

**AS-2812**  
**B. Sc. (Fifth Semester) Examination 2013**  
**CHEMISTRY**  
**CBT 502**  
**(Inorganic Chemistry-iii)**

*Time Allowed: Three hours*

*Maximum Marks: 30*

**Section- 'A'**  
**(Short Answer Type Questions)**

**10x1= 10**

*Note: Attempt all the questions. Each question carries 1 mark.*

1. Choose the correct alternatives:
  - (i) (c) diamagnetic
  - (ii) (c) Pt(II)
  - (iii) (a) 2
  - (iv) (b)  $\Delta S = 0$
  - (v) (b) Gd
  - (vi) Curie-Wiess equation.

**Ans.**

Materials that display exchange behaviour can usually be treated with a modification of Curie law's and given by following Curie-Wiess equation:

$$\chi_M = C/(T-\Theta)$$

$\chi_M$  = magnetic susceptibility ; T= absolute temperature;  $\Theta$  is a constant with units of temperature.  $C = N\mu_0\mu^2/3k$

- (vii) Explain why the stability of  $\text{Co}^{3+}$  complex >  $\text{Co}^{2+}$  complex even if the ionic size of central metal ion is almost same.

**Ans.**

Charge/radius ratio for the central ion is called ionic potential or polarising power of the cation. In case of  $\text{Co}^{3+}$  the ionic potential is higher due to high charge on it than  $\text{Co}^{2+}$  and because of this reason the stability of former is greater than later.

- (viii) Write statement of John-Teller theorem.

**Ans.**

This theorem states that "any non-linear molecular system possessing degenerate electronic states will be unstable and undergo distortion to form a system of lower symmetry and lower energy and thus will remove degeneracy".

- (ix) Predict the different types of electronic transition for  $d^2$  high spin octahedral complex.

**Ans.**

Three transitions are possible:



(x) Write down the electronic configuration and ground state term symbol for Sm.



### Section- 'B'

#### (Long Answer Type Questions)

5x4= 20

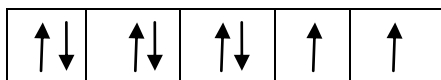
*Note: Attempt any five questions. Each question carries 4 marks.*

2. Explain why:-

(a) All the octahedral Ni(II) complexes are outer orbital.

The electronic configuration of Ni(II) is as follows:

*d*-orbital



According to VBT the 8- electron present in Ni(II) can not be rearranged if it forms inner orbital octahedral complex because in that case it requires two empty *d*-orbital to form  $d^2sp^3$  hybrid orbital which is not possible . This is why all the octahedral Ni(II) complexes form outer orbital complex.

(b) Tetrahedral Ni(II) complexes show magnetic moments up to 4.1BM.

The observed magnetic moment of Ni(II) is higher than spin-only values due to spin-orbit coupling which may be measured with this formula:

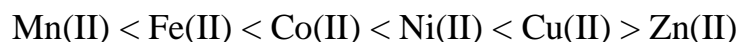
$$\mu = \mu_{\text{spin-only}} \left( \frac{1 - \alpha\lambda}{\Delta} \right)$$

$\lambda$  is negative in case of more than half-filled ion and for Ni(II) and additionally the value of  $\Delta_t$  is smaller than  $\Delta_o$  therefore it shows magnetic moment upto 4.1 BM in its tetrahedral complex in case of certain weak ligand like I.

