PHYSICOCHEMICAL STUDIES OF SOME TRIVALENT METAL β-DIKETONATES

BY

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ABSTRACT

Forty trivalent metal chelates of 2-thenoylacetone, 2-thenoyltrifluoroacetone, 2-furoylacetone, 2-furoyltrifluoroacetone, benzoylacetone, benzoyltrifluoroacetone and nicotinoyltrifluoroacetone (where metal(III) = Al, Cr, Mn, Fe and Co) as well as some mixed ligand β-diketonate complexes of iron(III), have been prepared and their spectroscopic and magnetic properties have been examined. Among the series of compounds studied, $Al(fbd)_3$, $Mn(fbd)_3$, $Al(tftbd)_3$, $Co(tftbd)_3$, $Cr(tffbd)_3$, $Mn(tffbd)_3$, $Co(tffbd)_3$, $M(tbd)_3$, $M(tfpybd)_3$ (where M = Al, Cr, Mn, Fe and Co), $Fe(bzac)_2$ (tftbd), $Fe(tftbd)_2(bzac)$, $Fe(fbd)_2(tbd)$ and $Fe(tbd)_2(fbd)$ have been investigated for the first time.

The effects of 3-pyridyl, 2-thienyl, 2-furyl, phenyl and trifluoromethyl substituents have been discussed in relation to the lowest spin-allowed transition, $\pi_3 - \pi_4^*$ and νM-O, νC$\underline{---}$O and νC$\underline{---}$C$\underline{---}$C stretching vibrations. Substitution of a methyl group in 2,4-pentanedione - by a furyl ring, and a methyl group in 1-(2-furyl)-1,3-butanedione by a trifluoromethyl are found to strengthen the C$\underline{---}$O and C$\underline{---}$C$\underline{---}$C and weaken the M-O bonds of the chelate rings; while the 2-thienyl group shifts the M-O and C$\underline{---}$O to lower, and C$\underline{---}$C to higher frequencies. The

phenyl substituent, as expected, strengthens the M-O and $\underline{C---C}$ bonds and weakens the $\underline{C---O}$ bonds. The most sensitive M-O stretching modes follow the order Co(III) >Al(III) > Cr(III) > Mn(III) > Fe(III). However, the lowest spin-allowed $\pi_3 - \pi_4^*$ transition of the β-ketoenolate anion, although found to be metal sensitive, does not follow the same trend. Trifluoromethyl group substitution resulted in the bathochromic shift of the $\pi_3 - \pi_4^*$ transitions.

The ligand field energy parameters D_q, f(ligand), B_{35} and β_{35} have been calculated and the following order of nephelauxetic effect in the ligands has been derived:

Htffbd > Htbd > Hfbd > Hacac > Hbztfac >
Htftbd > Hbzac > Htfpybd.

While the spectrochemical series of the ligands depicted by the magnitude of f(ligand) parameter also follow the order:

$\text{tfpybd}^- < \text{bztfac}^- < \text{fbd}^- < \text{tffbd}^- < \text{tbd}^- <$
$\text{acac}^- \sim \text{bzac}^- < \text{tftbd}^-$

The reflectance spectra and magnetic properties of these compounds revealed that they are very similar to the corresponding tris-(2,4-pentanedionato) metal(III) octahedral complexes.

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CERTIFICATION BY SUPERVISORS

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Dedicated to my parents, Apeke and Tashi Masa who by the sweat of the brow, have made the attainment of this height possible.

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ABBREVIATIONS

Hacac - 2,4 - pentanedione

Htfacac - 1,1,1-trifluoro-2,4-pentanedione

Htbd - 1 - (2-thienyl)-1,3-butanedione

Htftbd - 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione

Hfbd - 1 - (2-furyl) - 1, 3-butanedione

Htffbd - 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione

Hbzac - 1 - phenyl - 1, 3-butanedione

Hbztfac - 4,4,4-trifluoro-1-phenyl-1,3-butanedione

Htfpybd - 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione

Hdbm - 1, 3-diphenyl-1,3-propanedione

Hdpm - 2,2,6,6 - tetramethyl - 3,5-heptanedione

IBMK - isobutylmethyl ketone

ESR - electron spin resonance

CFSE - crystal field stabilization energy

IR - infrared

UV-VIS - ultraviolet-visible

ε - molar extinction coefficient

GC-MS - gas chromatography-mass spectrometry

ECGC - electron capture gas chromatography

LASER - light amplification by stimulated emission of radiation.

