbitals on nickel are empty, so we can form a set of empty sp^3d^2 hybrid orbitals by mixing the $4d_{x^2-y^2}$, $4d_{z^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals. These hybrid orbitals then accept pairs of nonbonding electrons from six ammonia molecules to form a complex ion.



The valence-bond theory therefore formally distinguishes between "inner-shell" complexes, which use $3d$, $4s$ and $4p$ orbitals to form a set of d^2sp^3 hybrids, and "outer-shell" complexes, which use $4s$, $4p$ and $4d$ orbitals to form sp^3d^2 hybrid orbitals.

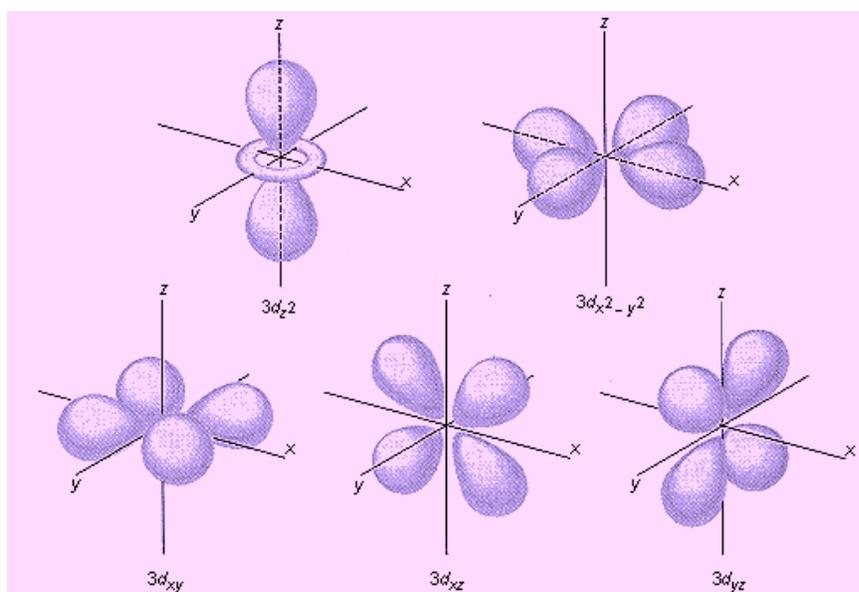
3. $\text{Fe}(\text{III})$ --- d^5 --High spin-octahedral will have sp^3d^2 hybrids, Low spin-will have d^2sp^3 hybrids
4. $\text{Cr}(\text{III})$ --- d^3 , d^2sp^3

CRYSTAL FIELD THEORY

In crystal field theory, a ligand lone pair is modeled as a point negative charge. This theory tried to describe the effect of the electrical field of neighboring ions on the energies of the valence orbitals of an ion in a crystal. Crystal field theory made the following assumptions:

1. Ligands are treated as point charges
2. There is no interaction between metal orbitals and ligand orbital
3. The d-orbitals on the metal all have the same energy (degenerate) in the free atom. This is destroyed when a complex is formed because the orbital

Crystal field theory was developed by considering two compounds: manganese(II) oxide, MnO, and copper(I) chloride, CuCl.

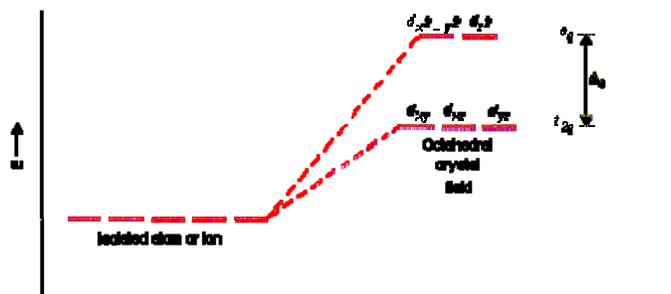


Octahedral Crystal Fields

For this model, the 6-point negative charges representing the ligands interact strongly with the central metal ion and the stability of the complex stems in large part from the attractive interaction between opposite charges.