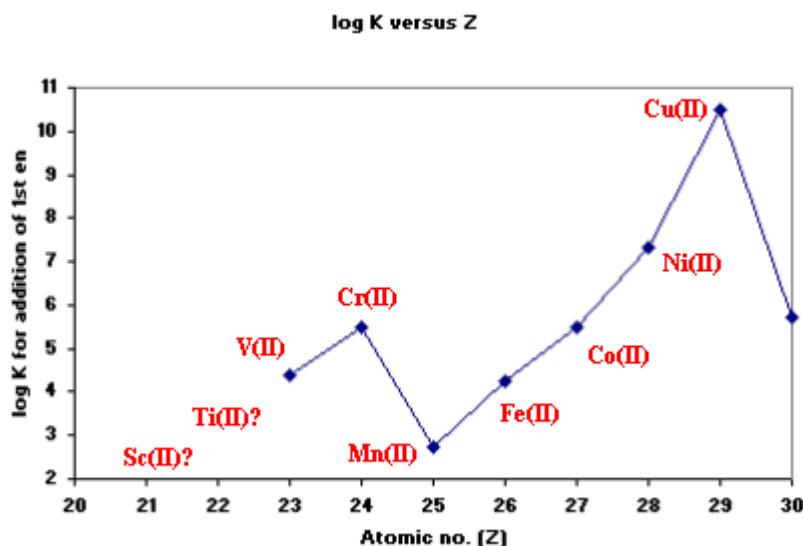
3. Discuss Irving-William order of stability of divalent ions of first row transition elements.

Irving William order from net

The general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:



This trend is essentially independent of the ligand. In the case of 1,2-diaminoethane (en), the first step-wise stability constants ( $\log K_1$ ) for M(II) ions are shown below.

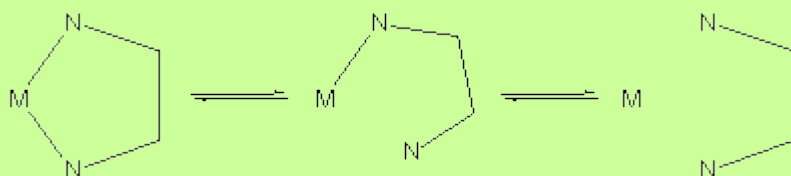


4. Write the effect of the following properties on the stability of metal complexes:  
(a) Charge and size

The larger the number of the chelate rings in a complex, the greater its stability.

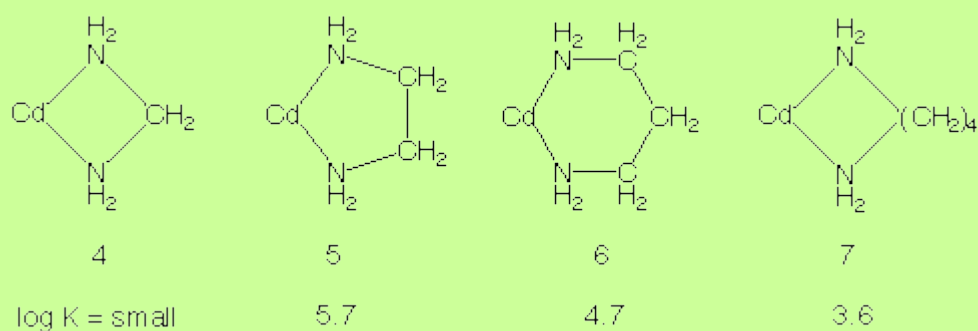
The increased stability of complexes containing chelating ligands over those containing comparable monodentate ligands can be envisaged as having the following physical basis. Suppose we have a metal ion in solution, and we attach to it a monodentate ligand, followed by a second monodentate ligand. These two processes are completely independent of each other. But suppose we have a metal ion and we attach to it one end of a chelating ligand (it's

reasonable to assume that when we put a chelate ligand onto a metal, it happens in a stepwise fashion, i.e. one end attaches first and then the other end). The point is that the attachment of the second end of the chelate is now no longer an independent process: once one end is attached, the other end, rather than floating around freely in solution, is anchored by the linking group in reasonably close proximity to the metal ion, and is therefore more likely to join onto it than a comparable monodentate ligand would be.



Similarly, for the reverse reaction, the dissociation of two monodentate ligands from the metal centre again consists of two independent processes, whereas for a chelate ligand, if one end dissociates, it is still held in the vicinity by the linking group and is therefore more likely to reattach itself to the metal. To get complete dissociation of the bidentate ligand we have to break the other metal-ligand bond before this happens.

One further point about chelating ligands. Certain ring sizes are more preferable than others. Here are some data for cadmium complexes of didentate amines of the type  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ , where  $n = 1-4$ , i.e. ring sizes 4-7.