RT - room temperature

LNT - liquid nitrogen temperature

LHT - liquid helium temperature

B.M. - Bohr Magneton

C.g.S. - Centimetre - gram - second

pm - picometer (10^{-12}meter).

CHAPTER 1

INTRODUCTION

1.1 General behaviour of β-diketones

β-Diketones participate in tautomeric equilibria where an apparently pure compound is actually a mixture of two or three substances having keto and enol structures (Fig.1a) [1, 2]. Generally β-diketones are weak acids and their pKa values are given in Table 1. The enolate anion (Fig 1b) has a five-atom π-network extending over the two oxygen and the three non-terminal carbon atoms. Six electrons occupy the resulting π-type molecular orbitals. The enolate anion will have a C_{2v} symmetric structure often represented as in Fig 1b, if R_1, R_2 and R_3 are treated as point masses and R_1 and R_2 are equal. One of the most fascinating features of the chemistry of this class of compounds is the variety of ways in which their enolate anions (Fig 1b) can bond to metallic and or semimetallic atoms or ions, to give varied molecular structures. Among the metal β-diketonates, metal acetylacetonates (R_1=R_2=CH_3;R_3= H) have received the greatest attention and can most often be thought of as prototypes for other β-ketoenolate complexes.

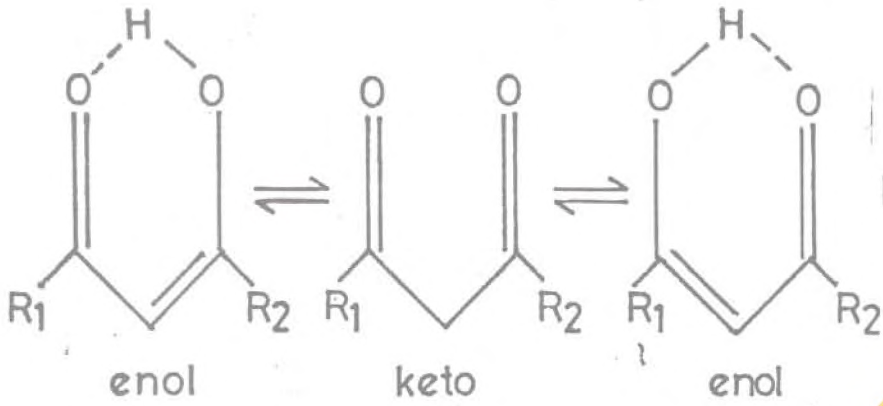


Fig. 1(a) Keto - enol tautomerism

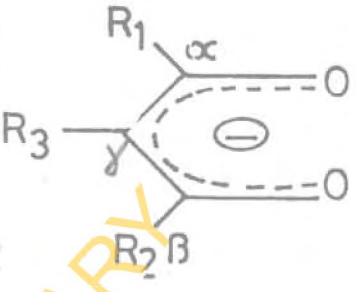


Fig. 1(b) β-keto - enolate anion

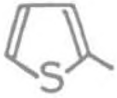
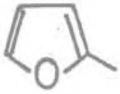
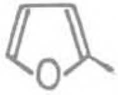
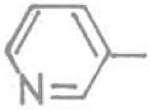
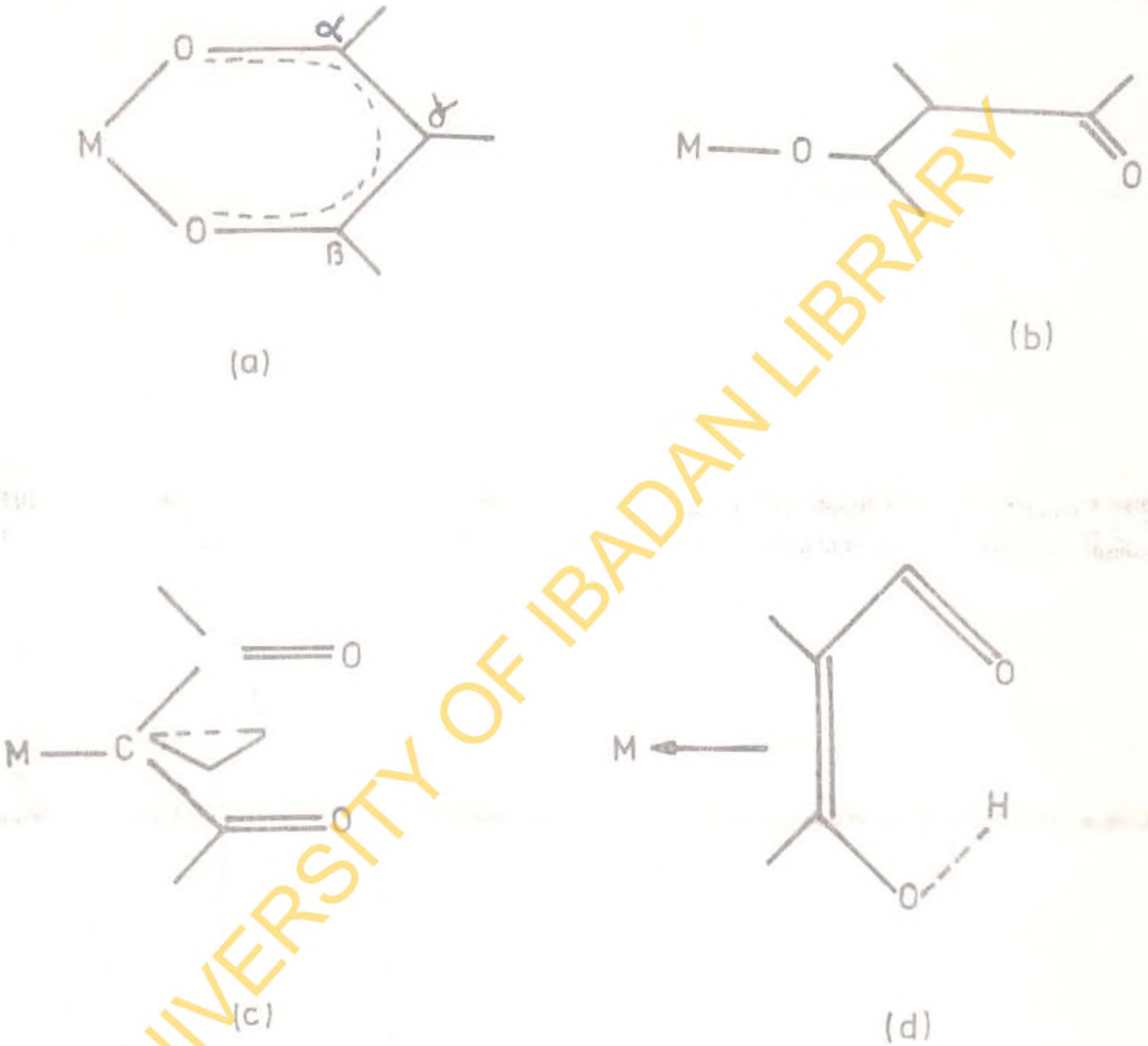
Abbreviations	R$_1$	R$_3$	R$_2$
Htbd	CH_3	H	
Htftbd	CF_3	H	
Hfbd	CH_3	H	
Htffbd	CF_3	H	
Hbzac	CH_3	H	
Hbztfac	CF_3	H	
Htfpybd	CF_3	H	

TABLE 1 pK_a's of β-Diketones.

