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Paper: C9T: Inorganic Chemistry

Topic: Coordination Chemistry

Part 5(Last part)

Comments- Study the whole lesson thoroughly. Specially application of "**applications of 18 -electron rule to metal carbonyls"** is very important.

[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

18-electron Rule :

In nitrosyl and carbonyl complexes the valence electron of the metal ion and the 'e' donated by the ligand is equal to 18. The complexes having the 18 electrons in the valence shell of central metal ion are the stable complexes. It is called 18-e rule.

In case of $[Cr(CO)_6]$ complex the no. of e in the valence shell of $Cr = 6$, the 'e' donated by 6-CO molecule $= (6\times2) = 12$. Therefore the total no. of e in the valence shell of the metal ion $= (12+6) = 18$. Hence $[Cr(CO)_6]$ complex obeys 18-e rule and it is a stable complex.

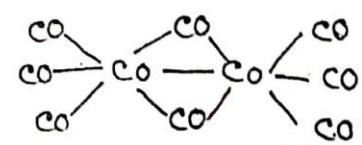
$[Fe(CO)_5]$, $[Ni(CO)_4]$, $[Mn_2(CO)_{10}]$ $[Co_2(CO)_8]$ obey 18-e rule

$[Fe(CO)_5] \Rightarrow [8+(5\times2)] = 18$

$[Mn_2(CO)_{10}] \Rightarrow [14+20+2] = 36.$

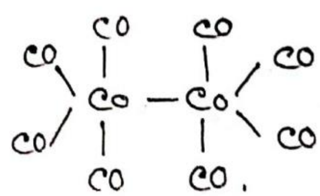
$[Co_2(CO)_8] \Rightarrow$

In solid state :



$[9+6+2+1] = 18$

In solution :



$[9+8+1] = 18$

with the help of this unpaired 'e' the value of magnetic moment (μ) canbe calculated.

In case of $[Cu(NH_3)_4]^{+2}$ ion EAN of Cu^{+2} is = 35. Hence the no of unpaired 'e' is = [36 (Atomic no. of crypton) − 35]

= 1.

Hence $\mu_{s.o} = \sqrt{n(n+2)} = \sqrt{1 \times (1+2)} = 1.732$ BM

In case $[Cr(NH_3)_6]^{3+}$ = [(24 − 3) + 12]

= 33.

The no. of unpaired 'e' = 3.

$\therefore \mu_{s.o} = \sqrt{3 \times 5} = \sqrt{15} = 3.87$ BM

Stability of Complex Compound :

In studying the formation of complex compound in soln two kinds of stability have to be distinguished ; these are given below ;

i) Thermodynamic stability :-

Thermodynamic stability can be classified into stable and unstable compounds.

- Stable complexes are those which posses sufficient stability to retain their identity in soln.
- Unstable complexes are those which are reversibily dissociated in soln into their components.

ii) Kinetic Stability :

Kinetic stability can be classified into ⇒ i) Labile complex ii) Innert complex

Labile complexes are those whose one or more ligand in the co-ordination sphere canbe rapidly replaced by other ligands. The ability of a complex to replace its one or more ligand by other ligand is called lability.

Innert complexes are those whose one or more ligand can either not be replaced or can be replace with difficulty by other ligands.

Kinetic Vs. Thermodynamics stability :

Since the terms labile and innert show the rates at which substitution of one ligand by other occurs, these term represent kinetic stability of complexes. These terms should not be confused with or used for thermodynamic stability terms [unstable and stable] Although thermodynamically stable complexes may be labile or innert and unstable complexes which are usually labile may also be innert. There is no correlation between thermodynamic and kinetic stability terms..

eg: $Hg(CN)_4]^{2-}$ which is thermodynamically very stable [formation const $= 10^{42}$] is labile. Since in sol^n it exchanges CN^- ligands with labelled CN ions [^{14}CN] at a very fast rate.

$$[Hg(CN)_4]^{2-} + 4\,^{14}CN^- \rightleftharpoons [Hg(^{14}CN)_4]^{2-} + 4CN^-$$

Thus the stability of this complex does not ensure its innertness.

On the other hand $[Co(NH_3)_6]^{3+}$ complex which is thermodynamically unstable can remain unchange in acid sol^n for weeks. Thus this complex is unstable but innert in acid sol^n.

It may be concluded that the innert complexes are not necessarily thermodynamically stable and labile complexes are not necessarily thermodynamically unstable

Condition for the formation of labile complexes.

We expect that in an octahedral complexes with e' in the antibonding eg* orbitals, the ligands will be relatively weakly bound and hence may be displaced easily. This leads us that all high spin d^4, d^5, d^6, complexes as well as complexes with d^7, d^8, d^9 and d^{10} configurations should be labile. Again when a complex has less than 3 three 'd' electrons, it will have one, two or three t_{2g} orbitals vacant; the metal can now be approached by another ligands along the directions of these vacant t_{2g} orbitals with relatively less electrostatic repulsion. This implies that a substitution reaction via a seven coordinate activated complexes will be favoured for such configurations, making the complex labile.