In the presence of the octahedral crystal field, d orbitals are split into a lower energy triply degenerate set (t_{2g}) and a higher energy doubly degenerate set (e_g) separated by Δ_o or $10Dq$ (**crystal field splitting energy**). The energy difference between the actual distribution of electrons and that for all electrons in

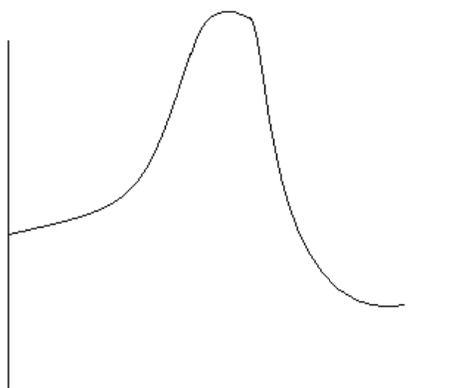
the uniform field levels is called the **crystal field stabilization energy (CFSE)**[This is the measure of the net energy of occupation of the d orbitals relative to their mean energy]. The energy level in which the negative charge due to the ligands is evenly distributed over a sphere instead of being localized at six points defines the barycentre of the arrays of levels. The two e_g orbitals lie $\frac{3}{5}\Delta_o$ above the barycentre and the three t_{2g} orbitals lie at $\frac{2}{5}\Delta_o$ below it.



[The Dq notation has mathematical origins in CFT but Δ_o is preferred because of its experimentally determined origin.]

The size of Δ_o can be measured easily using UV-Vis spec.

Example: $[Ti(OH_2)_6]^{3+}$, hexaaquatitanium(III) ion ($Ti=d^1$). The complex absorbs light of the current wavelength (energy) to promote the electron from the t_{2g} level to the e_g level. ($20300cm^{-1}=493nm$)



$$1kJmol^{-1}=83.7cm^{-1}$$

$$\Delta_o = \frac{20300}{83.7} = 243kJmol^{-1}$$

The single d electron occupies an energy level $\frac{2}{5}\Delta_o$ which is below the average energy of the d orbitals because of the CFSE of the d-orbitals.

$CFSE = \frac{2}{5} \times 243 = 97 \text{ kJ mol}^{-1}$ As a result the complex is stable.

The magnitude of Δ_o depends on three factors

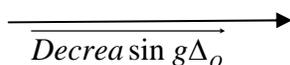
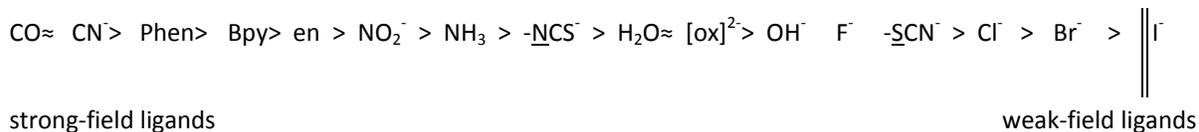
1. the nature of the ligands
2. the charge of the metal ion
3. The position of the metal in the periodic table (whether the metal is in 1st, 2nd or 3rd row)

The strength of the crystal field are classified either as weak field or strong field

Δ_o (weak field) < Δ_o (strong field)

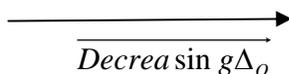
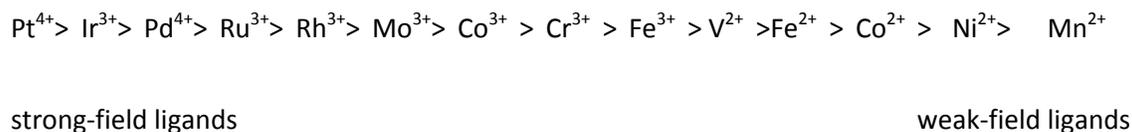
Explanation for Factors

Factor 1: The spectrochemical series of ligands:



NB: Ligands with same donor atoms are close together in the series.

