# CHAPTER III

# RESULTS, DISCUSSION AND CONCLUSION

## 3.1 General Features

### 3.1.1 Solution spectra of metal acetylacetonates

Generally, most of the metal acetylacetonates exhibit 3 bands in the ultraviolet region :

220-240 $m\mu$ (varying intensities),

270 $m\mu$ (very strong intensities), and

300-350 $m\mu$ (varying intensities).

The 220-240 $m\mu$ band is assigned as $\sigma_L \rightarrow 3d$ transition which involves the transfer of an electron from the ligand to the metal. The band near 270 $m\mu$ is assigned as the $\pi_L \rightarrow \pi_L^*$ transition. The 300-350 $m\mu$ band is assigned as $3d \rightarrow \pi_L^*$ transition, which involves the transfer of an electron from the metal to the ligand.

It is interesting to note that strong peaks involving metal transitions (metal $\leftrightarrow$ ligand) correspond to strong force constants of metal-oxygen bond.[20] (see Fig. 3 )

| Complex | Force constant (dynes/cm) |
|---|---|
| Cr (III) | $2.3 \times 10^5$ |
| Co (III) | $2.4 \times 10^5$ |
| Cu (II) | $2.2 \times 10^5$ |
| Pd (II) | $2.65 \times 10^5$ |
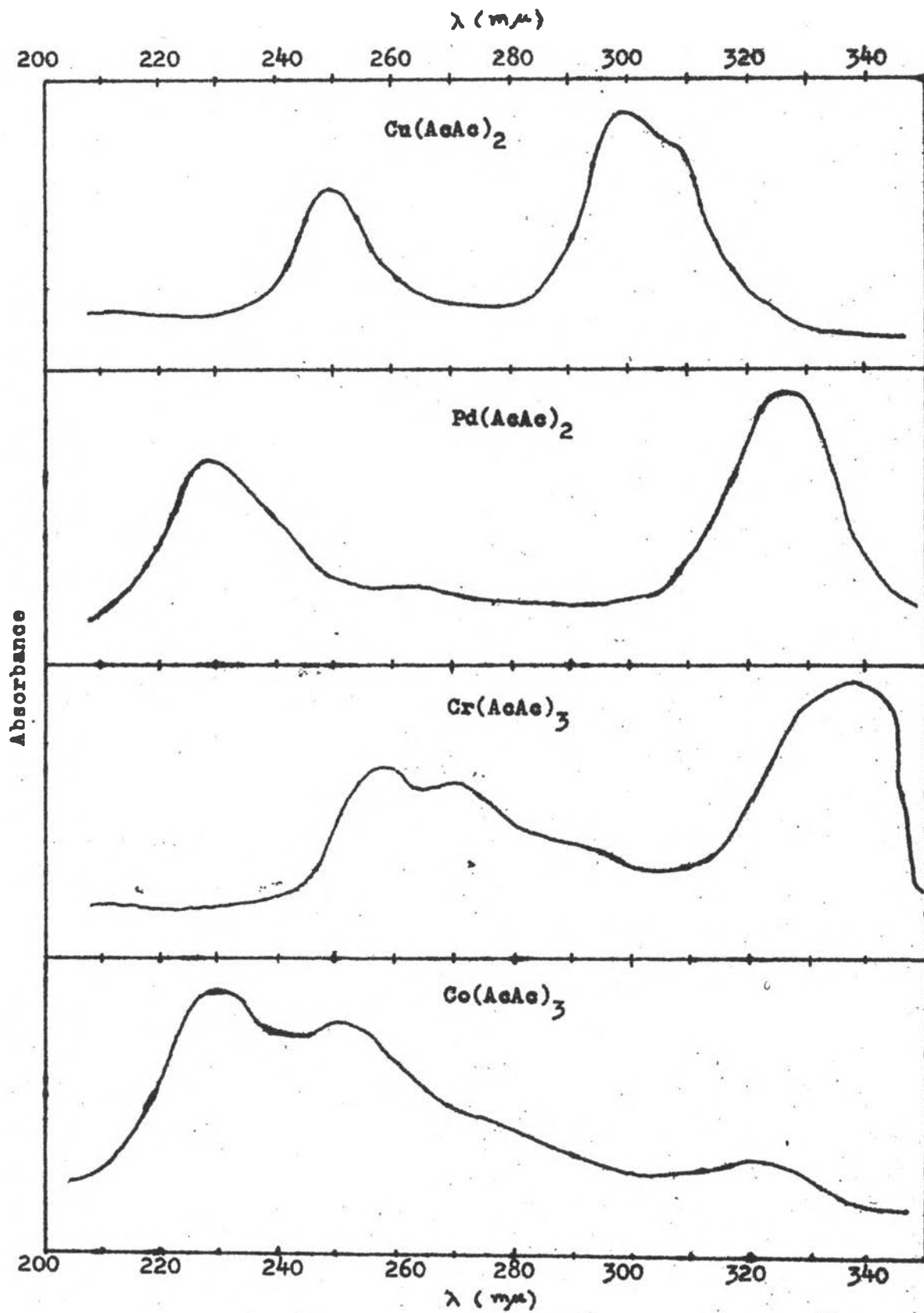
Fig. 3 Typical ultraviolet spectra of Cu(AcAc)$_2$, Pd(AcAc)$_2$, Cr(AcAc)$_3$, and Co(AcAc)$_3$.

And the weak metal transition peaks (Fig.4-8,12,13) correspond to weak force constants.[20]

| Complex | Force constant (dynes/cm) |
|---------|---------------------------|
| Mn (II) | $1.3 \times 10^5$ |
| Zn (II) | $1.3 \times 10^5$ |
| Co (II) | $1.5 \times 10^5$ |
| Mn (III) | $1.6 \times 10^5$ |
| Fe (III) | $1.7 \times 10^5$ |
| Ni (II) | $2.0 \times 10^5$ |

## 3.1.2  Solution spectra of (AcAc)

The spectra in the ultraviolet region for (AcAc) shows only one strong band at $\sim 270$ m$\mu$ ( $\pi \rightarrow \pi^*$ ). When the acetylacetonate is chelated to the metals, the ultraviolet spectum show two extra bands (220-240 m$\mu$ , 300-350 m$\mu$ ) plus one or two weak shoulders in some metal acetylacetonates. This incidentally support the above assign-ments concerning metal transitions $3d \rightarrow 3d$ , $3d \rightarrow \pi_L^*$ .

## Classification of Solvents.

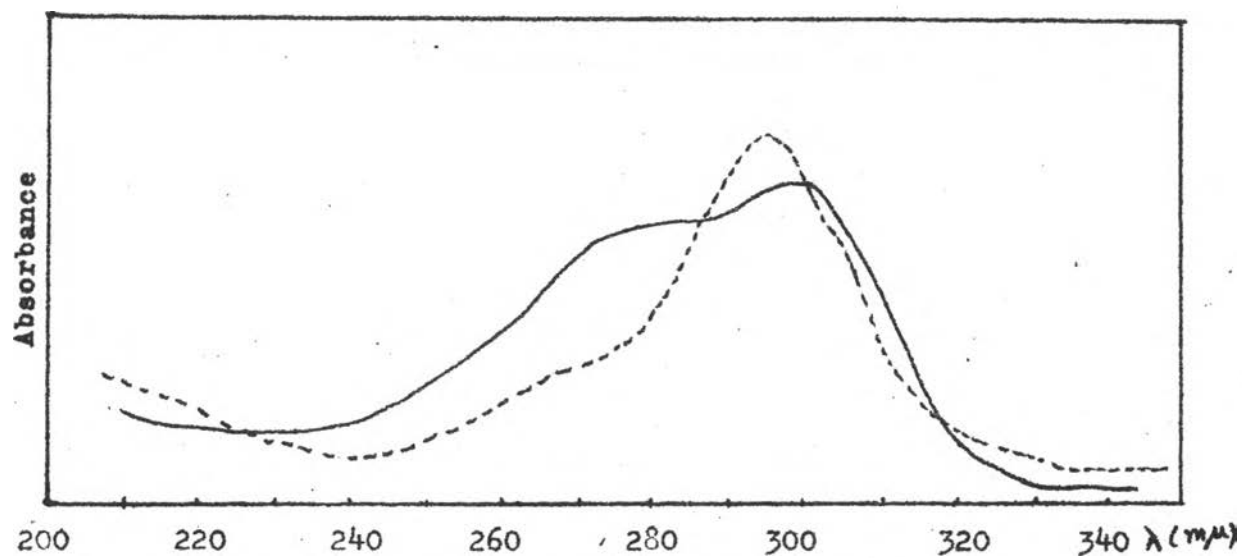| Solvent | Classification | | |
| --- | --- | --- | --- |
| | Polarity | H-bonding | Coordination |
| Isooctane | | | |
| Heptane | | | |
| Hexane | Non-polar | Non H-bonding | Non-coordinating |
| Cyclohexane | | | |
| Dioxane | | | |
| Chloroform | | | |
| Dichloromethane | | | |
| Dichloroethane | | | |
| n-Butyl alcohol | | | |
| Iso-propyl alcohol | Polar | H-bonding | Coordinating |
| n-Propyl alcohol | | | |
| Ethyl alcohol | | | |
| Methyl alcohol | | | |
| Water | | | |

Fig. 4    The ultraviolet spectrum of Ni(AcAc)$_2$:
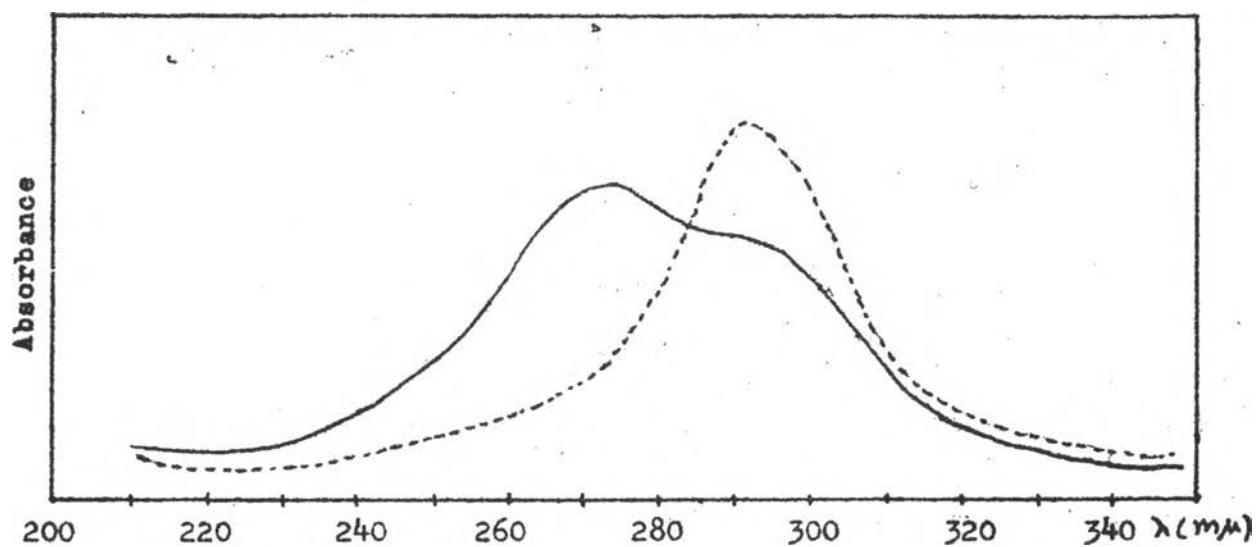————— , in hexane;
— — — — — , in ethyl alcohol.