β-Diketone	pK_a	Reference
Hexafluoroacetylacetone	4.40	[3]
Furoyltrifluoroacetone	5.40	[4]
Benzoyltrifluoroacetone	6.20	[3]
Thenoyltrifluoroacetone	6.50	[3]
Trifluoroacetylacetone	6.50	[3]
Benzoylacetone	9.20	[3]
Furoylacetone	9.30	[4]
Acetylacetone	9.80	[3]
Thenoylacetone	10.00	[4]
Dibenzoylmethane	10.30	[4]
Dipivaloylmethane	11.77	[4]

There are four different ways as shown in Fig. 2, in which a β-ketoenolate anion may function as a ligand in bonding to metals and semimetals. Though the most commonly found coordination [5] is through the two oxygen atoms of the ligand (Fig. 2a), coordination through the γ-carbon atoms has been established conclusively by X-ray crystallographic methods for a platinum (IV) complex [6] and also for a Werner complex, $KPt(acac)_2Cl$ [7] (Fig. 3). Bonding of the metal ion to the carbon-carbon double bond of the enol form is not crystallographically established as yet, but the elegant work of Lewis and coworkers [7 - 9] has proved beyond doubt that a platinum(II) - olefin bond exists in the acidified Werner complex, $HPt(acac)_2Cl$ (Fig.4). In general, therefore, the metals most likely to form carbon bonded complexes are the second and third row transition elements at the right hand side of the periodic table with an increased tendency toward formation in going from the second to the third row transition elements [10].



(a) (b)

(c) (d)

Fig. 2 Acetylacetone as a ligand showing different modes of coordination.

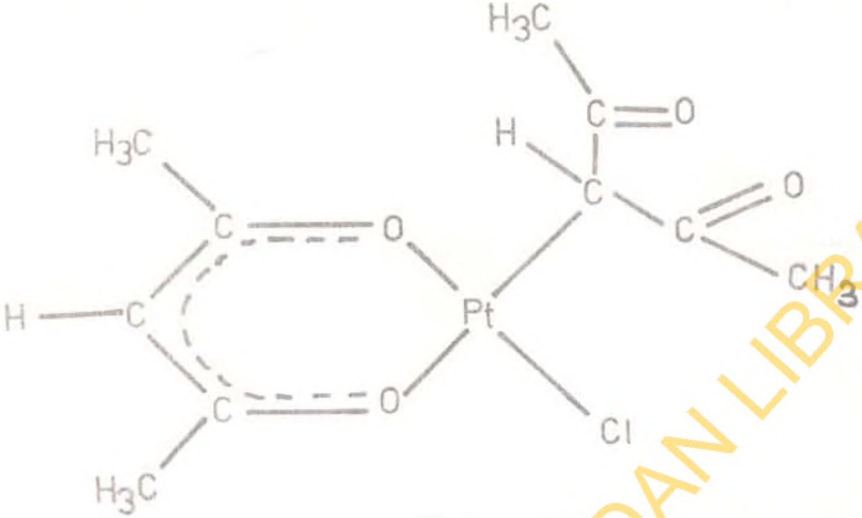


Fig. 3 $[Pt(acac)_2\,Cl]^{\ominus}$ anion.