When  $n = 1$ , the resulting four-membered ring is too strained at the  $\text{sp}^3$ -hybridized carbon which wants to try to have bond angles of  $109^\circ$ . It is worth pointing out, however, that there are lots of perfectly stable four-membered chelate rings that contain an  $\text{sp}^2$ -hybridized carbon in that position, such as carboxylates ( $\text{O}_2\text{CR}$ ), dithiocarbamate ( $\text{S}_2\text{CNR}_2$ ), xanthate ( $\text{S}_2\text{COR}$ ) and so on. When  $n = 2$ , the resulting five-membered ring is obviously the most stable one available, though  $n = 3$  (six-membered ring) isn't bad either. When we get to  $n = 4$ , you can see that the stability of the seven-membered ring is starting to drop again. This is because in

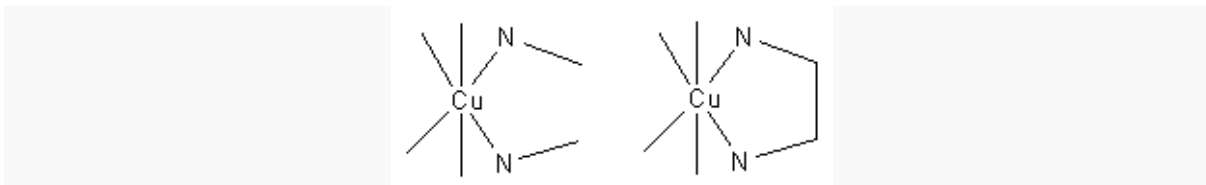
order to accommodate the longer hydrocarbon chain, the two nitrogens are being forced too far apart. The angle occupied by a chelate ligand, in this case the N-Cd-N angle, is called the *bite angle*, and obviously in an octahedral complex, it's going to be happiest at 90°. If we try to force the nitrogens too far apart so that they have a much bigger bite angle, eventually something will have to give, and one end of the ligand will dissociate. Hence the lower stability constant.

Chelating ligands all have the same basic design principles: two or more donor atoms (which can of course be the same or different) are joined by linking spacer groups. When you consider that there is an almost unlimited choice of spacer groups, and a vast number of combinations of donor atoms (and, if appropriate, substituents on those atoms), you will appreciate that there is an almost limitless number of chelate ligands we can prepare, and by changing things like donor atom, bite angle, electronic properties and so on we can fine tune the desired properties of the ligand. Notable recent successes, for example, include Jacobsen's asymmetric epoxidation catalyst which contains an optically active ligand.

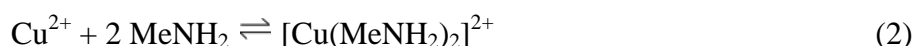
### *Any other example of chelate ring size*

(b) Chelate effect

#### **The Chelate effect**



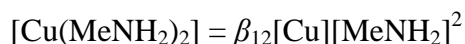
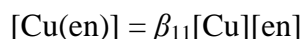
$\text{Cu}^{2+}$  complexes with methylamine (left) and ethylenediamine (right). Consider the two equilibria, in aqueous solution, between the copper(II) ion,  $\text{Cu}^{2+}$  and ethylenediamine (en) on the one hand and methylamine,  $\text{MeNH}_2$  on the other.



In (1) the bidentate ligand ethylenediamine forms a chelate complex with the copper ion. Chelation results in the formation of a five-membered ring. In (2) the bidentate ligand is replaced by two monodentate methylamine ligands of approximately the same donor power, meaning that the enthalpy of formation of Cu—N bonds is approximately the same in the two reactions. Under conditions of equal copper concentrations and when the concentration of methylamine is twice the concentration of ethylenediamine, the concentration of the complex (1) will be greater than the concentration of the complex (2). The effect increases with the number of chelate rings so the concentration of the EDTA complex, which has six chelate rings, is much higher than a corresponding complex with two monodentate nitrogen donor

ligands and four monodentate carboxylate ligands. Thus, the phenomenon of the chelate effect is a firmly established empirical fact: under comparable conditions, the concentration of a chelate complex will be higher than the concentration of an analogous complex with monodentate ligands.