Factors 2&3: Identity of the central metal ion



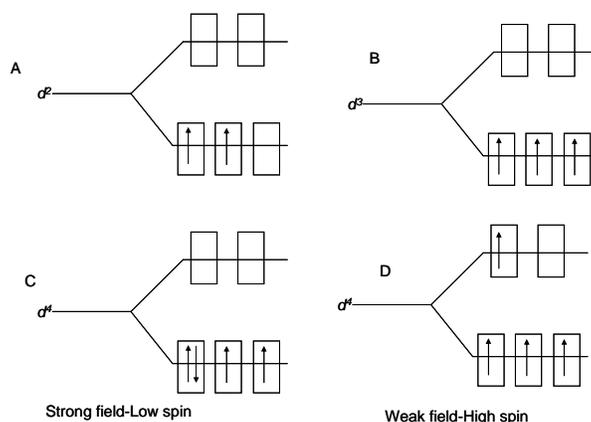
The value of Δ_o increases with increasing oxidation number of the central metal ion. The variation of oxidation number reflects the smaller size of more highly charged ions and consequently shorter metal-ligand distances and stronger interaction energies.

The value of Δ_o increases down the group. This reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interaction of the ligands.

High and Low spin octahedral complexes

The ground state configuration of a complex reflects the relative values of the CFSE parameter and the pairing energy.

Demonstration



For C: When the electrons pair up as for C above, it experiences a strong coulombic repulsion between the spin-paired electrons which is called pairing energy P.

C is t_{2g}^4 , $CFSE=1.6 \Delta_o$, therefore, the pairing energy is P and the net stabilization is $1.6 \Delta_o - P$.

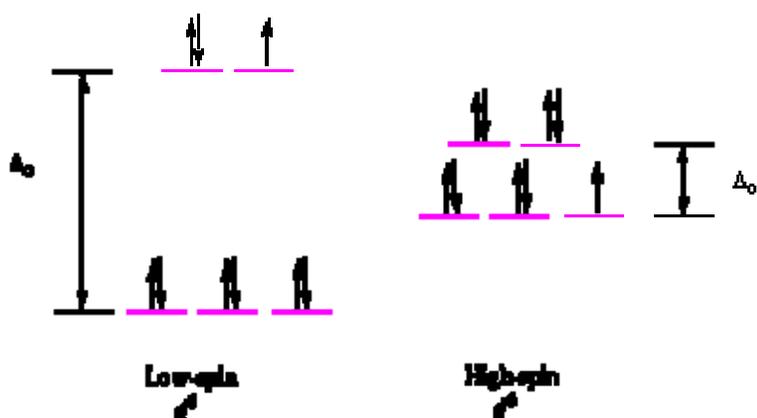
For D: There is no pairing energy. D is $t_{2g}^3 e_g^1$, $CFSE=-(3 \times 0.4 \Delta_o) + 0.6 \Delta_o = 0.6 \Delta_o$

Therefore, if $\Delta_o < P$ this is for high spin(Weak field), If $\Delta_o > P$, this is for low spin(Strong field)

d^n	High spin=Weak field		Low spin=Strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4 \Delta_o$		
d^2	$t_{2g}^2 e_g^0$	$-0.8 \Delta_o$		
d^3	$t_{2g}^3 e_g^0$	$-1.2 \Delta_o$		
d^4	$t_{2g}^3 e_g^1$	$0.6 \Delta_o$	$t_{2g}^4 e_g^0$	$-1.6 \Delta_o + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0 \Delta_o + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4 \Delta_o$	$t_{2g}^6 e_g^0$	$-2.4 \Delta_o + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8 \Delta_o$	$t_{2g}^6 e_g^1$	$-1.8 \Delta_o + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2 \Delta_o$		
d^9	$t_{2g}^6 e_g^3$	$-0.6 \Delta_o$		
d^{10}	$t_{2g}^6 e_g^4$	0		

Eg for d^6 , $CFSE = -(4 \times 0.4 \Delta_o) + (2 \times 0.6) = -0.4 \Delta_o$

Low spin $d^6 = 2.4 \Delta_o + 2P$ and not $3P$ because for spin pairing associated with the two pairs of electrons in excesses of the one in the high spin configuration.

