

CHAPTER I

INTRODUCTION

It is well known that solvent shift studies throw light on bond properties of solutes as well as solute - solvent interaction. Literature in organic compounds is extensive, but not so in inorganic compounds. Quite aside from the intrinsic interests, divalent and trivalent metal acetylacetonates are chosen for infrared solvent shift studies, because it is the first time, so far as is known, that a "bonded" system has been studied.

1.1 Theory of Solvent Shifts

From the passage of a gaseous state to a state of solution produces three characteristic effects in the vibrational spectrum of a solute:

- a) the rotational structure of the bands disappears or is replaced by a very simple contour;
- b) the band peaks do not correspond with the pure vibrational frequencies of the molecule in the gaseous state;
- c) the band half-widths are changed and their band intensities are enhanced.

Only one of these three effects is studied here, that of b) solvent shifts.

One of the simplest and earliest attempts to explain the effect of solvents on solute vibrational frequencies was that of

Kirkwood¹ and of Bauer and Magat². This was based on the model of an oscillating point dipole in a spherical cavity in a continuous dielectric medium. The observed solvent shifts were supposedly due to the interaction between solute dipole and the induced polarization of surrounding solvent molecules. This treatment led to the well-known Kirkwood-Bauer-Magat (KBM) relation

$$\Delta \nu / \nu = C (\epsilon - 1) / (2\epsilon + 1) \quad (\text{I})$$

where $\Delta \nu$ is the change in frequency on going from vapour to solution phase ν is the vapour-phase frequency, ϵ is the dielectric constant of the solvent and C is a constant.

This equation has been widely used and tested and found to be inadequate in many instances.^{3-5a} In the electrostatic model leading to equation (I) it is clear that only the electronic contribution to the solvent polarization can follow the vibrational frequencies of the solute (ca. 10^{-14} sec⁻¹). Molecular dipole relaxations are characterized by much lower frequencies (ca. 10^{11} sec⁻¹) so that dipole orientation cannot be involved in the vibrational interactions. On this simplification as exerting separate and superimposed effects, Bayliss and his collaborators⁶ claimed that in non-polar solvents, only electron polarization is involved. This system can be described by replacing ϵ in equation (I) by n^2 , where n is the refractive index of the solvent at the appropriate frequency.

$$\Delta \nu / \nu = C (n^2 - 1) / (2n^2 + 1) \quad (\text{II})$$

In polar solvents, they expect an electronic component of $\Delta \nu$ as

given by (II), and a superimposed orientation component for which no simple theory exists. When tested, there are still deviations despite the improvement of (II). They are partly due to the refractive indices being determined at visible frequencies and not in the I.R. region. But the main reason is because equation (II) is a gross simplification, which ignores interactions between neighbours.

Buckingham⁷ analyzes the problem quantum mechanically in a general manner by introducing the effect of solute-solvent interactions on the vibrational spectrum of a dissolved molecule, but still utilises the basic KBM model of a diatomic oscillator in a spherical solvent cavity. The frequency shift after simplification is found to be for polar solvents:-

$$\frac{\Delta \nu}{\nu} = C + C_{\epsilon} \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) + C_n \left(\frac{n^2 + 1}{2n^2 + 1} \right) \quad (\text{III})$$

and in non-polar solvents

$$\frac{\Delta \nu}{\nu} = C + \frac{1}{2} (C_{\epsilon} + C_n) \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \quad (\text{IV})$$

where C , C_{ϵ} , and C_n are constants depending on both solute and solvent.

Although providing a more thorough treatment of the perturbing effect of the solvent medium, this is still an over-simplified model, as Buckingham himself stresses. And it should only be expected to apply to those cases in which the equilibrium solute dipole moment greatly exceeds the induced moments. Moreover, it

is confined to diatomic molecules, although it should apply reasonably well to essentially isolated bond vibrations in polyatomic molecules. Practical applications of these relationships confirm the improvement of a few cases. But $\nu(X-H)$ frequencies still exhibit considerable deviations. These unquestionably arise from specific association interactions between solute and solvent molecules and it is evident that a comprehensive solvent theory must include a term to take these into account.

Caldow and Thompson⁸ try to explain the effect of specific association interactions for solvents of type R-H. It is possible to relate the observed shifts with quantitative measures of electron density at likely centres of interaction, based on the Taft σ^* inductive factor of the residue R and adding this term as a fourth term $C_4 \sigma^*$ to Buckingham's equations. They conclude that the dielectric factor contributes about 30% of the total frequency shifts exhibited by C = O dipolar.

The present theoretical situation can be summed up by saying that equation (III) and (IV) should be suitably modified with a specific interaction term.