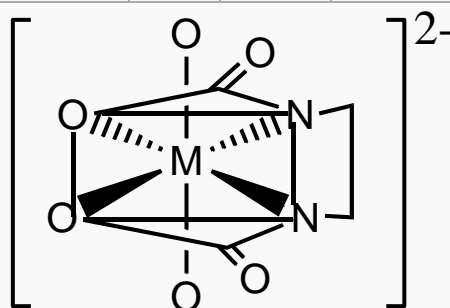
The thermodynamic approach to explaining the chelate effect considers the equilibrium constant for the reaction: the larger the equilibrium constant, the higher the concentration of the complex.



When the analytical concentration of methylamine is twice that of ethylenediamine and the concentration of copper is the same in both reactions, the concentration  $[\text{Cu}(\text{en})]^{2+}$  is much higher than the concentration  $[\text{Cu}(\text{MeNH}_2)_2]^{2+}$  because  $\beta_{11} \gg \beta_{12}$ .

The difference between the two stability constants is mainly due to the difference in the standard entropy change,  $\Delta S^\ominus$ . In equation (1) there are two particles on the left and one on the right, whereas in equation (2) there are three particles on the left and one on the right. This means that less entropy of disorder is lost when the chelate complex is formed than when the complex with monodentate ligands is formed. This is one of the factors contributing to the entropy difference. Other factors include solvation changes and ring formation. Some experimental data to illustrate the effect are shown in the following table.

Equilibrium	$\log \beta$	$\Delta G^\ominus$	$\Delta H^\ominus / \text{kJ mol}^{-1}$	$-T\Delta S^\ominus / \text{kJ mol}^{-1}$
$\text{Cd}^{2+} + 4 \text{MeNH}_2 \rightleftharpoons \text{Cd}(\text{MeNH}_2)_4^{2+}$	6.55	-37.4	-57.3	19.9
$\text{Cd}^{2+} + 2 \text{en} \rightleftharpoons \text{Cd}(\text{en})_2^{2+}$	10.62	-60.67	-56.48	-4.19



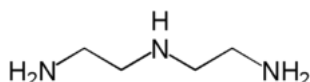
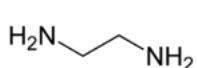
Metal-EDTA complex

These data show that the standard enthalpy changes are indeed approximately equal for the two reactions and that the main reason why the chelate complex is so much more stable is that the standard entropy term is much less unfavourable, indeed, it is favourable in this instance. In general it is difficult to account precisely for thermodynamic values in terms of changes in solution at the molecular level, but it is clear that the chelate effect is predominantly an effect of entropy. Other explanations, including that of Schwarzenbach, are discussed in Greenwood and Earnshaw.

The chelate effect increases as the number of chelate rings increases. For example the complex  $[\text{Ni}(\text{dien})_2]^{2+}$  is more stable than the complex  $[\text{Ni}(\text{en})_3]^{2+}$ ; both complexes are octahedral with six nitrogen atoms around the nickel ion, but dien (diethylenetriamine, 1,4,7-

triazahexane) is a tridentate ligand and en is bidentate. The number of chelate rings is one less than the number of donor atoms in the ligand. EDTA (ethylenediaminetetracetic acid) has six donor atoms so it forms very strong complexes with five chelate rings. Ligands such as DTPA, which have eight donor atoms are used to form complexes with large metal ions such as lanthanide or actinide ions which usually form 8- or 9- coordinate complexes.

5-membered and 6-membered chelate rings give the most stable complexes. 4-membered rings are subject to internal strain because of the small inter-bond angle in the ring. The chelate effect is also reduced with 7- and 8- membered rings, because the larger rings are less rigid, so less entropy is lost in forming them.