Some eg. of labile and inert octahedral complexes for various 'd' configuration illustrate this simple generalization

Labile		Inert	
d-confi.	example	d-config.	example
d^0	$[TiCl_6]^{2-}$	d^3	$[V(H_2O)_6]^{2+}$
d^1	$[Ti(H_2O)_6]^{3+}$	d^4 (LS)	$[Cr(CN)_6]^{4-}$
d^2	$[V(O\text{-}phen)_3]^{3+}$	d^5 (LS)	$[Fe(CN)_6]^{3-}$
d^4 (HS)	$[Cr(H_2O)_6]^{2+}$	d^6 (LS)	$[Fe(CN)_6]^{4-}$
d^5 (HS)	$[Mn(H_2O)]^{2+}$		
d^6 (HS)	$[Fe(H_2O)_6]^{2+}$		
d^7 (HS)	$[Co(H_2O)_6]^{2+}$		
d^8	$[Ni(en)_3]^{2+}$		
d^9	$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

EAN - Rule [Effective Atomic Number Rule]

On the basis of the concept of coordinate bond it is suggested that after the ligands have donated a certain no. of electron to the central metal ion to L-M bonding, the total no. of 'e' on the central atom, including those gained from ligand (L) in the bonding is called the EAN. (Effective atomic No) of the central metal ion. In many cases this total no. of e (EAN) surrounding the co-ordinated metal ion is equal to the atomic no. of the inert gas. This is called EAN rule.

When the EAN is 36 (crypton) 54 (Xenon), 86 (Radon) rule is said to be followed. Therefore the EAN of the central metal ion in a given complex is given by -

$$EAN = (Z - x) + ny$$

Z = Atomic no. of metal atom.
x = Oxidation state of the central metal ion.
n = no. of ligand
y = no. of 'e' donated by one ligand.

eg: In case of $Ni(CO)_4$,
EAN = [atomic no. of Ni atom + 'e' donated by four 'CO' gr]
= [28 + 8] = 36.
Hence $[Ni(CO)_4]$ complex obeys EAN rule.

Application of EAN Rule :

With the help of this rule the magnetic property of complex ion can be predicted. It has been observed that the complex ion whose central atom obeys this rule are diamagnetic.

Since the EAN of Co^{+3} ion in $[Co(NH_3)_6]^{3+}$ ion = 36, this ion obeys EAN rule. and hence $[Co(NH_3)_6]^{3+}$ ion is diamagnetic.

The complex ion whose central metal atom does not obey EAN rule are generally paramagnetic. The no. of unpaired 'e' present in the complex ion different between EAN of the central metal atom and the atomic no. of the nearest inert gas.

Q. The stepwise formation constants for complexes in general follow the order $K_1 > K_2 > K_3$. But for Fe^{+2} with 1,10-phenanthroline complex, the order is $K_1 > K_2 < K_3$. – Explain.

In general, the values of stepwise formation constants decrease regularly from K_1 to K_n i.e, $K_1 > K_2 > K_3 \cdots > K_n$. The steady decrese in the values of $K_1, K_2, \ldots K_n$ with increasing no. of ligands is due to the fact that as more and more ligands move into the coordination zone less and less aqua molecules are available to face ligands for replacement. With progressive intake of ligands the metal ion becomes less eletron greedy. In case of charged ligands the more important factors responsible for the steady decrease are coulombic, steric hindrence and statistical factors.

a) Coulombic factor :

This factor involve increasing electrostatic repulsion b/w the ligands.

b) Steric hindrence :

If the ligands are bulkier than than the water molecules which they replace, there will be steric hindrence in the formation of the complexes.

c) Statistical factor

A species like $[Ni(H_2O)_6]^{2+}$ has 6-sides from which it can lose a molecule of H_2O. But $[Ni(H_2O)_5L]^{2+}$ (L = ligand) has 5-sides from which it can lose a molecule of H_2O under identical conditions and hence has a lower probability for exchange of H_2O molecule than $[Ni(H_2O)_6]^{2+}$.

This applies to any step.

But for Fe^{+2} with 1,10-phenanthroline (o-phen) complex, the order is $K_1 > K_2 < K_3$.
This is due to the chelate effect. In case of the formation of $[Fe(H_2O)_4(o\text{-}phen)]^{2+}$ and $[Fe(H_2O)_2(o\text{-}phen)_2]^{2+}$ complexes chelate effect is less important than the previous factors [coulombic, steric and statistical]. But in case of the formation of $[Fe(o\text{-}phen)_3]^{2+}$ complex, the chelate effect is the predominating factor than the previous factors [coulombic, steric hindrance and statistical]. i.e., $[Fe(o\text{-}phen)_3]^{2+}$ complex is exceptionally stable complex due to its chelate effect. That is why Fe^{+2} with 1,10-phenanthroline complex the order is $K_1 > K_2 < K_3$.