

Quadrant II – Transcript and Related Materials

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Notes

Effective Atomic Number (EAN) rule

Introduction: In carbonyls, the CO molecule is bonded to the metal through the carbon atom. There are three types of metal –CO linkages.

The CO molecule behaves as (a) a monodentate ligand, (b) a bridge between two metal atoms and (c) less frequently, a bridge between three metal atoms.

The monodentate, terminal CO groups are most common e.g. $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, the ketonic or doubly bridged CO groups occur in polynuclear carbonyls e.g. $\text{Co}(\text{CO})_8$ and $\text{Fe}(\text{CO})_9$ and the triply bridging type has been found on only few compounds, e.g. $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$.

In a terminal MCO group, the CO donates 2 electrons to an empty metal orbital. In bridging $\text{M}(\text{CO})\text{M}$ group it is assumed that each M-C bond is formed by one metal electron and one carbon electron.

Maximum number of electrons bonds, a metal might form with CO molecules is limited by the number of vacant orbitals available on the metal atom or by the geometric considerations in the space around it.

The number of available orbitals is obtained from the EAN or 18-electron rule, a modified EAN rule.

Definition: In complexes the metal atom/ion accepts electron pairs from the ligands till the total number of electrons associated with the metal become equal to the atomic number of the next inert gas element in the periodic table.

Example- Ni(CO)_4

Z (atomic number) for Nickel =28, electrons donated by 4 CO ligands= $4 \times 2 = 8$

So, $28 + 8 = 36$ (corresponding to atomic number of inert gas Kr(Krypton))

Most of the metals in complexes obey the rule and are diamagnetic in nature. Examples are metal carbonyls like Ni(CO)_4 , Fe(CO)_5 , Cr(CO)_6

In order to attain the EAN next inert gas configurations, metals with even atomic number combine with integral number of CO ligands and obey the rule. On the other hand metals with odd atomic number dimerise forming polynuclear carbonyls and obey the rule.

Example- $\text{Mn}_2(\text{CO})_{10}$, Z (atomic number) for Mn =25. Each Mn is co-ordinated to 5 CO ligands which donate 10 electrons to Mn. In addition there is an electron from Mn-Mn bond.

Electrons donated by 5 CO ligands= $5 \times 2 = 10$ for each Mn atom. So, $25 + 10 + 1 = 36$ (corresponding to atomic number of inert gas Kr(Krypton))

In V(CO)_6 Vanadium has an odd atomic number of 23, electrons donated by 6 CO ligands= $6 \times 2 = 12$. So, $23 + 12 = 35$. So in the case of V(CO)_6 it does not obey the rule and is paramagnetic in nature

18 Electron rule

This is an alternative statement to EAN rule to explain stability

In transition metals the ns, np and (n-1)d orbitals and the total number of valence electrons that can be accommodated is 18.

Therefore according to this rule stable electronic configuration of 18 will result when ns, np and (n-1)d orbitals are completely filled by utilising lone pair of electrons from CO ligands.