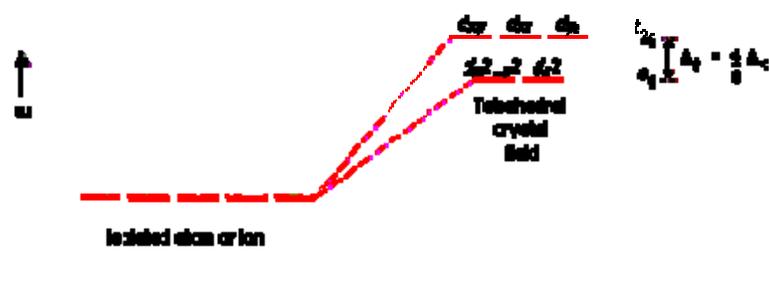


Tetrahedral Crystal Fields

Here the e orbitals lie below the t_2 orbitals. The effect of a tetrahedral crystal field on a set of d orbitals is to split them into 2 sets: the e pair (which points directly at the ligands) lies lower in energy than the t_2 triplet (which points more directly towards the ligands).

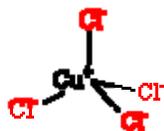
$$\Delta_t = \frac{4}{9} \Delta_o$$

The pairing energy is invariably more favorable than Δ_t and only high spin tetrahedral complexes are commonly encountered. CFSE calculated as in octahedral but with reverse of $e = \frac{3}{5} \Delta_t$ and $t_2 = -\frac{2}{5} \Delta_t$.



The d^n complexes have these configuration: $e^1, e^2, e^2 t_2^1, e^2 t_2^2, e^2 t_2^3, e^3 t_2^3, e^4 t_2^3, e^4 t_2^4, e^4 t_2^5, e^4 t_2^6$ as n increases from 1 to 10.

Example: Each Cu^+ ion in copper(I) chloride is surrounded by four Cl^- ions arranged toward the corners of a tetrahedron, as shown in the figure below. CuCl is therefore a model for a tetrahedral complex in which a transition-metal ion is coordinated to four ligands.

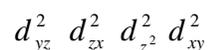


Once again, the negative ions in the crystal split the energy of the d atomic orbitals on the transition-metal ion. The tetrahedral crystal field splits these orbitals into the same t_{2g} and e_g sets of orbitals as does the octahedral crystal field.

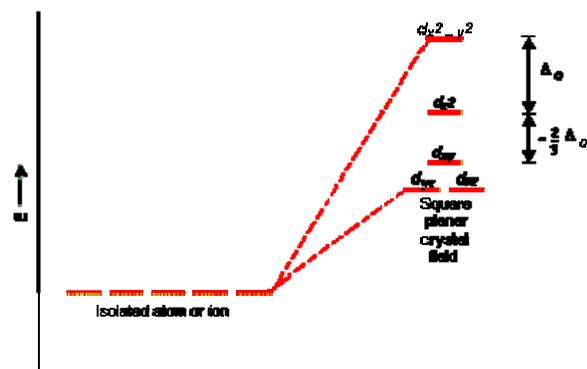
To understand the splitting of d orbitals in a tetrahedral crystal field, imagine four ligands lying at alternating corners of a cube to form a tetrahedral geometry, as shown in the figure below. The $d_{x^2-y^2}$ and d_z^2 orbitals on the metal ion at the center of the cube lie between the ligands, and the d_{xy} , d_{xz} , and d_{yz} orbitals point toward the ligands. As a result, the splitting observed in a tetrahedral crystal field is the opposite of the splitting in an octahedral complex. Because a tetrahedral complex has fewer ligands, the magnitude of the splitting is smaller. The difference between the energies of the t_2 and e orbitals in a tetrahedral complex (Δ_t) is slightly less than half as large as in octahedral (Δ_o).