Fig. 5    The ultraviolet spectrum of Ni(AcAc)$_2$:
————— , in chloroform;
— — — — — , in methyl alcohol.
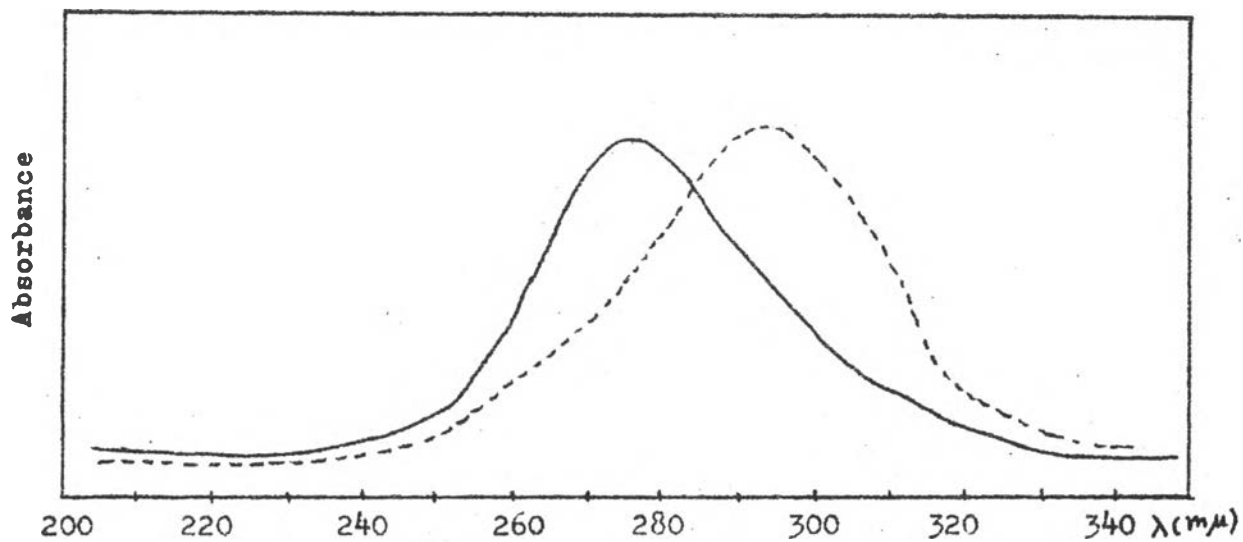
Fig. 6        The ultraviolet spectrum of Co(AcAc)$_2$:

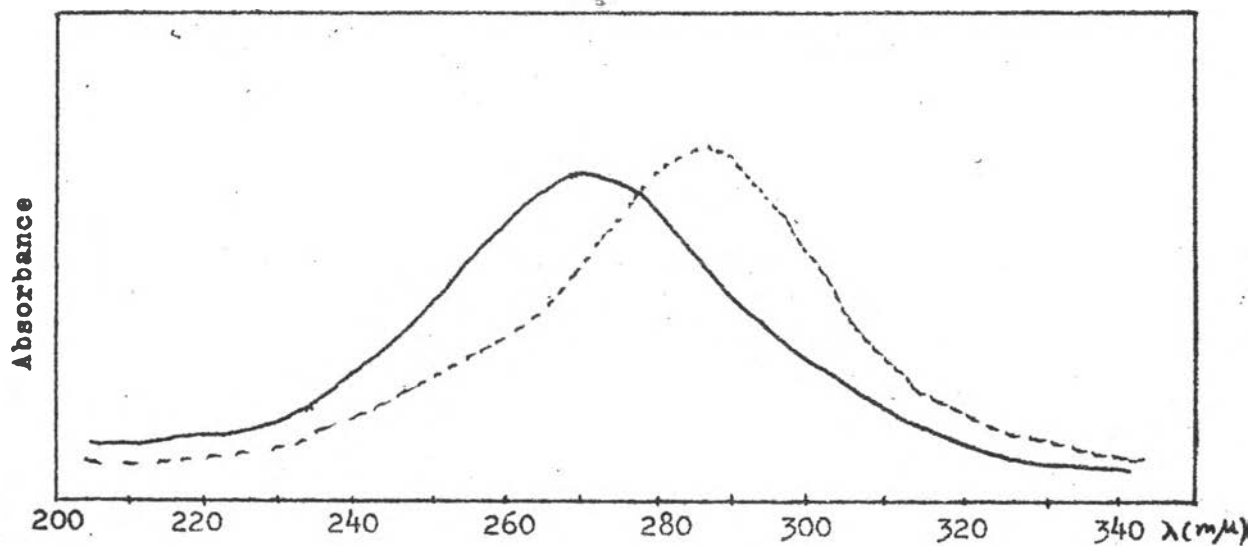————————— , in cyclohexane;

— — — — — — , in water.



Fig. 7        The ultraviolet spectrum of Zn(AcAc)$_2$:

————————— , in isooctane;

— — — — — — , in n-propyl alcohol.
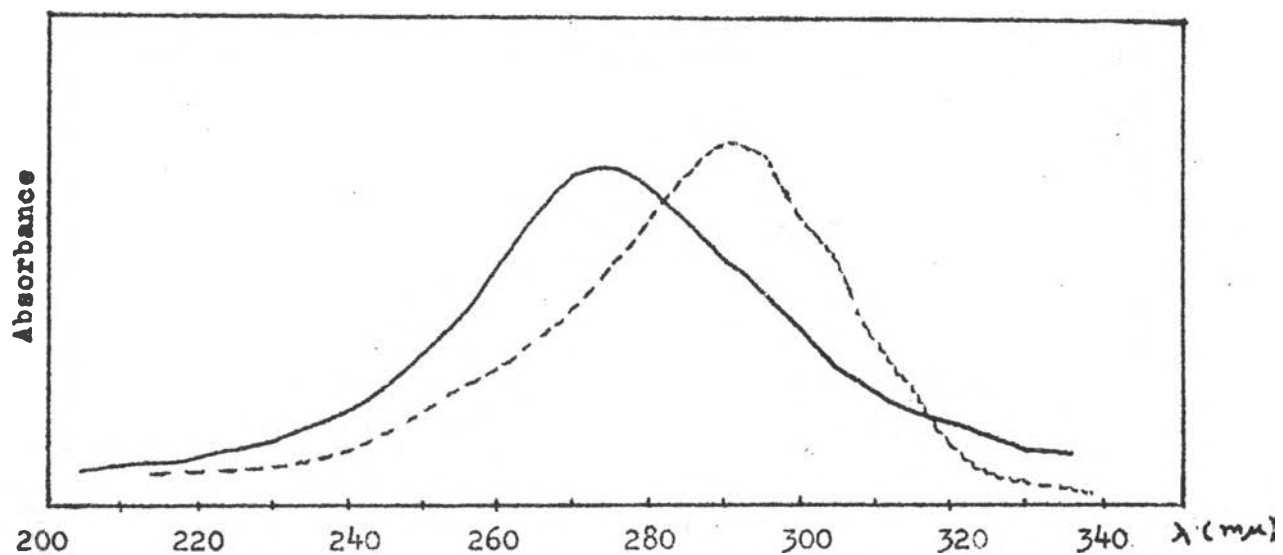
Fig. 8    The ultraviolet spectrum of Mn(AcAc)$_2$ :

————————— , in heptane;

— — — — — , in  methyl alcohol.
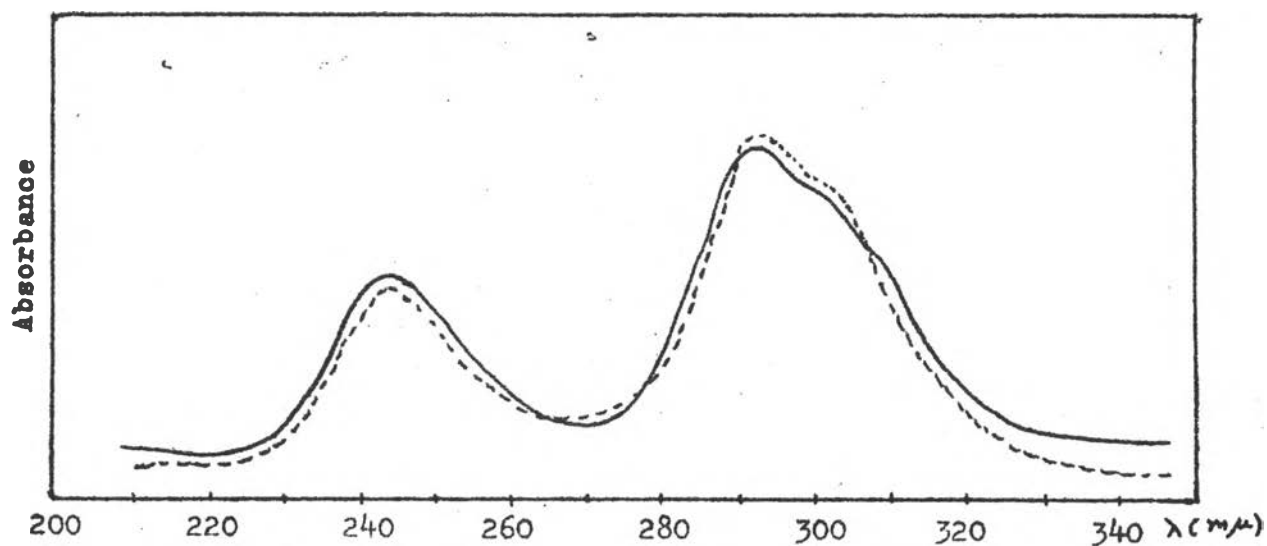


Fig. 9    The ultraviolet spectrum of Cu(AcAc)$_2$ :

————————— , in hexane;

— — — — — — , in water.
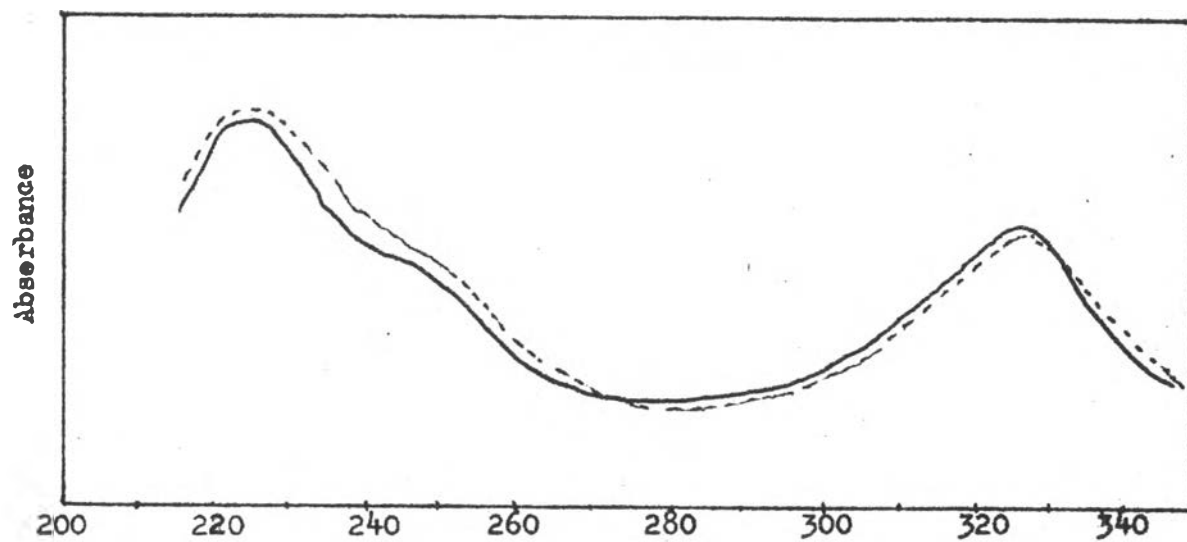
**Fig. 10**   The ultraviolet spectrum of Pd(AcAc)$_2$ :