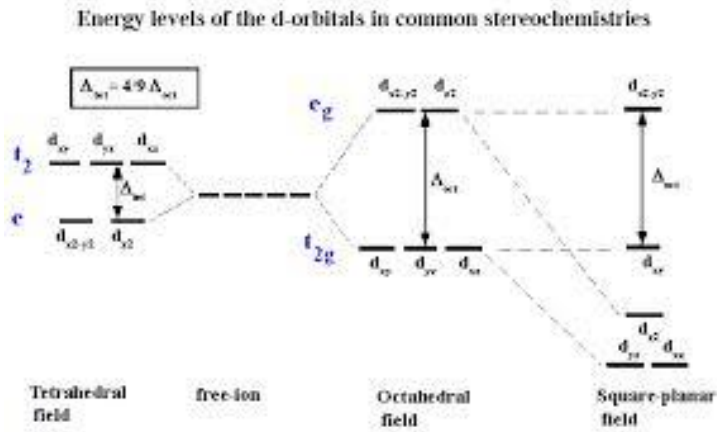
5. Write the main postulates of CFT and write the electronic configuration of central metal ion for the following complexes:
- Ethylenediamine (en) Diethylenetriamine (dien)
- $[\text{CoF}_6]^{3-}$
  - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
  - $[\text{Fe}(\text{CN})_6]^{4-}$
  - $[\text{RhCl}_6]^{3-}$

***Main postulates of CFT:***

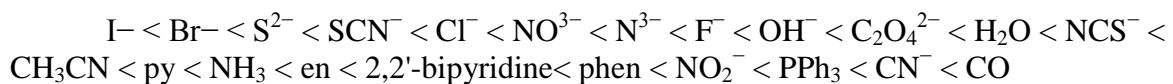
Crystal field theory (CFT) advanced by Bethe and Van Vleck was originally applied mainly to ionic crystals and is, therefore called Crystal Field Theory. Orgel popularised its application for inorganic chemistry during 1952.

- CFT considers a complex formation is a result of combination of central metal ion surrounded by other ions or molecules with electrical dipoles i.e. ligands. It regards these ligands as point charges or as point dipoles.
- CFT does not consider covalent bonding in complexes, but bonding between metal cation and ligands arises from electrostatic attraction between the nucleus of the metal cation and partial negative charge invariably present on the ligands. The bonds between the metal and the surrounding ligands are thus purely ionic. The repulsive forces are responsible for causing the splitting of the *d*-orbital of the metal cation.
- The CFT does not facilitate for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons i.e. it does not consider any orbital overlap.
- CFT gives a representation of bonding that is purely an electrostatic or coulombic between positively charged cation and negatively charged anions or dipolar ligand molecules.

***Splitting of d-orbital in different ligand field symmetry:***



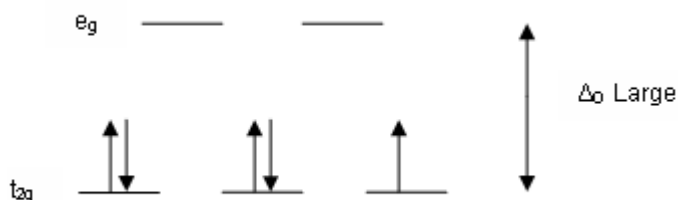
The **spectrochemical series** is an empirically-derived list of ligands ordered by the size of the splitting  $\Delta$  that they produce (small  $\Delta$  to large  $\Delta$ ):



It is useful to note that the ligands producing the most splitting are those that can engage in metal to ligand back-bonding.

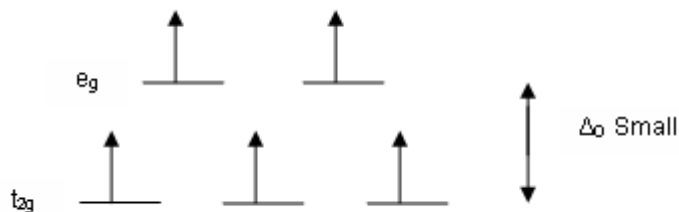
Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy. This splitting is affected by the following factors:

1. The nature of the metal ion.
2. The metal's oxidation state. A higher oxidation state leads to a larger splitting.  
the arrangement of the ligands around the metal ion.
3. The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy d groups.



