

CHAPTER II

EXPERIMENT

2.1 Reagent2.1.1 Solids

Acetylacetonates of the following metals were purchased from Merck-Schuchardt:-

Chromium (III)

Cobalt (III)

Cobalt (II)

Copper (II)

Iron (III)

Manganese (III)

Manganese (II)

Nickel (II)

Palladium (II)

Zinc (II)

2.1.2. Liquids

The solvents, from Merck and BDH which were not analar grade were double-distilled and were dried with drying agents prior to use.

2.2 ProcedureUltra-violet spectral measurements

All spectra were measured at $\sim 25^{\circ}\text{C}$ on a Perkin-Elmer Model 124 double beam grating spectrophotometer, using 1-cm. quartz cells and 1.0 nm spectral slit-width. The solutions measured were all $\sim 10^{-4}$ M.

H-bonding spectra were recorded as a function of time.

The time at which the complex dissolved in the solvent was taken as zero time. Wavelengths given are reliable to $\pm 0.5 \text{ m}\mu$.

ALL $\Delta\lambda$ 'S are relative to iso-octane.

2.3 Acetylacetonone and its Metal Complexes

Acetylacetonone is a mixture of two forms having keto (Fig. 2 A) and enol (Fig. 2 B) structures. It is a weak acid (pK_a 8.8)¹¹ and one proton can be lost easily to give the enolate anion. This enolate anion has a five-atom π network extending over the two oxygen and three non-terminal carbon atoms. Six electrons thus occupied are delocalized into a symmetric structure. This can be conveniently called quasi-aromatic form (Fig. 2 C).

The metal complexes which are studied here can be classified into 2 groups:-

2.3.1 Trivalent metal complexes, include cobalt (III), chromium (III), iron(III), and manganese (III) acetylacetonates. Their geometries have been established by X-ray crystallography^{12,13} (Fig. 2 D) and their symmetries are D_3 i.e. a distorted octahedral. The acetylacetonone chelate being planar and symmetrical, i.e. quasi-aromatic form.

2.3.2 Divalent metal complexes, include palladium (II), copper (II), nickel (II), cobalt (II), zinc (II), and manganese(II) acetylacetonates. The (Pd) complex has a planar configuration with a distorted octahedral co-ordination of the Pd atom.¹⁴ Cu (II) complex has a bonded bridge structure with the central carbon atom acting as a bridge between the two nearly square planar Cu (AcAc)₂ units.¹⁵ The remaining complexes are oligomer with polymerization via chelated oxygen bridge. Crystallographic