An alternative empirical approach has been developed by Bellamy and his co-worker.⁹

$$\left[\frac{(\nu_{\text{vap}} - \nu_{\text{soln}})}{\nu_{\text{vap}}} \right]_A = S \left[\frac{(\nu_{\text{vap}} - \nu_{\text{soln}})}{\nu_{\text{vap}}} \right]_B \quad (V)$$

where A and B are different compounds in the same solvent. By this means the effects of macroscopic properties of the solvent are internally compensated and the deviation of the gradient, s, from

unity indicates differing microscopic solvent - solute interactions. In general, correlation is good. Numerous applications¹⁰ of the treatment have demonstrated its value both in assessing interactions and in establishing band assignments.

1.2 Acetylacetone and its Metal Complexes

Acetylacetone is a mixture of two forms having keto (Fig. 1 A) and enol (Fig. 1 B) structures. It is a weak acid ($pK_a \sim 8.8$)¹¹ and the 3rd proton can be lost easily to give the enolate anion. This enolate anion has a five-atom π net work extending over the two oxygen and three nonterminal carbon atoms. Six electrons occupy the resulting π -type molecular orbitals. The enolate anion could thus be delocalized into a symmetric structure. This can be conveniently called quasi-aromatic form (Fig. 1. c).

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

a) Trivalent metal complexes, which include cobalt (III), chromium (III), iron(III), and manganese (III) acetylacetonates. Their geometries have been established by X-ray crystallography^{12 13} (Fig. 1 D) and their symmetries are D_3 i.e. a distorted octahedral. The acetylacetone chelate being planar and symmetrical, i.e. quasi-aromatic form.

b) Divalent metal complexes, which 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)