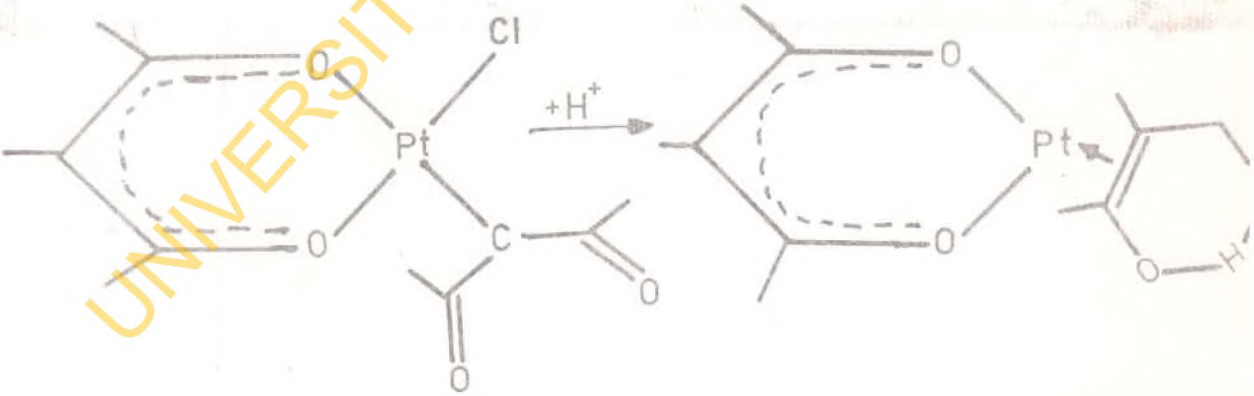


Fig. 4 Werner Complex ; $HPt(acac)_2\,Cl$

The occurrence of oxygen-chelated acetylacetonate complexes can be appreciated from the fact that such complexes have been reported for all the main group transition elements (except Technetium) and lanthanide elements (except Promethium) as well as numerous main group and actinide elements. Various aspects of this subject have received extensive treatment in several review articles [11 - 14]; and it is known that when the coordination number of the metal exceeds twice the charge on the metal ion, and if the ligands sterically allow it, polymerization (or adduct formation of the metal β-ketoenolate complex occurs. Crystallographic evidence for polymerization exists for species like $[Ni(acac)_2]_3$ [15], $[Co(acac)_2]_4$ [16] $Fe(acac)_2$ [5] and $[(CH_3)_3Pt(acac)]_2$ [17], while there is also an evidence for polymerization from molecular weight determinations of $Mn(acac)_2$, $Ln(acac)_3$, (Ln=lanthanides) [5]. $Zn(acac)_2$ appears to crystallize as a trimer [14, 15, 18, 19] while $Cr(acac)_2$ [5] as a polymer.

For monomeric six-coordinated complexes with trivalent metals, an octahedral coordination of oxygens about the metal is expected and it has been confirmed for the structures of $Al(acac)_3$ [6], $Fe(acac)_3$ [20], $Cr(acac)_3$ [21] and $Mn(acac)_3$ [22].

The $Mn(acac)_3$ molecule however, is known from structural analysis as having two average Mn – O bond distances 195pm and 200pm [23] in a compressed MnO_6 octahedron compatible with the predicted Jahn-Teller distortion and consistent with the electronic spectra.

1.2 Preparative methods of metal β-diketonates

Under the appropriate conditions, the enolic protons of 1,3-diketones can be replaced by different metals or their salts, forming metal derivatives which are characteristic of the various β-diketones. Five major preparative methods are encountered and these are described below.

(i) The first method involves direct reaction of β-diketones with metal salts. The reaction may either occur in an aqueous solution and, or, in a non-aqueous medium. The metal salts usually used are: acetates, nitrates, oxalates, oxychlorides and chlorides [24].

$$M^{n+} + nRCOCH_2COR' \xrightarrow{EtOH(95\%)} M(RCOCHCOR')_n + nH^+$$

In the course of such a reaction, there is an increase in concentration of free acid in solution which therefore makes the reaction come to an equilibrium short of completed reaction. A pH control is therefore essential for the reaction to go to completion and this is achieved by buffering the solution. For this reason, the use of metal acetates iw widely reccommended for such preparations as illustrated in the reactions below.

(a) $MnCl_2 + 2\ Hacac + 2NaAc \rightarrow Mn(acac)_2 + 2NaCl + 2HAc$

(b) $4Mn(acac)_2 + KMnO_4 + 7Hacac + HAc \rightarrow 5Mn(acac)_3 + KAc + 4H_2O$.