————————— , in hexane;

— — — — — — , in methyl alcohol.
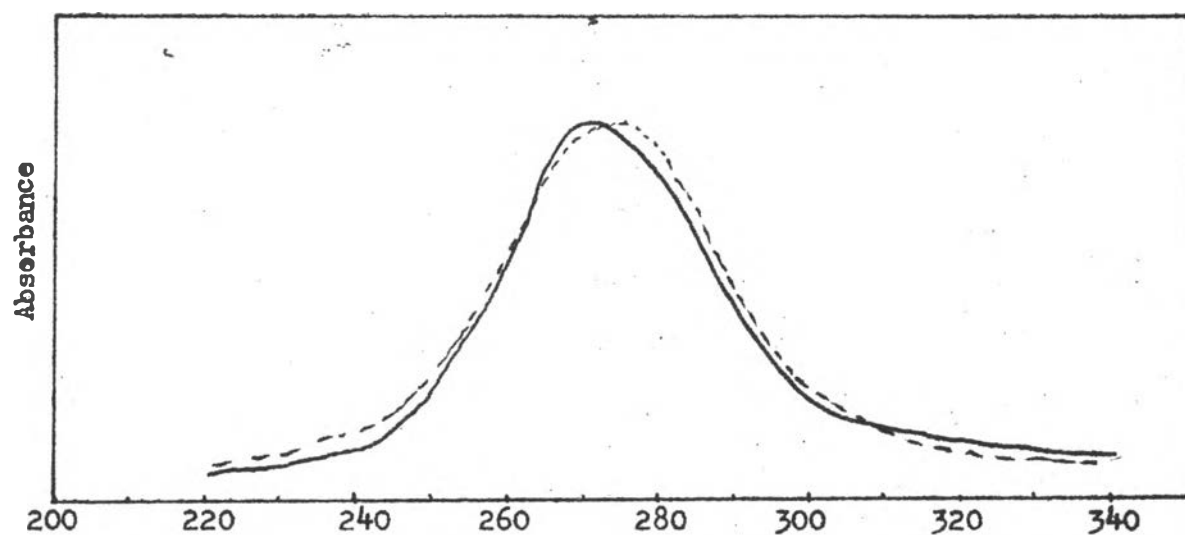


**Fig. 11**   The ultraviolet spectrum of (AcAc) :

——————— , in isooctane;

— — — — — — , in methyl alcohol.
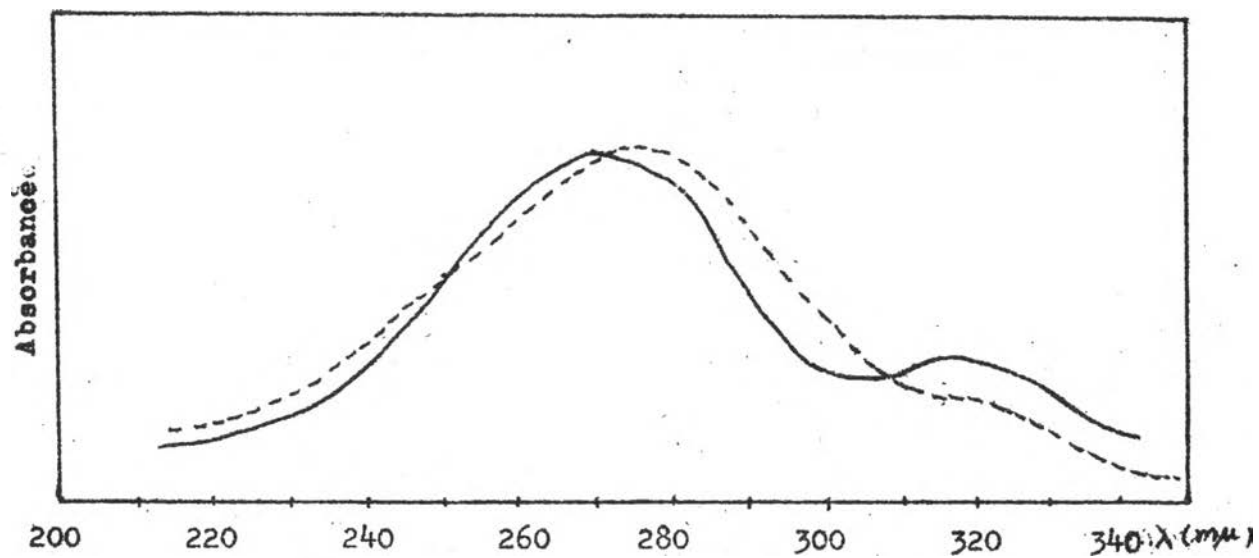
Fig. 12    The ultraviolet spectrum of Mn(AcAc)$_3$:

───────── , in hexane;

- - - - - - - , in n-butyl alcohol.
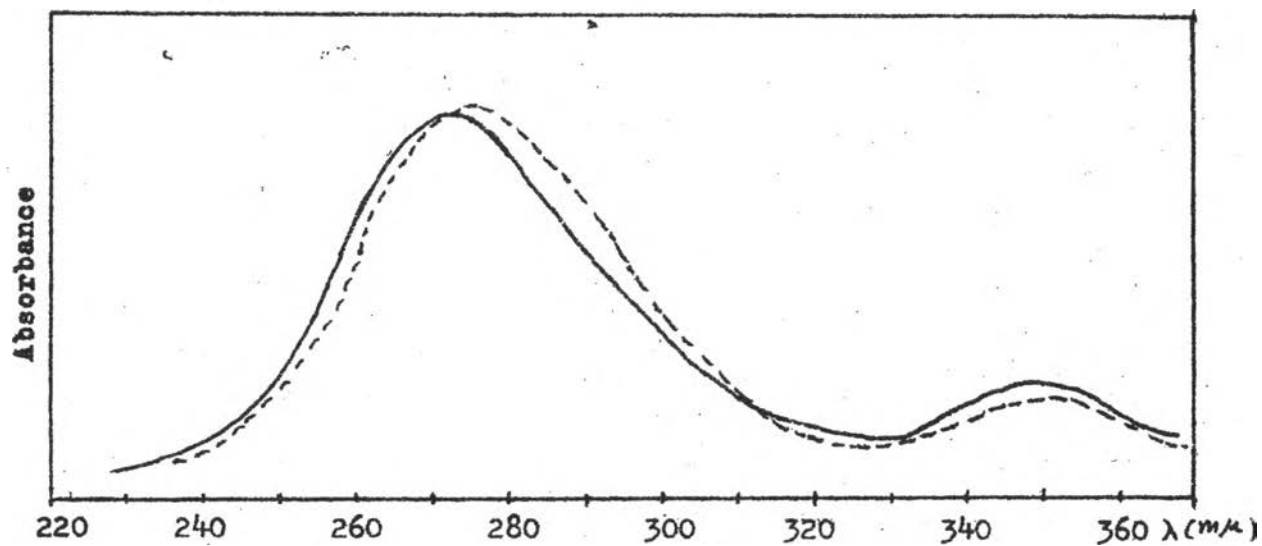


Fig. 13        The ultraviolet spectrum of Fe(AcAc)$_3$:

───────── , in hexane;

- - - - - - - , in ethyl alcohol.
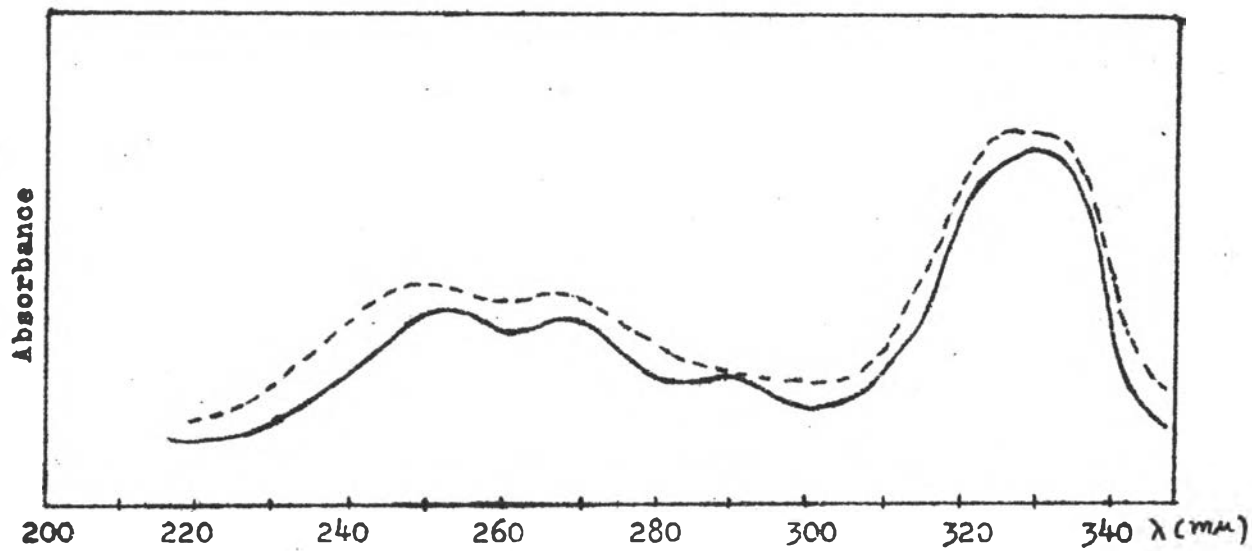
Fig. 14 The ultraviolet spectrum of Cr(AcAc)$_3$ :

————————— , in hexane;

— — — — — , in ethyl alcohol.
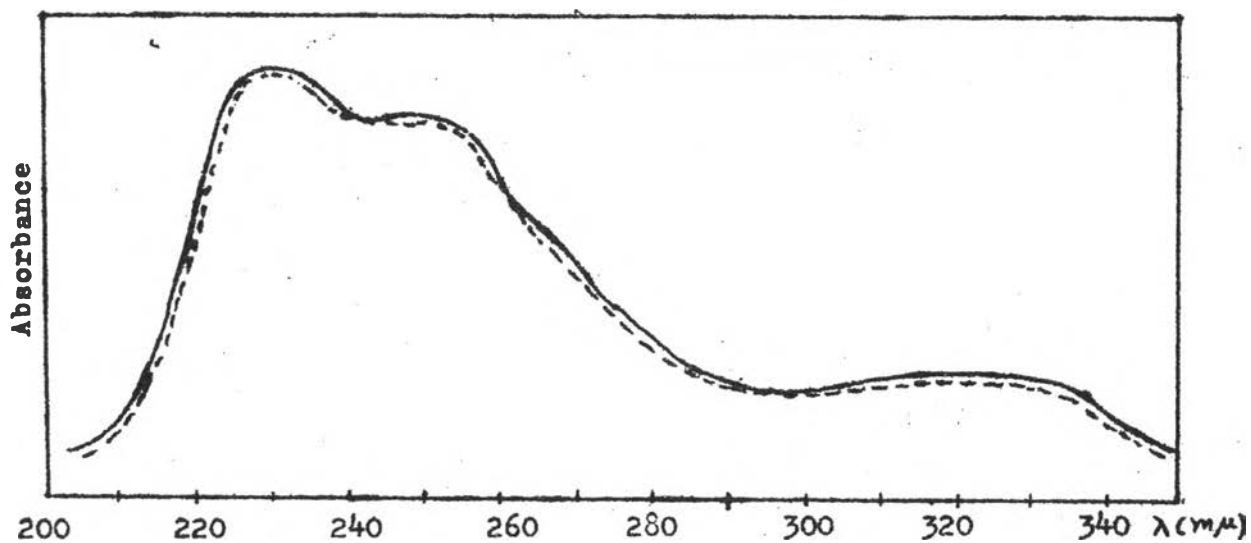


Fig. 15   The ultraviolet spectrum of Co(AcAc)$_3$ :

————————— , in heptane;

— — — — — , in methyl alcohol.