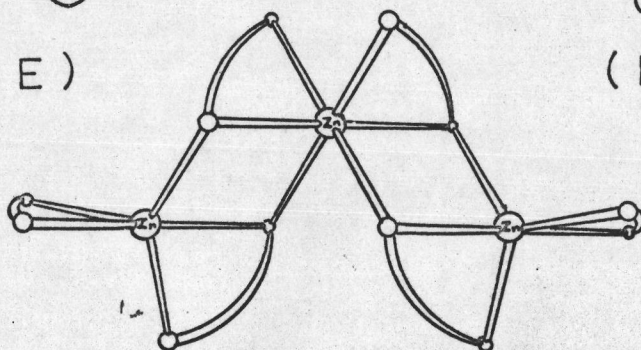
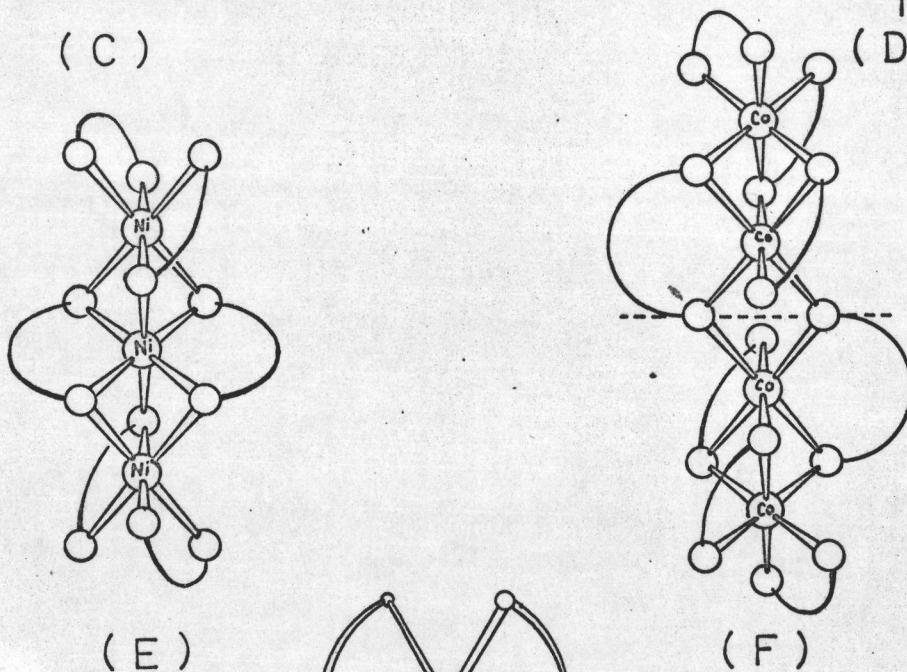
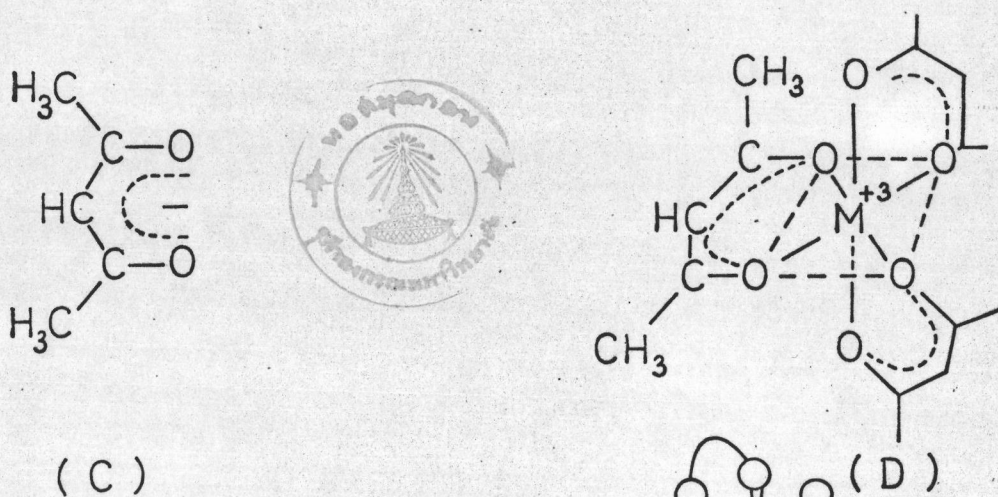
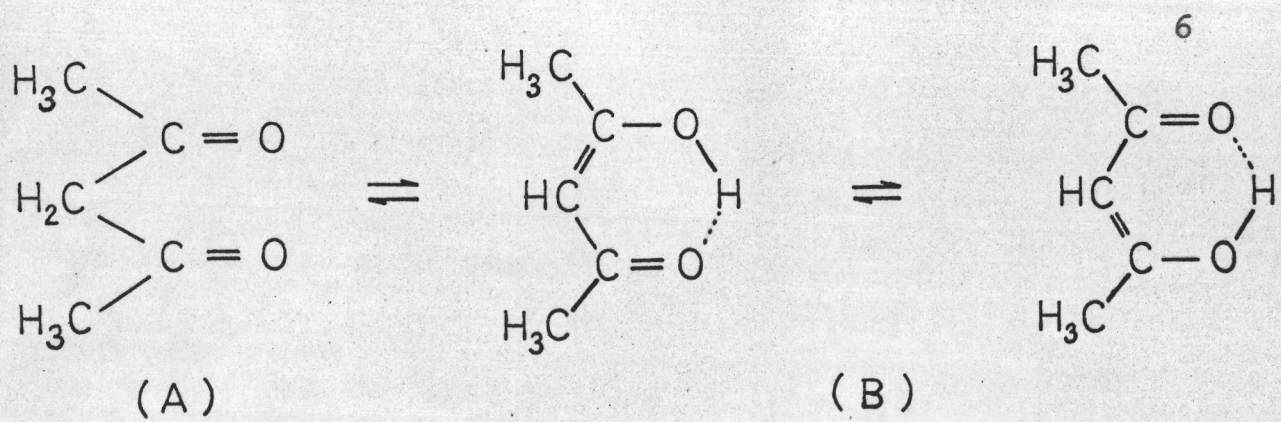


Fig. 1

complex has a bonded bridge structure with the central carbon atom acting as a bridge between the two nearly square planar $\text{Cu}(\text{acac})_2$ units.¹⁵ The remaining complexes are oligomer with polymerization via chelated oxygen bridges. Crystallographic evidences for polymerization has been definitely established to date with $[\text{Ni}(\text{acac})_2]_3$ ¹⁶ (Fig. 1.E), $[\text{Co}(\text{acac})_2]_4$ ¹⁷ (Fig. 1.F), and $[\text{Zn}(\text{acac})_2]_3$ ¹⁸ (Fig. 1.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).

The infrared spectra of metal acetylacetonate complexes have been studied extensively. In 1956, Meck and Funk²⁰ assigned the infrared spectra of acetylacetonate and its metal complexes on an empirical basis. In 1960, Nakamoto and Martell²¹ carried out an approximate normal co-ordinate analysis of $\text{Cu}(\text{acac})_2$. Prior to 1960, no spectral data were available below 400 cm.^{-1} and no isotopically substituted acetylacetonate complexes were studied. Since then a number of investigators²²⁻²⁵ have extended their measurements to the far-infrared region. The spectra of metal complexes containing C^{13} - and O^{18} - labeled acetylacetones have been obtained.^{26,27} A rigorous normal co-ordinate analysis considering all the atoms in the molecule has been made for $\text{M}(\text{acac})_2$ and $\text{M}(\text{acac})_3$ - type complexes.²⁸