B.Sc. (Honours) Part-II

Paper-IIIB

Topic: Effective atomic number (EAN)

UG

Subject-Chemistry

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Effective atomic number (EAN)

In the 1920s, N.V. Sidgwick recognized that the metal atom in a simple metal carbonyl, such as $[Ni(CO)_4]$, has the same valence electron count (18) as the noble gas that terminates the long period to which the metal belongs. Sidgwick coined the term 'inert gas rule' for this indication of stability, but it is now usually referred to as the **18–electron rule or EAN Rule**.

It becomes readily apparent, however, that the 18-electron rule is not as uniformly obeyed for d-block organometallic compounds as the octet rule is obeyed for compounds of Period 2 elements and we need to look more closely at the bonding to establish the reasons for the stability of both the compounds that have the 18-electron configurations and those that do not.

The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbitals, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that the combination of these nine A.O.s with ligand orbitals creates nine M.O.s that are either metal-ligand bonding or non-bonding.

✓ Ligands (donor-acceptor ligands) like carbonyls, carbenes, arenes, isonitriles, etc. forms complexes that tend to follow the ean rule or the 18 electron rule. Because the rule is obeyed with rather high frequency by organometallic compounds, especially those having carbonyl and nitrosyl ligands (π acceptor ligands), it has considerable usefulness as a tool for predicting formulas of stable compounds.

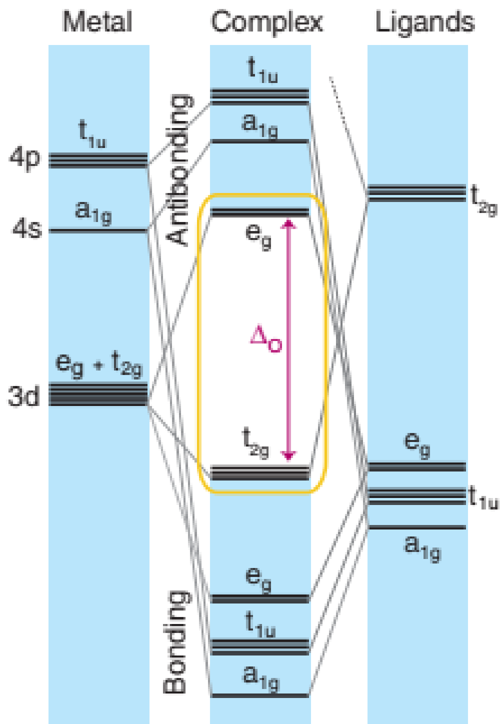

Figure 1 The energy levels of the molecular orbitals of an octahedral complex with strong-field ligands.

18 Electron Rule in Octahedral Complexes

Figure 1 shows the energy levels that arise when a strong-field ligand such as carbon monoxide bonds to a d-metal atom.

Carbon monoxide is a strong-field ligand, even though it is a poor σ donor because it can use its empty π* orbitals to act as a good π acceptor. In this picture of the bonding, the t_{2g} orbitals of the metal atom are no longer nonbonding, as they would be in the absence of π interactions, but are bonding.

The energy-level diagram shows six bonding MOs that result from the ligand–metal σ interactions, and three bonding MOs that result from π interactions. Thus up to 18 electrons can be accommodated in the nine bonding MOs.

Compounds that have this configuration are remarkably stable; for instance, the 18-electron $[Cr(CO)_6]$ is a colourless, air-stable compound.

An indication of the size of the HOMO-LUMO gap (Δ_O) can be gained from a consideration of its lack of colour, which results from a lack of any electronic transitions in the visible region of the spectrum; that is, Δ_O is so large that such transitions are shifted to the UV.

The only way to accommodate more than 18 valence electrons in an octahedral complex with strong-field ligands is to use an antibonding orbital. As a result, such complexes are unstable, being particularly prone to electron loss and acting as reducing agents.

Compounds with fewer than 18 electrons will not necessarily be very unstable. However, such complexes will find it energetically favourable to acquire extra electrons by reaction and so populate their bonding MOs fully.

Example: Calculate the effective atomic number of the following complexes:

- K4$[Fe(CN)_6]$
- $[Co(NH_3)]Cl_3$

1. $K_4[Fe(CN)_6]$

Number of electrons in Fe^{2+} = 24

Number of electrons by Six CN = 2×6 = 12

Total number of electrons possessed by Fe^{2+} = 24 + 12 aherefore, the effective atomic number = 36.

2. $[Co(NH_3)]Cl_3$

Number of electrons in Co^{+3} = 24

Number of electrons by Six NH_3 = 2×6 = 12

Total number of electrons possessed by Co^{+3} = 24 + 12

Therefore, the effective atomic number = 36.

Direct Shortcut method:

$$\mathbf{EAN} = [(Z_M \times N_M + e^{-}\text{by } \sigma \text{ bond} \times N_M + e^{-}\text{pair by } L \times N_L)]\frac{1}{N_M}$$

$$\mathbf{Where\ Z_M} = \text{Atomic mass of central Metal atom}$$

$$\mathbf{N_M} = \text{Number of central Metal Atom}$$

$$\boldsymbol{N_L} = \text{Number of Ligand}$$

Calculate of EAN of $Ru_3\,(CO)_{12}$

$$\mathbf{EAN} = [(Z_M \times N_M + \ e^{-} \text{by } \sigma \text{ bond} \times N_M + \ e^{-} \text{pair by L} \times N_L)]\frac{1}{N_M}$$

$$\mathbf{EAN} = [44 \times 3 + \ 3 \times 2 + \ 2 \times 12)]\frac{1}{3} = \mathbf{54\ (Xe)}$$