## Table 1

### Solvent Shifts of Acetylacetonate

| Solvent | $\lambda$ (m$\mu$) | $\Delta\lambda$ (m$\mu$) |
|---|---|---|
| Isooctane | 270 | 0 |
| Heptane | 270 | 0 |
| Hexane | 270 | 0 |
| Cyclohexane | 271 | +1 |
| Dioxane | 271 | +1 |
| Chloroform | 273 | +3 |
| Dichloromethane | 272 | +2 |
| Dichloroethane | 272 | +2 |
| n-Butyl alcohol | 274 | +4 |
| Iso-propyl alcohol | 274 | +4 |
| n-Propyl alcohol | 273 | +3 |
| Ethyl alcohol | 273 | +3 |
| Methyl alcohol | 272 | +2 |
| Water | 274 | +4 |

## Table 2

### Solvent Shifts of Ni(AcAc)$_2$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) |
|---------|---------|---------|---------|---------|
| Isooctane | 270 | 0 | 296(315)[*] | 0 |
| Heptane | 272 | +2 | 296(315) | 0 |
| Hexane | 270 | 0 | 296(315) | 0 |
| Cyclohexane | 270 | 0 | 296(314) | 0 (-1) |
| Dioxane | 274 | +4 | 296(310) | 0 (-4) |
| Chloroform | 274 | +4 | 295(312) | -1(-3) |
| Dichloromethane | 274 | +4 | 295(313) | -1(-2) |
| Dichloroethane | 273 | +3 | 295(314) | -1 (-1) |
| n-Butyl alcohol | - | - | 294(310) | -2 (-5) |
| Iso-propyl alcohol | - | - | 294(310) | -2 (-5) |
| n-Propyl alcohol | - | - | 294(310) | -2 (-5) |
| Ethyl alcohol | - | - | 293(310) | -3 (-5) |
| Methyl alcohol | - | - | 295(310) | -1 (-5) |
| Water | - | - | 295(310) | -1 (-5) |

[*]Band which appear as shoulders or inflexions on the side of a more intense band are enclosed in parentheses.

Table 3

Solvent Shifts of Co(AcAc)$_2$

| Solvent | $\lambda$ (m$\mu$) | $\Delta\lambda$ (m$\mu$) |
|---|---|---|
| Isooctane | 272 | 0 |
| Heptane | 274 | +2 |
| Hexane | 274 | +2 |
| Cyclohexane | 275 | +3 |
| Dioxane | 263 | -9 |
| Chloroform | 279 | +7 |
| Dichloromethane | 275 | +3 |
| Dichloroethane | 273 | +1 |
| n-Butyl alcohol | 283 | +11 |
| Iso-propyl alcohol | 283 | +11 |
| n-Propyl alcohol | 283 | +11 |
| Ethyl alcohol | 282 | +10 |
| Methyl alcohol | 283 | +11 |
| Water | 289 | +17 |

Table  4

Solvent Shifts of $Zn(AcAc)_2$

| Solvent | $\lambda$ ($m\mu$) | $\Delta\lambda$ ($m\mu$) |
|---|---|---|
| Isooctane | 271 | 0 |
| Heptane | 272 | +1 |
| Hexane | 271 | 0 |
| Cyclohexane | 271 | 0 |
| Dioxane | 273 | +2 |
| Chloroform | 274 | +3 |
| Dichloromethane | 274 | +3 |
| Dichloroethane | 274 | +3 |
| n-Butyl alcohol | 283 | +12 |
| Iso-propyl alcohol | 283 | +12 |
| n-Propyl alcohol | 283 | +12 |
| Ethyl alcohol | 283 | +12 |
| Methyl alcohol | 284 | +13 |
| Water | 289 | +18 |

Table  5

Solvent Shifts of Mn(AcAc)$_2$

| Solvent | $\lambda$ (m$\mu$) | $\Delta\lambda$ (m$\mu$) |
|---|---|---|
| Isooctane | 270 (310)* | 0 |
| Heptane | 271 (311) | +1 (+1) |
| Hexane | 271 (312) | +1 (+2) |
| Cyclohexane | 271 (312) | +1 (+2) |
| Dioxane | 272 | +2 |
| Chloroform | 273 | +3 |
| Dichloromethane | 273 | +3 |
| Dichloroethane | 273 (312) | +3 (+2) |
| n-Butyl alcohol | 292 (305) | +22 (-5) |
| Iso-propyl alcohol | 291 (305) | +21 (-5) |
| n-Propyl alcohol | 292 (307) | +22 (-3) |
| Ethyl alcohol | 291 (305) | +21 (-5) |
| Methyl alcohol | 292 (306) | +22 (-4) |
| Water | 292 | +22 |

Table  6

Solvent Shifts of Cu(acac)$_2$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) | $\lambda_3$ (m$\mu$) | $\Delta\lambda_3$ (m$\mu$) |
|---|---|---|---|---|---|---|
| Isooctane | 244 | 0 | 294 | 0 | (305)* | 0 |
| Heptane | 244 | 0 | 294 | 0 | (305) | 0 |
| Hexane | 244 | 0 | 294 | 0 | (305) | 0 |
| Cyclohexane | 245 | +1 | 294 | 0 | (305) | 0 |
| Dioxane | - | - | 294 | 0 | (305) | 0 |
| Chloroform | - | - | 295 | +1 | (305) | 0 |
| Dichloromethane | 245 | +1 | 294 | 0 | (305) | 0 |
| Dichloroethane | 245 | +1 | 295 | +1 | (305) | 0 |
| n-Butyl alcohol | 243 | -1 | 293 | -1 | (305) | 0 |
| Iso-propyl alcohol | 242 | -2 | 293 | -1 | (305) | 0 |
| n-Propyl alcohol | 242 | -2 | 293 | -1 | (305) | 0 |
| Ethyl alcohol | 242 | -2 | 294 | 0 | (305) | 0 |
| Methyl alcohol | 240 | -4 | 293 | -1 | (305) | 0 |
| Water | 238 | -6 | 293 | -1 | (305) | 0 |

* Band which appear as shoulders or inflexious on the side of a more intense band are enclosed in parentheses.

Table  7

Solvent Shifts of $Pd(AcAc)_2$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) | $\lambda_3$ (m$\mu$) | $\Delta\lambda_3$ (m$\mu$) |
|---|---|---|---|---|---|---|
| Isooctane | 226 | O | (250) | O | 328 | O |
| Heptane | 226 | O | (250) | O | 328 | O |
| Hexane | 226 | O | (250) | O | 328 | O |
| Cyclohexane | 226 | O | (250) | O | 328 | O |
| Dioxane | - | - | (250) | O | 325 | -3 |
| Chloroform | - | - | (250) | O | 326 | -2 |
| Dichloromethane | - | - | (250) | O | 325 | -3 |
| Dichlorocthane | - | - | (250) | O | 327 | -1 |
| n-Butyl alcohol | 225 | -1 | (250) | O | 326 | -2 |
| Iso-propyl alcohol | 225 | -1 | (250) | O | 326 | -2 |
| n-Propyl alcohol | 224 | -1 | (250) | O | 325 | -3 |
| Ethyl alcohol | 224 | -1 | (250) | O | 325 | -3 |
| Methyl alcohol | 224 | -1 | (250) | O | 325 | -3 |
| Water | - | - | (245) | -5 | 322 | -6 |

* Band which appear as shoulders or inflexions on the side of a
more intense band are enclosed in parentheses.

Table 8

Solvent shifts of Mn(AcAc)$_3$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) |
|---|---|---|---|---|
| Isooctane | 268 | 0 | 319 | 0 |
| Heptane | 269 | +1 | 319 | 0 |
| Hexane | 268 | 0 | 319 | 0 |
| Cyclohexane | 270 | +2 | 319 | 0 |
| Dioxane | 271 | +3 | 319 | 0 |
| Chloroform | 272 | +4 | 321 | +3 |
| Dichloromethane | 273 | +5 | 321 | +3 |
| dichloroethane | 272 | +4 | 321 | +3 |
| n-Butyl alcohol | 274 | +6 | 310 | -9 |
| Iso-propyl alcohol | 278 | +10 | 310 | -9 |
| n-Propyl alcohol | 291 | +23 | 310 | -9 |
| Ethyl alcohol | 273 | +5 | 310 | -9 |
| Methyl alcohol | 271 | +3 | 310 | -9 |
| Water | 283 | +15 | - | - |

Table  9

Solvent Shifts of $Fe(AcAc)_3$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) | $\lambda_3$ (m$\mu$) | $\Delta\lambda_3$ (m$\mu$) |
|---|---|---|---|---|---|---|
| Isooctane | (237)[*] | 0 | 271 | 0 | 352 | 0 |
| Heptane | (237) | 0 | 271 | 0 | 352 | 0 |
| Hexane | (237) | 0 | 271 | 0 | 352 | 0 |
| Cyclohexane | (236) | -1 | 272 | +1 | 352 | 0 |
| Dioxane | (236) | -1 | 273 | +2 | 352 | 0 |
| Chloroform | - | - | 273 | +2 | 352 | 0 |
| Dichloromethane | - | - | 273 | +2 | 352 | 0 |
| Dichloroethane | - | - | 273 | +2 | 352 | 0 |
| n-Butyl alcohol | (235) | -2 | 272 | +1 | 352 | 0 |
| Iso-propyl alcohol | (235) | -2 | 272 | +1 | 350 | -2 |
| n-Propyl alcohol | (235) | -2 | 272 | +1 | 349 | -3 |
| Ethyl alcohol | (235) | -2 | 272 | +1 | 349 | -3 |
| Methyl alcohol | (235) | -2 | 273 | +2 | 349 | -3 |
| Water | - | - | 274 | +3 | 349 | -3 |