Square-Planar Complexes

The crystal field theory can be extended to square-planar complexes, such as $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. A d^8 configuration, coupled with a strong ligand field favours the formation of square planar complexes. The arrangement becomes energetically favorable when there are eight d electrons and the crystal field is strong enough to favour the low spin arrangement.



The splitting of the d orbitals in these compounds is shown in the figure below.



Many square planar complexes are found for the $4d^8$ and $5d^8$ complexes eg in $\text{Rh}(\text{I})$, $\text{Ir}(\text{I})$, $\text{Pt}(\text{II})$, $\text{Pd}(\text{II})$ and $\text{Au}(\text{III})$ where there is a large ligand field splitting. $3d$ metal complexes eg $[\text{NiX}_4]^{2-}$ with X as halogen is usually tetrahedral because CFSE is quite small. But if the ligand is high up in the spectrochemical series, it results in the formation of the square planar complex eg $[\text{Ni}(\text{CN})_4]^{2-}$.

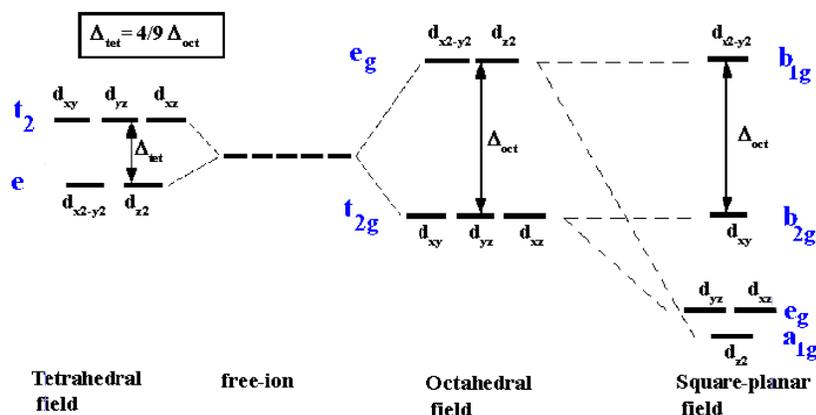
Questions:

1. Why is $[\text{NiCl}_4]^{2-}$ paramagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ diamagnetic?
2. Why is $[\text{NiCl}_4]^{2-}$ tetrahedral and paramagnetic while $[\text{Pd}(\text{Cl})_4]^{2-}$ and $[\text{Pt}(\text{Cl})_4]^{2-}$ are square planar and diamagnetic?—due to larger CFSplitting energy observed for 2nd and 3rd metal ion compared with their 1st row congener.
3. Explain why the $\text{Co}(\text{NH}_3)_6^{3+}$ ion is a diamagnetic, low-spin complex, whereas the CoF_6^{3-} ion is a paramagnetic, high-spin complex

Note

Compounds in which all of the electrons are paired are diamagnetic — they are repelled by both poles of a magnet. Compounds that contain one or more unpaired electrons are paramagnetic — they are attracted to the poles of a magnet. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of unpaired electrons in the complex. We can therefore determine whether a complex is high-spin or low-spin by measuring the strength of the interaction between the complex and a magnetic field.

Crystal field d orbital splitting diagrams for common stereochemistries.