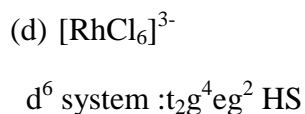
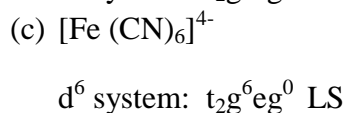
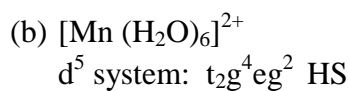
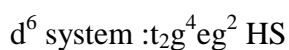
**Low Spin**  $[Fe(NO_2)_6]^{3-}$  crystal field diagram





### High Spin $[\text{FeBr}_6]^{3-}$ crystal field diagram

#### Electronic Configuration



6. Write selection rule for electronic transition of metal complexes and explain why  $d-d$  transition is not purely forbidden. Describe the molar absorptivities ( $\epsilon$ ) for various types of electronic transitions observed in complexes.

#### Selection rule (Brief description of Laporte and Spin Selection rule)

*Laporte or Orbital selection rule:*

$\Delta l = \pm 1$ : Only allowed transitions are those with change of parity: gerade ( $g$ ) to ungerade ( $u$ ) or vice versa or allowed but not  $g \rightarrow g$  or  $u \rightarrow u$ . Since all the  $d$  orbitals have gerade symmetry in centrosymmetric molecules, this means that all  $d-d$  transitions in octahedral complexes molecules, this means that all  $d-d$  transitions in octahedral complexes are formally forbidden. In  $Td$  complex, there is no center of symmetry and thus orbitals have no  $g$  or  $u$  designation.

*Spin selection rule*

A second selection rule states that any transition for which  $\Delta S \neq 0$  is forbidden and  $\Delta S = 0$  is allowed.

Table: Molar absorptivities ( $\epsilon$ ) for various types of electronic transitions observed in complexes.

Type of transition	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	Typical complexes
Spin forbidden Laporte forbidden	$10^{-3} - 1$	Many octahedral complexes of $d^5$ ions, e.g., $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
Spin allowed Laporte forbidden	$1 - 10$	Many octahedral complexes, e.g., $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
	$10 - 10^2$	Some square planar complexes, e.g., $[\text{PdCl}_4]^{2-}$
	$10^2 - 10^3$	Six-coordinate complexes of low symmetry; many square planar complexes, particularly with organic ligands
Spin allowed Laporte allowed	$10^2 - 10^3$	Some metal-to-ligand charge transfer bands in molecules with unsaturated ligands
	$10^2 - 10^4$	Acentric complexes with ligands such as acac or those having P, As, etc. as donor atoms
	$10^3 - 10^6$	Many charge transfer bands; transitions in organic species

7. Describe lanthanide contraction and its consequences.

The decrease in size of elements in the lanthanide series with increase in atomic number due to the poor screening power of the 'f' orbital is known as lanthanide contraction (Due to this poor shielding it is more strongly attracted by the nuclear charge resulting in decreased radius). This effect is also found in transition series where it is due to imperfect shielding of 'd' orbitals.

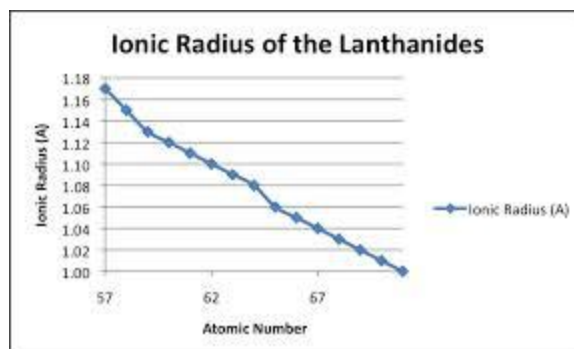


Fig: Crystal or ionic radii of  $\text{Ln}^{3+}$  ions as a function of their atomic numbers.

### Consequences:

Description of the following points at least with one example:

1. Anomalous behaviour of post-lanthanide elements
  - (a) Atomic and ionic radii of post lanthanide elements
  - (b) High density of post-lanthanide elements
2. Basic character of oxides,  $\text{Ln}_2\text{O}_3$  and hydroxides,  $\text{Ln}(\text{OH})_3$
3. Small variation in the properties on account of lanthanide contraction allows the separation of lanthanides by the method based on fractional crystallization and basicity differences.
4. Occurrence of Y with heavy lanthanides.