Table   10

Solvent Shifts of $Cr(AcAc)_3$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta\lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta\lambda_2$ (m$\mu$) | $\lambda_3$ (m$\mu$) | $\Delta\lambda_3$ (m$\mu$) |
|---|---|---|---|---|---|---|
| Isooctane | 254 | 0 | 271 | 0 | 335 | 0 |
| Heptane | 254 | 0 | 271 | 0(1) | 335 | 0 |
| Hexane | 254 | 0 | 271 | 0 | 335 | 0 |
| Cyclohexane | 255 | +1 | 271 | 0 | 335 | 0 |
| Dioxane | 254 | 0 | 271 | 0 | 334 | -1 |
| Chloroform | 255 | +1 | 273 | +2 | 335 | 0 |
| Dichloromethane | 255 | +1 | 272 | +1 | 334 | -1 |
| DIchloroethane | 255 | +1 | 272 | +1 | 334 | -1 |
| n-Butyl alcohol | 255 | +1 | 271 | 0 | 333 | -2 |
| Iso-propyl alcohol | 255 | +1 | 270 | -1 | 333 | -2 |
| n-propyl alcohol | 255 | +1 | 270 | -1 | 331 | -4 |
| Ethyl alcohol | 255 | +1 | 270 | -1 | 331 | -4 |
| Mathyl alcohol | 255 | +1 | 270 | -1 | 331 | -4 |
| Water | 255 | +1 | 270 | -1 | 330 | -5 |

Table 11

Solvent Shifts of Co(AcAc)$_3$

| Solvent | $\lambda_1$ (m$\mu$) | $\Delta \lambda_1$ (m$\mu$) | $\lambda_2$ (m$\mu$) | $\Delta \lambda_2$ (m$\mu$) | $\lambda_3$ (m$\mu$) | $\Delta \lambda_3$ (m$\mu$) |
|---|---|---|---|---|---|---|
| Isooctane | 227 | 0 | 256 | 0 | 325 | 0 |
| Heptane | 227 | 0 | 256 | 0 | 325 | 0 |
| Hexane | 228 | +1 | 255 | -1 | 325 | 0 |
| Cyclohexane | 228 | +1 | 256 | 0 | 324 | -1 |
| Dioxane | 227 | 0 | 256 | 0 | 325 | 0 |
| Chloroform | - | - | 257 | +1 | 325 | 0 |
| Dichloromethane | - | - | 258 | +2 | 324 | -1 |
| Dichloroethane | - | - | 258 | +2 | 325 | 0 |
| n-butyl alcohol | 228 | +1 | 256 | 0 | 323 | -2 |
| Iso-propyl alcohol | 228 | +1 | 256 | 0 | 323 | -2 |
| n-Propyl alcohol | 229 | +2 | 256 | 0 | 323 | -2 |
| Ethyl alcohol | 228 | +1 | 255 | -1 | 323 | -2 |
| Methyl alcohol | 229 | +1 | 255 | -1 | 323 | -2 |
| Water | 228 | +1 | 254 | -2 | 323 | -2 |

## 3.2 Solvent Effect Study of the Polymeric/Adducted and Monomeric Species of $M(AcAc)_2$

Numerous $M(AcAc)_2$ are known to exist as oligomers in the solid state or in solutions of weakly coordinating solvents[24]. Some metal (II) complexes can associate in solvent of low coordinating power[30]. It has become clear that[26] the steriochemical behavior of $M(AcAc)_2$ compounds of the first-row transition metal (except copper) tends to have a coordination number greater than four. Provided they have no access to additional donor molecules they try to satisfy this tendency by forming oligomers in which there are bridging oxygen atoms. Thus in addition to the trimer $[Ni(AcAc)_2]_3$ (Fig. 2F) in which there are three octahedra fused together on their faces; there is the $[Co(AcAc)_2]_4$ tetramer, in which there are four octahedrally coordinated cobalt atoms with the octahedra sharing either faces or edges (Fig. 2F). The trimeric $[Zn(AcAc)_2]_3$ has been found to consist of six-coordinated and two five-coordinated zinc atoms. $Mn(AcAc)_2$ is trimeric, believed to be similar to $[Ni(AcAc)_2]_3$[26]

3.2.1 <u>Polymer and monomer equilibrium</u>

The Ni(AcAc)$_2$ complex in any noncoordinating solvents ( Fig 4 ) exhibits a monomer-oligomer equilibrium which is indicated by the intensities of the monomeric band ( 270 m$\mu$ ) and polymeric band ( 296 m$\mu$ ). The intensity of the polymeric band gradually decreases indicating polymeric species have now become largely monomeric. [Ni(AcAc)$_2$]$_z$ is known to exhibit mainly monomers in high dilutions ( 10$^{-4}$ - 10$^{-5}$ M ) in non-coordinating solvents[30] and so must retain their planar structures in solution without increasing the coordination number to six.

It is to be noted that, the oligomer species of Co(AcAc)$_2$, Zn(AcAc)$_2$ and Mn(AcAc)$_2$ do not show the polymer-monomer equilibrium as in Ni(AcAc)$_2$. This may due to the solubilities of these complexes: the order being Zn$^{2+}$ > Mn$^{2+}$ > Co$^{2+}$ > Ni$^{2+}$ . Also the order of the stability in M(AcAc)$_2$ is Ni > Co > Zn > Mn . Thus the less stable and the more soluble complexes, can dissociate quickly and easily in to monomers in dilute solution, in so doing, escape detection.

Ni(AcAc)$_2$ $_3$

(296 m$\mu$)
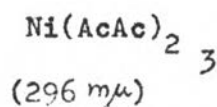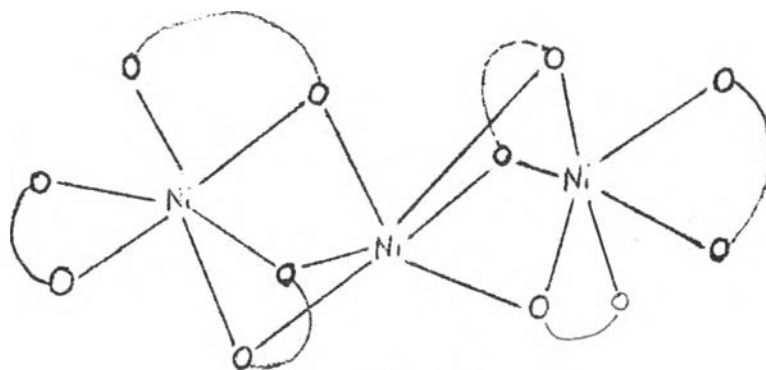
In non-coordinating solvent ( at high conc.)
Trimeric species.

O( alcohol,water)

O ( alcohol,water)

Ni(AcAc)$_2$.2S

(295 m$\mu$)
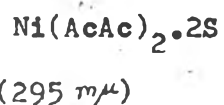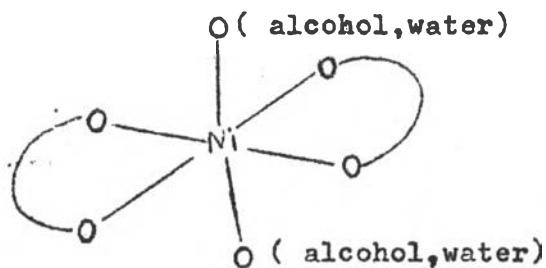
In coordinating solvent
Adducted, 6-coordinated, octahedral species.
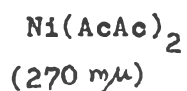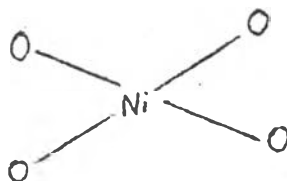
Ni(AcAc)$_2$

(270 m$\mu$)

In non-coordinating solvent ( at high dilution $10^{-4} - 10^{-5}$ M.)
4-coordinated planar species.

Fig. 16

### 3.2.2 Adducted species

The UV spectra of $Ni(AcAc)_2$ in a coordinating solvent shows a strong band at 294 m$\mu$. The band at 270 m$\mu$ which occur in non-coordinating solvents, has completely disappeared. This is because $Ni(AcAc)_2$ is now fully six coordinated. The trimeric units of Ni(II) acetylacetonate are broken by the coordinating solvents. As in Fig. 5 dissolution of $Ni(AcAc)_2$ in methanol a coordinating solvent, produces a six-coordinated, pseudo-octahedral complex, has a band near 294 m$\mu$. Coordinating solvents

like alcohol and water interact with $Ni(AcAc)_2$ to occupy coordination sites on the nickel metal :- $Ni(AcAc)_2.2H_2O$ or $Ni(AcAc)_2.2CH_3OH$ [26]

Fig. 6 presents the UV spectra of $Co(AcAc)_2$ in a non-coordinating solvent and in a coordinating solvent. The non-coordinating solvent spectrum shows a strong band at 275 m$\mu$ (mono-meric band) while in a coordinating solvent, the spectrum shows a strong band at 283 m$\mu$ instead , which is the band corresponding to the adducted species of $Co(AcAc)_2.2S$ eg. $Co(AcAc)_2.2H_2O$ [26,27]

The UV spectrum of $Zn(AcAc)_2$ in a non-coordinating solvent and in a coordinating solvent is shown in Fig. 7 . In coordinating solvents( alcohol, water ) the spectra show a band at 283 m$\mu$ which is associated with the adducted complex $Zn(AcAc)_2.2S$ eg. $Zn(AcAc)_2.2H_2O$ [26]. And the band at 271 m$\mu$ which assumed to be associated with monomeric $Zn(AcAc)_2$ disappeared .

Fig . 8    presents the  UV  spectra of Mn(AcAc)$_2$ in a
non-coordinating solvent and a coordinating solvent. The compa-
rison of Mn(AcAc)$_2$ in both solvents show that in non-coordina-
ting solvent, the band near 270 m$\mu$ is associated with monomer
Mn(AcAc)$_2$. And in the coordinating solvent, the spectrum shows
a band at 292 m$\mu$ only. This indicates that most of the species
are adducted to the coordinating solvent molecules
eg. Mn(AcAc)$_2$.2H$_2$O [19]

The assignments of the monomer, polymer/adduct bands are
now presented in the following table .

Assignment of monomer and polymer/adduct band of $[ M(AcAc)_2 ]_n$

| Complex | monomer 4-coordinated band (m$\mu$) | polymer/adduct 6-coordinated band (m$\mu$) |
|---------|-------------------------------------|--------------------------------------------|
| Ni(AcAc)$_2$ | 270 | 296 |
| Mn(AcAc)$_2$ | 270 | 292 |
| Co(AcAc)$_2$ | 272 | 283 |
| Zn(AcAc)$_2$ | 271 | 283 |
| Cu(AcAc)$_2$ | 293 | —— |
| Pd(AcAc)$_2$ | 250 | —— |

It is to be noted that neither $Cu(AcAc)_2$ nor $Pd(AcAc)_2$ form adducts, because **their** preferred valence is four. Also $Pd(AcAc)_2$ does not form polymers. Fig. 10 shows that the **UV** spectrum of $Pd(AcAc)_2$ in any non-coordinating and coor--dinating solvents are similar.

The **UV** spectrum of $Cu(AcAc)_2$ is shown in Fig. 9 $Cu(AcAc)_2$ forms a dimer $\left[Cu(AcAc)_2\right]_2$, but the observed UV spectrum only shows one band at 290 mμ indicating that the dimer and monomer have the same band frequency. This is not surprising , since the structure of the dimer is very similar to that of the monomer. The bridge to form a dimer $\left[Cu(AcAc)_2\right]_2$ is through central **carbon** atom of the ligand; unlike other oligomers which are bridged via the oxygen atoms of the ligand .