Ligand field theories

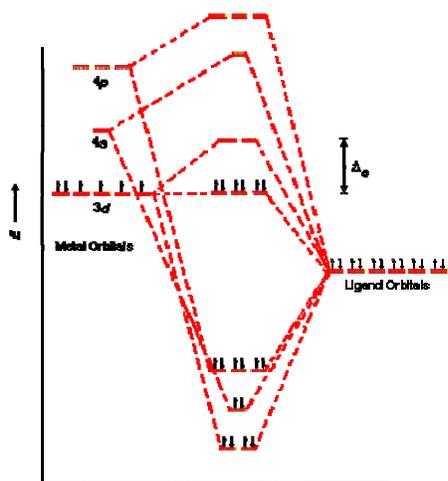
The valence-bond model and the crystal field theory explain some aspects of the chemistry of the transition metals, but neither model is good at predicting all of the properties of transition-metal complexes. The CFT is defective because it treats ligands as point charges and doesnot account for the overlap of ligand and metal atom orbitals. Also, it cannot account for the ligand spectrochemical series.

A third model, based on molecular orbital theory, was therefore developed that is known as ligand-field theory. [Ligand-field theory is more powerful than either the valence-bond or crystal-field theories. Unfortunately it is also more abstract]. This theory concentrates on the d-orbitals of the central metal atom. It provides a more substantial framework for understanding the origins of Δ_o .

Illustration of the application of the MOT to d-block metal complexes:

σ -bonding

The ligand-field model for an octahedral transition-metal complex such as the $\text{Co}(\text{NH}_3)_6^{3+}$ ion assumes that the 3d, 4s, and 4p orbitals on the metal overlap with one orbital on each of the six ligands to form a total of 15 molecular orbitals, as shown in the figure below.



An MO diagram for the formation of $[\text{ML}_6]^{n+}$ (where M is a first row metal) using the ligand group approach. The bonding only involves M-L σ -interactions.

Six of these orbitals are *bonding molecular orbitals*, whose energies are much lower than those of the original atomic orbitals. Another six are *antibonding molecular orbitals*, whose energies are higher than those of the original atomic orbitals. Three are best described as *nonbonding molecular orbitals*, because they have essentially the same energy as the 3d atomic orbitals on the metal.

Metal orbital	Symmetry Label	Degeneracy
S	a_{1g}	1
P_x, P_y, P_z	t_{1u}	3

$d_{x^2-y^2}, d_{z^2}$	e_g	2
d_{xy}, d_{yz}	t_{2g}	3

Each ligand provide one pair of electrons.

Explanation: *Ligand-field theory enables the 3d, 4s, and 4p orbitals on the metal to overlap with orbitals on the ligand to form the octahedral covalent bond skeleton that holds this complex together. At the same time, this model generates a set of five orbitals in the center of the diagram that are split into t_{2g} and e_g subshells, as predicted by the crystal-field theory. As a result, we don't have to worry about "inner-shell" versus "outer-shell" metal complexes. In effect, we can use the 3d orbitals in two different ways. We can use them to form the covalent bond skeleton and then use them again to form the orbitals that hold the electrons that were originally in the 3d orbitals of the transition metal.*

Example

1. Low spin $[\text{Co}(\text{NH}_3)_6]^{3+}$ - Has 18 electrons (valence 6 from $\text{Co}(\text{III})$ plus two each from each ligand) occupy the a_{1g} , t_{1u} , e_g and t_{2g} MOs bonding.
2. High Spin $[\text{CoF}_6]^{3-}$ Has 18 electrons available: 12 occupying the a_{1g} , t_{1u} and MOs(bonding), 4 electrons occupying the t_{2g} level and the remaining 2 electrons occupying the e_g^* level.

The energy separation of the t_{2g} and e_g^* level determine whether a complex is high spin or low spin.

Π -bonding

The metal d_{xy}, d_{yz} atomic orbitals (t_{2g} sets which are non-bonding in an $(\text{ML}_6)^{n+}$ - σ -bonded complex) may overlap with ligands orbitals of the correct symmetry to give Π -interactions. This renders the t_{2g} AO no longer nonbonding on the metal atom. There are two types of ligand: Π donor and Π -acceptor.

