DATE

# Evidence in Favour of Werner's Theory:

| Conductance measurement | Cryoscopic Measurement | Precipitation reactions |
|---|---|---|
| → Depends upon the no. of charges on the particles<br>→ As the no. of particle and charges increases molar conductance increases | → Depression in freezing point depends on the no. of particles<br>→ More the particle more will be the depression in freezing point. | |

1. Conductance Measurement:

| | No. of charges |
|---|---|
| $[Co(NH_3)_6]Cl_3$ | 6 |
| $[Co(NH_3)_5Cl]Cl_2$ | 4 |
| $[Co(NH_3)_4Cl_2]Cl$ | 2 |
| $[Co(NH_3)_3Cl_3]$ | 0 |

Conductance Order

$[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

→ Conductance increases

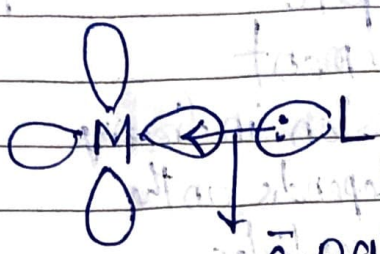
2. Depression in freezing point:

| Complex | No. of particles in |
|---|---|
| $[Co(NH_3)_6]Cl_3$ | 4 |
| $[Co(NH_3)_5Cl]Cl_2$ | 3 |
| $[Co(NH_3)_4Cl_2]Cl$ | 2 |
| $[Co(NH_3)_3Cl_3$ | 0 (undissociated) |

Shortcoming's of Werner's Theory:

1. It fails to explain the magnetic properties, spectral properties, thermodynamic stabilities and kinetic stabilities.
2. Structure determination from the number of isolated isomers.
3. Preference to certain coordination number and stereochemical configuration.

## Sidgwick Concept of Coordinate Bond:




ē pair donation from ligand

According to this theory ligands donate electron pairs to the metal (ion) resulting in the formation of coordinate covalent bond

## Demerit of Sidgwick's Theory:

→ Donation of electron pairs by ligand to the central metal causes build-up of electron density (negative charges) on the central metal (ion).

→ As a result of build-up of negative charge on the metal (ion), a partial ionic character is generated in the complex making it less stable.

## Sidwick's EAN Rule (Effective Atomic Number):

### The 18-Electron Rule:

According to this rule, the ligands donate the electron to the central metal (ion) through coordinate covalent bonds and the total number of electrons on the central metal (ion) including those gained from the ligands is the atomic number of the nearest noble gas. This is referred as the effective atomic number (EAN) rule.

→ For the transition metal complexes, this corresponds to the filling of (n-1)d, ns and np orbitals of the central metal (ion).

DATE

→ These 9 (5+1+3) valency orbitals can accomodate 18 valency electrons.
This is why EAN rule is also called as the 18-electron rule.

e.g. $[Co(NH_3)_6]^{3+}$

i) EAN:

No. of electrons donated by $Co^{3+}$ = 27 − 3
= 24

No. of electrons donated by six $NH_3$ = 6 × 2
= 12

EAN of $[Co(NH_3)_6]^{3+}$ = 24 + 12
= 36

ii) 18 $\bar{e}$ rule:

No. of electrons donated by $Co^{3+}$ = $3d^6 4s^0$
= 6 $e^-$

No. of electrons donated by six $NH_3$ = 6 × 2 = 12 $e^-$

Number of valence $\bar{e}$ electrons in $[Co(NH_3)_6]^{3+}$ = 6 + 12
= 18 $\bar{e}$

$[Fe(CN)_6]^{4-}$

i) EAN: $Fe^{2+}$ = 24
6 $CN^-$ = 6 × 2 $\bar{e}$
Total = 36

ii) 18 $\bar{e}$ $Fe^{2+}$ = 6 $\bar{e}$
6 $CN^-$ = 6 × 2 $\bar{e}$
Total = 18 $\bar{e}$

$Ni(CO)_4$:

EAN Ni = 28
4 CO = 4 × 2 $\bar{e}$
Total = 36 $\bar{e}$

18 $\bar{e}$ Ni = 10 $\bar{e}$
4 CO = 8 $\bar{e}$
Total = 18 $\bar{e}$

$[Ag(NH_3)_2]^+$ $_{47}Ag$

| EAN | | 18 $\bar{e}$ | |
|---|---|---|---|
| $Ag^+$ | = 46 | $Ag^+$ | = 10 $e^-$ |
| $2NH_3$ | = 04 | $2NH_3$ | = 04 $e^-$ |
| Total | = 50 $\bar{e}$ | Total | = 14 $\bar{e}$ |

**Note:** Complexes which follow the EAN or 18 $\bar{e}$ rule are considered to be stable.
18 $\bar{e}$ and EAN rules are similar but the 18 $\bar{e}$ rule is more advantageous because there is no need to remember the atomic number for each noble gas.

## Exceptions to EAN or 18 $\bar{e}$ Rule:

The complexes in which the metal cations or atoms have odd number of electrons never obey the EAN rule or 18 $\bar{e}$ rule because sum of total electrons or valence shell electrons and the electrons donated by the ligands is also and odd number.

Eg. $[Fe(CN)_6]^{3-}$

| EAN | | 18 $\bar{e}$ | |
|---|---|---|---|
| $Fe^{3+}$ | = 23 | $Fe^{3+}$ | = 5 |
| $6CN^-$ | = 12 $\bar{e}$ | $6CN^-$ | = 12 $\bar{e}$ |
| Total | = 35 $\bar{e}$ | Total | = 17 $\bar{e}$ |

## 16 $\bar{e}$ Rule:

The 18 $\bar{e}$ rule is also not applicable for the metals (e.g. Rh, Ir, Pd and Pt) residing at the right bottom corner of d-block elements.
Rh(I), Ir(I), Pd(0), Pt(0), Pd(II) and Pt(II) very often to prefer the 16 $\bar{e}$ rule instead of the 18 $\bar{e}$ rule.

For such systems the EAN is less than 2 compared to the atomic number of nearest inert gas.

e.g.

Pt(II), or Pd(II) $d^8$ system. $[PdCl_4]^{2-}$ $[Pt(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
16 e⁻
$[Pt(C_2H_4)Cl_3]^-$
18 e⁻

Ir(I) $d^8$ system (16 e⁻) $[Ir(CO)Cl(PPh_3)_2]$
18 e⁻

Pd(0) $d^{10}$ system $Pt(PPh_3)_3$ = 18 e⁻