### 3.2.2 Summary

By comparing the ultraviolet spectra of $M(AcAc)_2$ in non-coordinating and coordinating solvents, we have been able to conclude that the spectra of $M(AcAc)_2$, with the exceptions of $Cu(AcAc)_2$ and $Pd(AcAc)_2$ in non-coordinating solvents show monomeric ( 4-coordinated ) species and in solution of coordinating solvents most of the species are ( 6-coordinated ) octahedral species. The band which occurs near 270 mµ is assigned as the $\pi \longrightarrow \pi_L^*$ transition and it is associated with monomeric species. The band near 290 mµ corresponds to the $\pi_L \longrightarrow \pi_L^*$ transition in six-coordinated pseudo-octahedral metal(II) complexes, where the coordination about the metal arise from either polymerization or adduct interaction with the exception of $Cu(AcAc)_2$ and $Pd(AcAc)_2$ .

### 3.3  Hydrogen Bonding of $CHCl_3$ and $CH_2Cl_2$ to $M(AcAc)_2$ and $M(AcAc)_3$

The oxygen atom of acetylacetonate complexes as well as the chelate rings themselves, can function as sites for H-bond formation. The ability of these sites to function as lewis bases is shown by the fact that many of the $M(AcAc)_2$ complexes polymerize through the acetylacetonate oxygens.

Solvents capable of H-bonding significantly perturb the visible and near-infrared spectra of some metal $\beta$-keto enolate complexes.[4]  Clark et.al.[2] showed from vapour pressure measurment in halomethane solvents, specific interaction do occur, e.g. H-bonding.  X-ray[1] powder patterns indicate that the solvates of some metal acetylacetonates e.g. $Cr(AcAc)_3 \cdot 2CHCl_3$, $Fe(AcAc)_3 \cdot 2CHCl_3$, have patterns which differ from the parent compounds.  In a systematic infrared[3] study of the interactions between $CDCl_3$ and various alcohols with various $\beta$-ketoenolate complexes showed that H-bond formation do occur.

We have selected two interesting solvents for our H-bond studies: $CHCl_3$ and $CH_2Cl_2$.  We have assumed that a change in band contours is indicative of H-bonding, an assumption yet to be tested.

### 3.3.1 Changes in band contours

Mn(AcAc)$_3$. The electronic spectrum for the Mn(AcAc)$_3$ complex has been dicussed by the previous authors.[25] The band at 272 m$\mu$ has been assigned as the $\pi_L \rightarrow \pi_L^*$ transition and the 318 m$\mu$ band as the $d \rightarrow \pi_L^*$ transition.

The UV spectra for Mn(AcAc)$_3$ in CH$_2$Cl$_2$ at various time intervals is presented in Fig. 17

The intensity of the 318 m$\mu$ band ( $d \rightarrow \pi_L^*$ ) decreases as time passed. The disappearance of this 318 m$\mu$ band was completed within one week. This suggests that the 318 m$\mu$ band is at least partially disturbed by the interaction between the Mn(AcAc)$_3$ complex and the solvents CHCl$_3$ and CH$_2$Cl$_2$ due to formation of H-bonds.

Fe(AcAc)$_3$. The $\pi_L \rightarrow \pi_L^*$ transition is located at 272 m$\mu$ and the $d \rightarrow \pi_L^*$ transition at 351 m$\mu$. Fig. 18 shows the UV spectra for Fe(AcAc)$_3$ in CHCl$_3$. at various time intervals.

The 351 m$\mu$ band also disappeared within one week for both solvents (CHCl$_3$, CH$_2$Cl$_2$) which again suggests H-bond formation between Fe(AcAc)$_3$ and H-bonding solvents: CHCl$_3$, CH$_2$Cl$_2$.
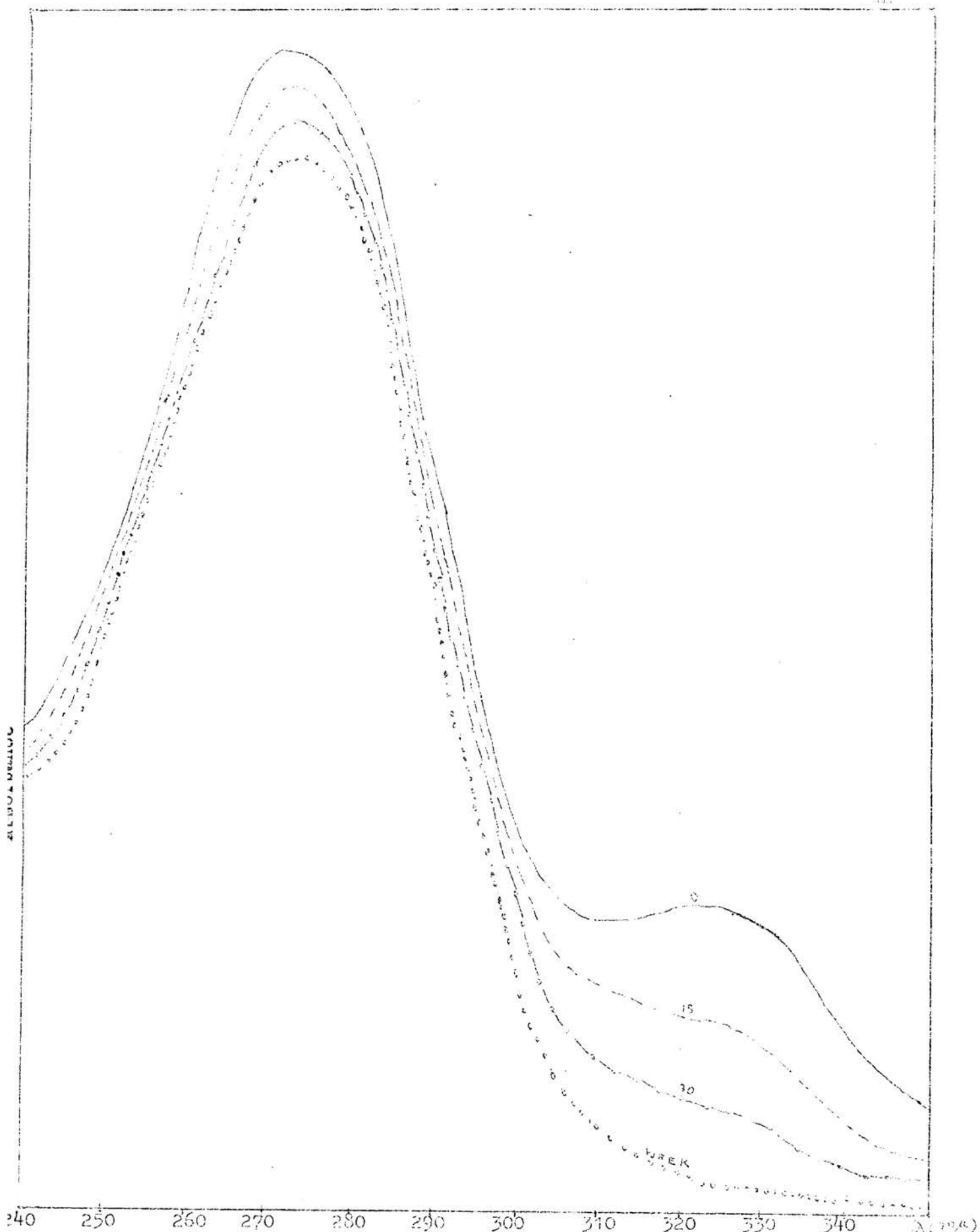
Fig. 17 The ultraviolet spectrum of $Mn(tcAc)_3$ in dichloromethane at various time intervals; —————, o min;————, 15 min;————, 30 min;............, week.
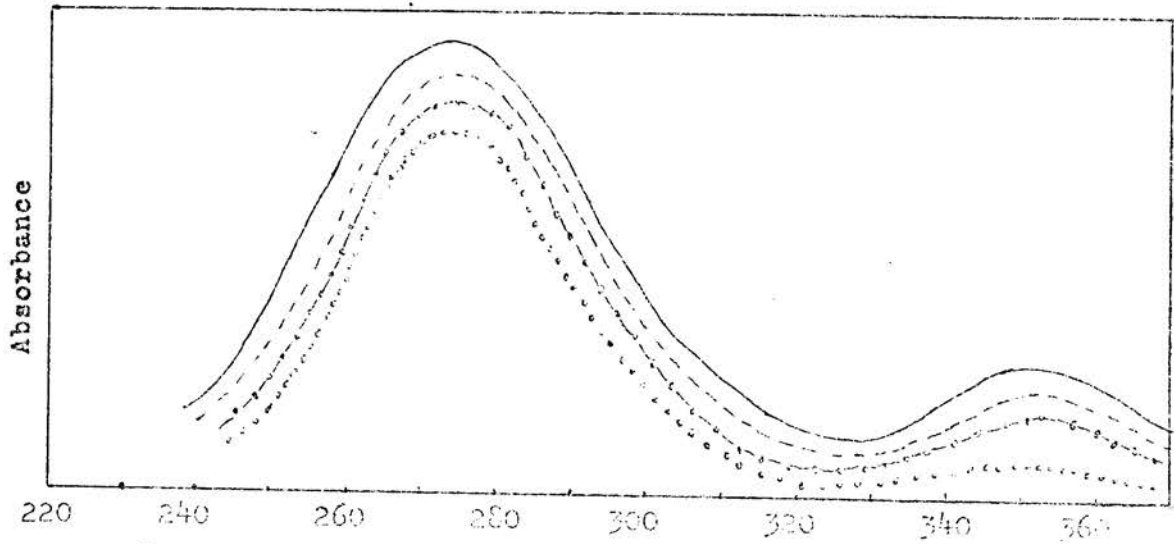
Fig. 18 The ultraviolet spectrum of Fe(AcAc)$_3$ in chloroform at various time intervals: ————, 0 min; — — — —, 15 min; — · — · — · —, 30 min; ············, week.
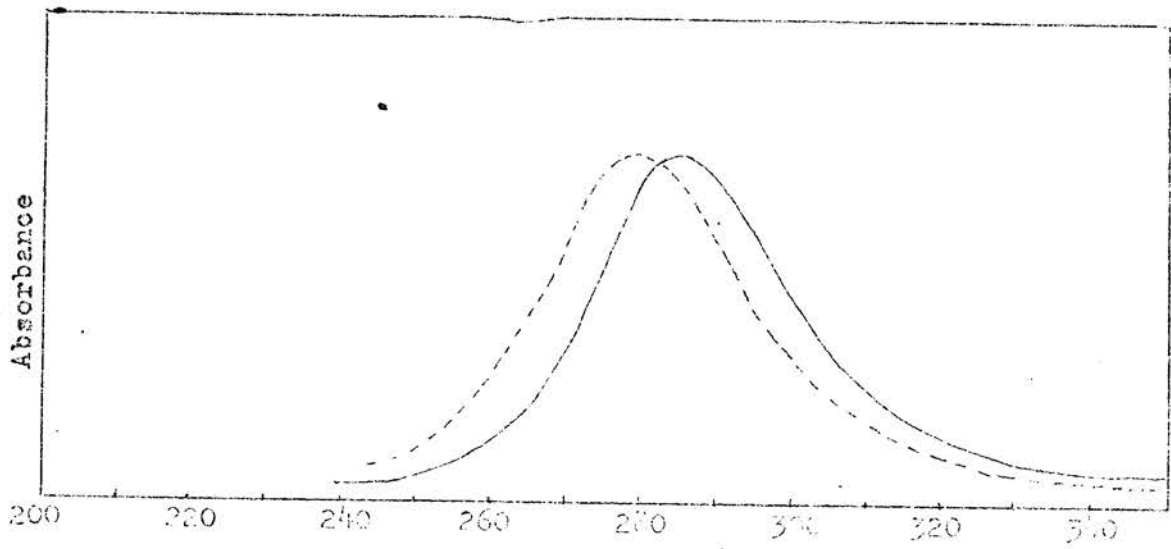