Π donor: This is a ligand that donates electrons to the metal centre in an interaction that involves a filled ligand orbital and an empty metal orbitals. This includes Cl^- , Br^- , OH^- , H_2O , I^- . The metal-ligand Π -interaction involves transfer of electrons from filled ligand p-orbitals to the emtal centre. Thus the electron density is transferred from the ligand to the metal. This type of complex is favored when the central metal has a high oxidation state and is short of electrons. This ligand Π orbitals are lower

in energy than the metal t_{2g} orbitals. The delocalization of π electrons from the ligand to the metal reduces the value Δ_o .

π -acceptors: Examples are CO, CN^- , NO^+ , N_2 and alkenes. The metal-ligand π bonds arise from the back donation of electrons from the metal centre to vacant antibonding orbitals on the ligands. The π -acceptors ligands have empty π orbitals. The π orbitals of the ligands are of higher energy than the metal t_{2g} orbitals. No electrons are added as the ligand π orbitals are empty but the π -interaction increases the value of Δ_o .

This accounts for the position of the strong field ligands at the right of the spectrochemical series.

JAHN-TELLER EFFECT

According to the Jahn-Teller theorem, any molecule or complex ion in an electronically degenerate state will be unstable relative to a configuration of lower symmetry in which the degeneracy is absent. The chief applications of this theorem in transition-metal chemistry are in connection with octahedrally coordinated metal ions with high-spin d^4 , low-spin d^7 , and d^9 configurations; in each of these cases the t_{2g} orbitals are all equally occupied (either all half filled or all filled) and there is a single electron or a single vacancy in the e_g orbitals. Either an e_g or an e_g^3 configuration gives rise to a doubly degenerate (E) ground state, and thus a distortion of the octahedron is expected. In other words, high-spin d^4 , low-spin d^7 , and d^9 ions should be found in distorted, not regular, octahedral environments. It has been found by experiment that, with few possible exceptions, this is the case. The exceptions do not necessarily constitute violations of the Jahn-Teller theorem, because the slightness of the distortions may be within experimental error.

PREPARATIONS OF COMPLEXES

A wide variety of methods are used in synthesizing coordination compounds. They are:

- 1) Substitution reaction in aqueous solution
- 2) Substitution reaction in non-aqueous solution
- 3) Substitution reaction in the absence of solvents (Direct combination reaction)
- 4) Thermal dissociation of solid complexes
- 5) Oxidation- Reduction reaction
- 6) Catalysis
- 7) Substitution reactions without metal- ligand cleavage
- 8) Trans effect
- 9) Preparation of cis-trans isomers
- 10) Preparation of optically active compounds
- 11) Preparation of metal carbonyls and organometallic compounds

Synthesis of complexes i.e coordination compounds is of two types:

- (i) Werner complexes and (ii) organometallic compounds (metal-carbon bond)

Several different but related experimental methods can be used to prepare metal complexes. The methods of choice depend upon the system in question, and not all methods are necessarily applicable to the synthesis of a particular compound. In addition, certain experimental procedures are expected to be carried out so as to isolate the product from the reaction mixture in pure and good yield.

REACTIONS OF METAL COMPLEXES

Complexes undergo substitution reactions i.e replacement reactions as their prominent reaction which include:

- i) Acid hydrolysis
- ii) Acid-catalysed aquation

- iii) Anation
- iv) Base hydrolysis
- v) Reactions without metal-ligand bond cleavage

STABILITY OF CHEMISTRY AND CHELATE EFFECT

To understand the solution of chemistry of metals; nature and stability of the complexes must be understood. Metal complexes are formed in solution by stepwise reaction and equilibrium constants can be written for each step.



$$K_1 = \frac{[ML]}{[M] + [L]}$$



$$k_n = \frac{[ML_n]}{[ML_{n-1}] + [L]}$$



$$\beta_n = \frac{[ML_n]}{[M] + [L]^n}$$

Factors that Affect Stability of Metal Complexes

The stability constant of a metal complexes depending upon :

- 1) The metal ion
- 2) The nature of the ligands

- 3) The solvents to be used
- 4) Chelate effect