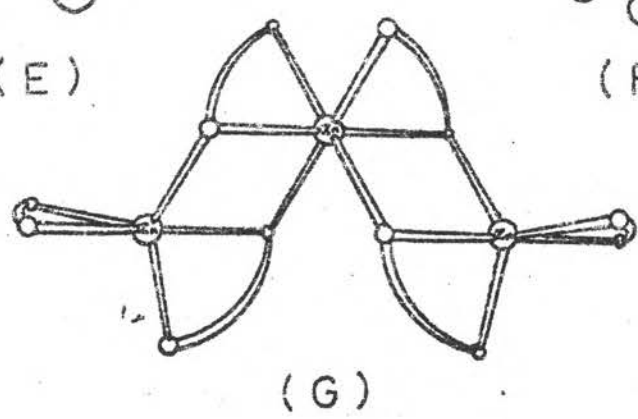
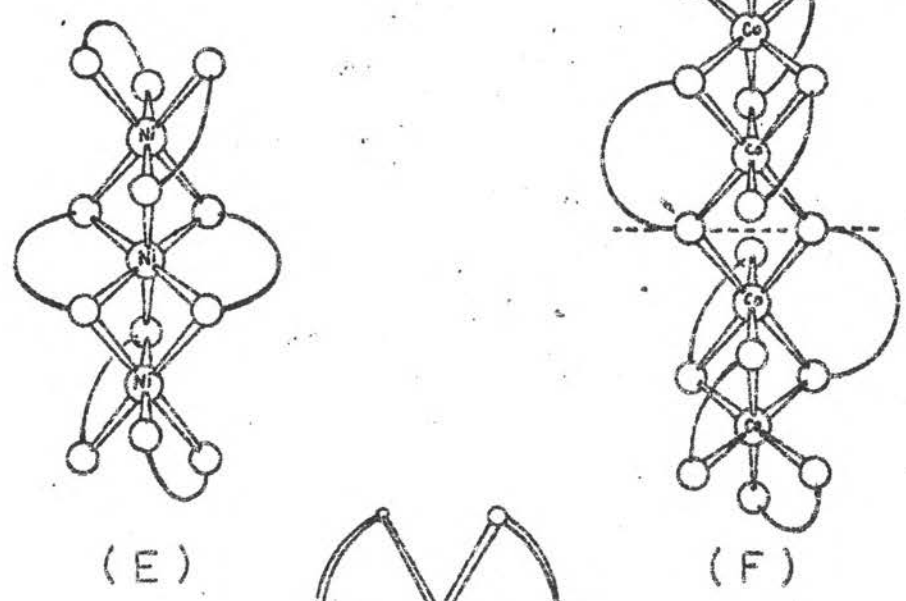
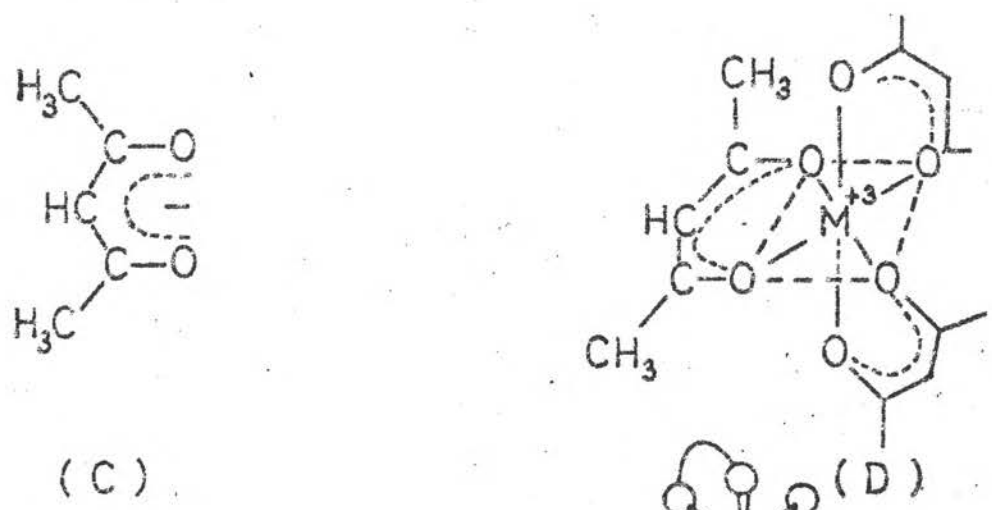
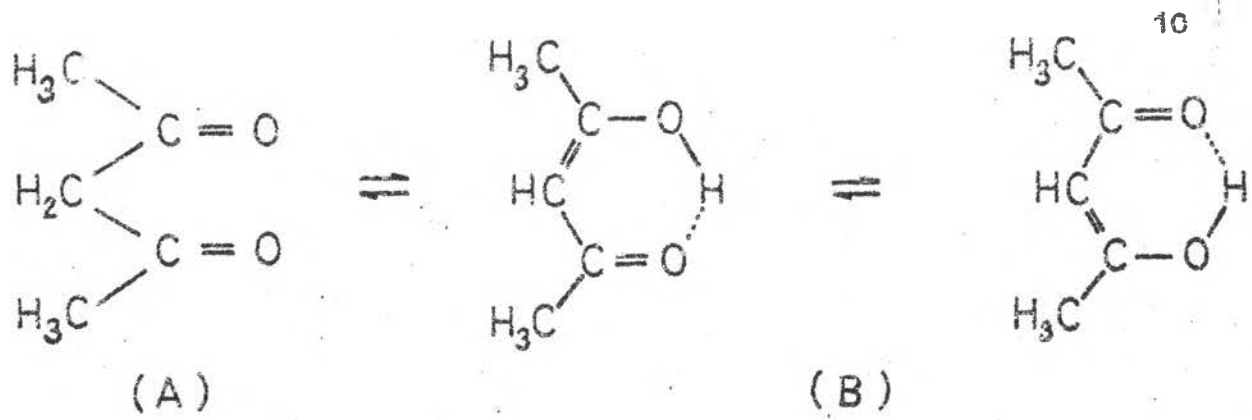


Fig. 2 [From P.H., M.Sc. Thesis (Chula 1974)]²⁰

evidences for polymerization has been definitely established to date with $[\text{Ni}(\text{AcAc})_2]_3$ ¹⁶ (Fig. 2 E), $[\text{Co}(\text{AcAc})_2]_4$ ¹⁷ (Fig. 2 F), and $[\text{Zn}(\text{AcAc})_2]_3$ ¹⁸ (Fig. 2 G); and molecular weight study indicates polymerization also for $[\text{Mn}(\text{AcAc})_2]_3$ ¹⁹ which is believed to have the same structure as Ni (II).

Polymeric species in M(II)

Cu(II) forms dimer and the monomer is planar, symmetry D_{2h} . Ni(II) and Mn(II) are believed to have identical structures, both are trimeric¹⁹. In Ni(II) there are nine possible structures of trimeric alone.¹⁷ Ni(II) and Mn(II) monomers are planar, symmetry D_{2h} .

Zn(II) is also trimeric, but the monomer is tetrahedral, symmetry D_{2d} . Co(II) forms tetramers, the monomer is also tetrahedral, symmetry D_{2d} .