Fig. 19 The ultraviolet spectrum of Co(AcAc)$_2$ in chloroform at various time intervals: ————, 0 min; — — — — —, 30 min.
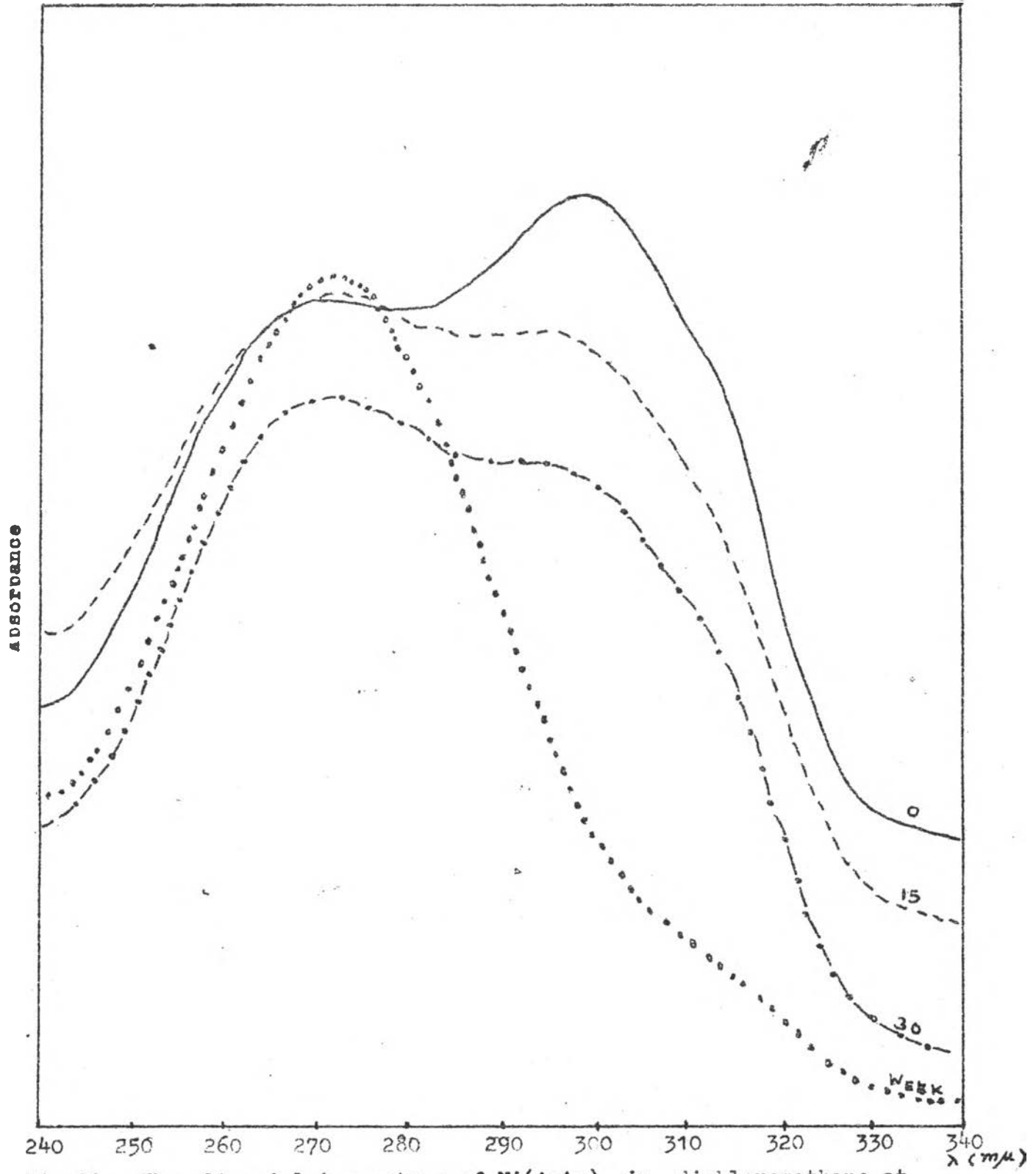
Fig.20  The ultraviolet spectrum of Ni(AcAc)$_2$ in dichloromethane at various time intervals: ————, 0 min; — — — — —, 15 min; —·—·—·—·—, 30 min; ··········, week.

<u>Ni(AcAc)$_2$</u> . The spectra of Ni(AcAc)$_2$ has been discussed in previous section. The UV absorption spectrum of Ni(AcAc)$_2$ in CH$_2$Cl$_2$ at various time intervals (Fig. 20 ) show that at time = 0 min. , the solutions exhibits monomeric species (272 m$\mu$ band) and oligomeric species (295 m$\mu$ band) at equilibrium.

As time progresses, the monomeric species predominate (intensity of 270 m$\mu$ is increased while that of 295 m$\mu$ is decreased.). Also within one week the shoulder at $\sim$ 311 m$\mu$ disappeared almost completely, indicating H-bonding.

Identical results have been obtained using CHCl$_3$ as a H-bonding solvent.

At concentration of 10$^{-5}$ M, Ni(AcAc)$_2$ in CHCl$_3$ show no oligomer band at 295 m$\mu$ (only 270 m$\mu$ band) and the shoulder band at 311 m$\mu$ also disappears within one week.

<u>Mn(AcAc)$_2$</u> . The UV. absorption spectrum of Mn(AcAc)$_2$ in solution of CHCl$_3$ and CH$_2$Cl$_2$ (which recorded at various time intervals) show evidence of H-bond formation. In a solution of CHCl$_3$ , the weak band at 310 m$\mu$ disappeared within 5 min. and in a solution of CH$_2$Cl$_2$ the disappearance of the 310 m$\mu$ band occured within one hour , once again suggesting H-bond formation.

3.3,2 <u>Frequency shifts</u>. The UV spectrum of Zn(AcAc)$_2$ and
Co(AcAc)$_2$ in solution of CHCl$_3$,CH$_2$Cl$_2$ (Fig. 19) which were recorded
at various time intervals, show no change in band contours for the
single 270 m$\mu$ band observed. hence ,no evidence of H-bond formation,
based on our assumption. This may be due to both Zn(AcAc)$_2$ and
Co(AcAc)$_2$ monomers are tetrahedral. Thus the solvent molecules
CHCl$_3$ , CH$_2$Cl$_2$ cannot H-bond to the complexes without excessive
crowding.

However ,both UV spectra show decisive frequency shifts.

| complex | CHCl$_3$ | CH$_2$Cl$_2$ |
|---------|----------|--------------|
| Zn(AcAc)$_2$ | 276-274 m$\mu$(within30min) <br> no further shifts | 276-274 m$\mu$(within30min) <br> no further shifts |
| Co(AcAc)$_2$ | 285-279 m$\mu$(within30min) <br> no further shifts | 288-282 m$\mu$(within30min) <br> 288-278 m$\mu$(within 24hour) <br> no further shifts |

The shift of frequencies dae be attributed to the change
in molecular structure i.e. the tetrahedral structure of Co(AcAc)$_2$
and Zn(AcAc)$_2$ change to planar forms in solution of CHCl$_3$ , CH$_2$Cl$_2$ .
At this stage H-bond formation is not observable.

It is interesting to note that in both solvents Co(AcAc)$_2$
requires more energy for changing; tetrahedral→planar.

| Complex | $CHCl_3$ | $CH_2Cl_2$ |
|---------|----------|------------|
| $Zn(AcAc)_2$ | 2 kcal/mole | 2 kcal/mole |
| $Co(AcAc)_2$ | 4 kcal/mole | 6 kcal/mole |

One can conclude that the bending force contant $Co-\hat{O}-C$ is stronger than $Zn-\hat{O}-C$ which agree with force constant calculations,[21]

$$Co(AcAc)_2 = 1.50 \times 10^5 \text{ dynes/cm}$$
$$Zn(AcAc)_2 = 1.30 \times 10^5 \text{ dynes/cm}$$

### 3.3.3 Compounds with no apparent changes in contour and frequency

$Co(AcAc)_3$, $Cr(AcAc)_2$ and $Pd(AcAc)_2$ dissolved in $CHCl_3$, $CH_2Cl_2$, show no spectral changes in both contours and frequency at various time intervals (15 min, 30 min, up to one week). Thus, we conclude that there is no UV spectral evidence for H-bonding with $CHCl_3$, $CH_2Cl_2$ for $Co(AcAc)_3$, $Cr(AcAc)_3$, $Cu(AcAc)_2$ and $Pd(AcAc)_2$.

Summary of hydrogen bonding of metal acetylacetonates in $CHCl_3$, $CH_2Cl_2$

| Complex | Method of detection | | | | |
| --- | --- | --- | --- | --- | --- |
| | UV (This work) | Visible[4] | IR[3] | Solvation[2] | X-ray |
| $Mn(AcAc)_3$ | $(CHCl_3,CH_2Cl_2)^a$ | $(CDCl_3)^a$ | $(CDCl_3)^a$ | | |
| $Fe(AcAc)_3$ | $(CHCl_3,CH_2Cl_2)^a$ | | $(CDCl_3)^a$ | $(CHCl_3,CH_2Cl_2)^a$ | $(CHCl_3)^a$ |
| $Ni(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^a$ | | | | |
| $Mn(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^a$ | | | | |
| $Co(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^b$ | | | | |
| $Zn(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^b$ | | $(CDCl_3)^b$ | $(CHCl_3)^b$ | |
| $Cr(AcAc)_3$ | $(CHCl_3,CH_2Cl_2)^b$ | | | | $(CHCl_3)^a$ |
| $Co(AcAc)_3$ | $(CHCl_3,CH_2Cl_2)^b$ | | $(CDCl_3)^a$ | | |
| $Cu(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^b$ | | | $(CHCl_3)^b$ | |
| $Pd(AcAc)_2$ | $(CHCl_3,CH_2Cl_2)^b$ | | | | |

a = H-bond occur with solvent in brackets;  b = H-bond do not occur with solvent in brackets.

From the table, it can be seen that our assumption for H-bonding formation is satisfactory.

### 3.3.4 Nature of H-bonding

It is believed that the H-bonding above is "trifurcated"[1]
for M(AcAc)$_3$ complexes, in which the H atom is linked equally
with 3 oxygen atoms on an octahedral face of the complex.

As for M(AcAc)$_2$ complexes, by the same argument it is
"bifurcated".

However, H-bonding with the chelate ring itself cannot
be ruled out.

The disapperance of the $\sim$ 320 m$\mu$ band suggests that significant
interactions between the chelate ring itself rather than
O atoms with CHCl$_3$, CH$_2$Cl$_2$, as it is known that the chelate ring
is completely delocalized[20] and also the Cl atom is strongly
electronegative thereby drawing electron from the chelate ring.

Finally the approximate magnitude of the H-bonding
formation may be obtained from the solvent red shifts of the
$\pi_L \rightarrow \pi_L^*$, 270 m$\mu$ band, they are tabulated below:-

| Complex | $\Delta$ H H-bonding (K cal/mole) |
|---|---|
| Ni(AcAc)$_2$ | 1.6 |
| Mn(AcAc)$_2$ | 1.2 |
| Mn(AcAc)$_3$ | 1.6 |
| Fe(AcAc)$_3$ | 0.8 |

This suggests the method of calculation is not satisfactory,

because the values are low by a factor of 2.5 . It is not really surprising since the organic $\pi \rightarrow \pi^*$ red shift criterion cannot really be applied to the inorganic ligand-crystal field system . Also the central symmetric field of the metal plays a part . Therefore, the $\pi \rightarrow \pi^*$ red shifts or the $n \rightarrow \pi^*$ blue shifts used as sole criteria for H-bonding in the inorganic system are suspect.

## 3.4 Solvent Shifts

### 3.4.1 $\pi \rightarrow \pi^*$ band

(AcAc)   The frequency shift observed in the band ($270\,m\mu$) of (AcAc), 'Table 1 shows a red shift of about $+4\,m\mu$ ($500\,cm^{-1}$) on going from non-polar solvent to polar solvent.

It can be added that the shift in the organic system are generally higher e.g. H-bond shifts for $\pi \rightarrow \pi^*$ transition in mesityloxide is about $1,000\,cm^{-1}$, in benzophenone about $900\,cm^{-1}$, the solvents being methyl alcohol and ethyl alcohol.

The smaller frequency shifts suggest that inter and intra H-bonding as well as some other solvation interactions come into play. They may affect opposite shifts . The reason could be the  electron in (AcAc) are almost completely delocalized . Therefore the rings as well as the oxygen atoms can serve as sites for inter H-bonding between solute and solvents and other molecular interactions.

<u>M(AcAc)</u>$_2$     The red shift of the $\pi_L \longrightarrow \pi_L^*$ band of Ni(AcAc)$_2$ , Co(AcAc)$_2$ , Zn(AcAc)$_2$ , Mn(AcAc)$_2$ are about +4 m$\mu$ ( 540 cm$^{-1}$ ) , +2 m$\mu$( 300 cm$^{-1}$ ) , +3 m$\mu$( 407 cm$^{-1}$ ) and +2 m$\mu$ ( 300 cm$^{-1}$ ) respectively, ( Table 2-5 ) as the solvent changes from isooctane to dichloroethane.However, when these M(AcAc)$_2$ are dissolved in alcohols and water , these divalent complexes form a new band at 290 m$\mu$. This is believed to be an adducted band . The equilibrium of monomers-oligomers of Ni(AcAc)$_2$ in non-coordinating solvents have already been noted previously.

The $\pi_L \longrightarrow \pi_L^*$ band for Cu(AcAc)$_2$ ( 294 m$\mu$ ) and Pd(AcAc)$_2$ ( 250 m$\mu$ ) do not show ( Table 6,7 ) any significant shifts in the spectra ( with the exception of -5 m$\mu$ for Pd(AcAc)$_2$ in water ) . This means that these two complexes interact weakly with the solvent molecules . A possible explanation being that these two metals form very strong   complexes[20] The ligands are held too tightly for strong solvent interactions . Also Cu(AcAc)$_2$ and Pd(AcAc)$_2$ prefer a valence of four .

$\underline{M(AcAc)_3}$    From tables. 8-9, it can be seen that red shifts of the 270 m$\mu$ band in $Fe(AcAc)_3$ and $Mn(AcAc)_3$ are greater in polar solvents as expected . $Mn(AcAc)_3$ has been reported to be partly dissociated in alcohols.[25] Our spectra seem to support this ; there are indications of frequency shifts as time progresses as in iso-propyl alcohol and water or slight changes in band contours as in ethyl alcohol and methyl alcohol for different runs . This also suggests H-bond formation , which supports our preliminary IR results.

For $Co(AcAc)_3$ the $\pi_L \rightarrow \pi_L^*$ transition ( Table 11,10 ) is ~ 256 m$\mu$ and $Cr(AcAc)_3$ ~ 270 m$\mu$ ( the band at ~ 255 m$\mu$ is assumed to be associated with the $\pi_L \rightarrow \pi_L^*$ transition ). The red shifts are quite small, suggesting weak interactions with solvents . The reason being both are strongly chelated to the ligands.

### 3.4.2  Metal ←→ Ligand band

(i) $d \rightarrow \pi_L^*$ , the blue shifts (except Mn) of the $d \rightarrow \pi_L^*$ band observed for $M(AcAc)_3$ and $M(AcAc)_2$ are presented in Tables 2 - 11.  They are summarised below.

| Complex | Configuration of d-electron* | Blue Shift | |
|---------|------------------------------|------------|------------|
| | | Non-coordinating | Coordinating |
| $Cr(AcAc)_3$ | $d^3 \quad d^0$ | 0 | -3 |
| $Mn(AcAc)_3$ | $d^3 \quad d^1$ | +1 | -9 |
| $Fe(AcAc)_3$ | $d^3 \quad d^2$ | 0 | -2 |
| $Mn(AcAc)_2$ | $d^3 \quad d^2$ | +2 | -5 |
| $Co(AcAc)_3$ | $d^4 \quad d^2$ | 0 | -2 |
| $Co(AcAc)_2$ | $d^5 \quad d^2$ | --- | --- |
| $Ni(AcAc)_2$ | $d^6 \quad d^2$ | -2 | -3 |
| $Pd(AcAc)_2$ | $d^6 \quad d^2$ | -1 | -3 |
| $Cu(AcAc)_2$ | $d^6 \quad d^3$ | 0 | 0 |
| $Zn(AcAc)_2$ | $d^6 \quad d^4$ | --- | --- |

* High spin

The result from the above table shows that the blue shifts of d $\longrightarrow \pi_L^*$ transition does not significantly depend upon the number of d-electrons.

However it is interesting to note that, both Ni(AcAc)$_2$ and Mn(AcAc)$_2$ show the same order of shifts in alcohols and water as they both have similar polymeric and monomeric structures. Mn(AcAc)$_3$, which shows greater blue shift in alcohol and water, indicates some H-bond interaction with these solvents. This is in agreement with the greater red shifts of $\pi_L \rightarrow \pi_L^*$ transition band, and slight changes in band contours in Mn(AcAc)$_3$, already mentioned.

### (ii) $\sigma_L \longrightarrow$ 3d band

This band of 230 m$\mu$ is only observed for Cu(AcAc)$_2$, Pd(AcAc)$_2$, Fe(AcAc)$_3$, Co(AcAc)$_3$ ( Table 6,7,9,11 ) all shifts are very small except Cu(AcAc)$_2$ in water 6 m$\mu$, but the pattern indicates the solvents shifts in coordinating solvents are more than those of the non-coordinating solvents.

All $\sigma_L \longrightarrow$ 3d bands are strong except for Fe(AcAc)$_3$, indicating a measure of $\sigma$ bond strengths.

### 3.5 Comparison of Infrared, Nuclear magnetic resonance and UV-visible methods of detections in hydrogen bonding.

The NMR measurements of H-bonding systems are few in number but great in promise. Effective use of this technique depends rather critically upon the possibility of varying the sample temperatures. At high temperatures, dissociation of H-bonded complexes can be obtained. While at low temperatures, the different H-bonded species may be observed individually.

We can profitably contrast the capabilities of the IR and NMR techniques. There are a number of the advantages in IR. methods: different H-bonded species can be studied in the stretching and bending region (4,000-50 cm ), lower concentrations can be used; gas and solid phases are readily studied; wider temperature range are accessible. On the other hand, there are some inherent capabilities of NMR measurements which give them unique value e.g., the specific role of the hydrogen atom in H-bonding interactions. With reference to the electronic redistribution accompanying H-bond formation, NMR shifts give new, though not yet well understood, information. Finally, the special power of the magnetic methods for determing rates of H-bond formation and rupture awaits exploitation.

The IR and NMR methods can thus be used as powerful supplementary tools.

It is to be expected that the UV-visible spectrum of a molecule may be altered by the formation of a H-bonds, if the chromophoric portion of the molecule is perturbed by the H-bond. Such is indeed the case: H-bond formation is often accompanied by readily measurable spectral changes, which contains interesting and useful information. Yet it is only within the last decade that UV-visible spectra have received concerted attention as a means of studying H-bonding.

The following generalizations about the effect of H-bonding on electronic transitions can be made:-

1. Electronic transition (both in emission and absorption) of either acidic or basic substances in solution may show shifts of the band maximum upon H-bond formation. In absorption spectra both positive and negative shifts, $\Delta \nu_a$, have been observed. These shifts correspond to energies, $h \Delta \nu_a$, usually in the order of, but smaller than, H-bond energies. In absorption spectra, no pronounced change of absorption coefficient accompanies the shifts, but vibrational fine structure may become diffuse.

2. The frequency shifts often provide quantitative determination of thermodynamic quantities: equilibrium constants, $\Delta H$ and $\Delta S$ of H-bond formation at different temperatures.

3. It is commonly accepted from organic literature that $n \longrightarrow \pi^*$ transition of a base always shift toward higher frequency upon H-bond formation (blue-shift)

4. In contrast, $\pi \longrightarrow \pi^*$ transitions usually shift toward lower frequencies (red shift) upon H-bond formation.

5. These shifts contain information concerning the difference of $\Delta H$ in H-bond formation between the ground and the excited states.

Of course, IR method can also give similar information as in 1 and 2 above. Thus, for a better understanding of H-bonding all 3 methods should be used.

## 3.6 Summary and Conclusion

By comparing the UV spectrum of $M(AcAc)_2$ in non-coordinating solvents and coordinating solvents, we can conclude that the spectra in non-coordinating solvents of $M(AcAc)_2$ show monomeric (4-coordinated) species; and in solutions of coordinating solvents most of the species are adducted (6-coordinated) species.

The UV spectra of some metal acetylacetonates showed time effects in two interesting H-bonding solvents: $CHCl_3$ and $CH_2Cl_2$, the assumption being that a change in band contours is indicative of H-bonding. By comparing this UV method with the other methods: visible, IR, solvation and X-ray; our results are in general agreement with the other methods mentioned.

It is believed that the oxygen atom of $\beta$-ketoenolate complexes, as well as the chelate rings themselves, can function as sites for H-bond formation. However many evidence support the oxygen atoms as the sites, the ability of the oxygen atom to functional as lewis base is shown by the fact that many of the $M(AcAc)_2$ complexes polymerise through the $\beta$-diketone oxygens.

Our studies of H-bonding in $CHCl_3$ and $CH_2Cl_2$ suggest that the solvents use the chelate rings rather than the oxygen atoms as sites. It is known that electrons in the chelate rings are

completely delocalized and also the chlorine atoms have high .
affinity for electrons. The disappearance of the $3d \rightarrow \pi_L^*$ band
suggests strong perturbations of electron transfer. This
indicates the perturbation would involve the entire delocalized
rings rather than the oxygen atoms.

Finally, we can now pose the question "How good is UV
method in detecting H-bond formation?" . We can only use the
change of band contours or frequency shifts ( red and blue
shifts ) as  indications. But, there are other molecular
interactions which need not be H-bonding e.g. association,
solvation . It is difficult, if not impossible, to distinguish
how much contribution to the frequency  shifts for example ,
is associated with a certain molecular interaction. Therefore,
the UV and indeed the visible methods for detecting H-bonding
can only be relegated to  supporting roles.