(Ac = acetate anion, Hacac = acetylacetone and HAc = acetic acid)

The pH control could also be achieved by gradually adding a weak base such as ammonia, however, one must be very careful to maintain the pH below a critical value otherwise a metal hydroxide or basic salt might contaminate the product. Occasionally the controlled addition of ammonia may also result in high local concentrations which may cause the precipitation of basic diketone derivatives. The difficulties may be avoided by the homogeneous generation of ammonia (adding urea to the solution and heating) [25] as illustrated in the preparation of $Cr(acac)_3$.

(a) $CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$

(b) $CrCl_3 + 3Hacac + 3NH_3 \rightarrow Cr(acac)_3 + 3NH_4Cl$

In aqueous solution, the reaction is usually limited by insufficient solubilities of many β-diketones, and this may be overcome by using a mixture of water with ethanol or dioxane; or by adding the β-diketone in an alcoholic solution, to the aqueous solution of the metal salt (buffered with sodium acetate) [26].

(ii) The second method involves a reaction of a soluble salt of a metal. This is very similar to the first method and the reaction involves the preliminary formation of the diketone in water by adding the minimum necessary amount of ammonia or sodium carbonate [27]. It is then equivalent to carrying out the reaction at a higher pH than by the use of the β-diketone alone. Under this condition, a number of substances other than the desired neutral chelate can be formed.

Among these, are (a) a mixed compound e.g., MchX (ch=β-diketone, X=halide, nitrate etc.) [27], resulting from the presence of insufficient β-diketone in the region of the reaction or to the formation of usually insoluble compounds, (b) metal hydroxide or basic chelate, e.g., MchOH [27], or (c) complex anions, e.g., Mch_3^- [27] resulting from the presence of excess β-diketone.

(iii) The third method is the reaction of metal carbonyls with β-diketones. This involves refluxing the appropriate mononuclear metal carbonyl with the neat β-diketone for two to four days [28]. This type of reaction is illustrated by the following general equation:

$$M(CO)_n + 3RCOCH_2COR' \rightarrow M(RCOCHCOR')_3 + \frac{3}{2} H_2 + nCO$$

(M = Co, Mo, Cr; R = CH_3 or CF_3; R' =CH_3 or CF_3)

(iv) The fourth method involves the reaction of metal salts of 2-ethylhexanoic acid, naphthenoic and stearic acids with the β-diketone in suitable organic solvents. The advantages of these metal salts and particularly of the ethylhexanoates is their appreciable solubility in organic solvents such as petroleum ether, benzene, and chloroform. Consequently the pH control which is often difficult during synthesis of metal chelates in water or strongly polar solvents, is no longer necessary. The metal acetylacetonates are precipitated in crystalline form, even at room temperature on mixing the β-diketone with the solution of the metal ethylhexanoate in benzene or petroleum ether. Iron(III), cobalt(II), cobalt(III), manganese(II), zirconium(IV), aluminium(III), calcium(II), zinc(II) and copper(II) acetylacetonates have been prepared by using this procedure [29].

(v) Lastly, the reaction of a β-diketone with a metal is usually carried out in an anhydrous inert medium. It has been used for obtaining derivatives of the alkali metals, alkaline earth metals, copper (in the presence of air), and aluminium (as an amalgam).

Apart from the above major categories of preparative methods, one could easily use an adaptation of any of them where suitable for the preparation of a particular metal β-diketonate desired.

1.3 Infrared Spectra

The infrared spectra of the metal acetylacetonate compounds have been studied extensively [30 - 40], however, the band assignments in the infrared have for long been a subject of controversy. These have been so mainly because most of the bands were assigned purely on empirical basis. Usually the bands of interest are those in the spectral range 1600 - 1250cm^{-1} and below 500cm^{-1} corresponding to vibrations of the basic O-C-C-C-O skeleton and the metal - ligand bonds respectively.

Nakamoto and Martell (1960) [39] carried out an approximate normal coordinate analysis on Cu(acac)$_2$ in an attempt to give a detailed description of the character of, among others, the absorption bands at about 1600 and around 1500cm^{-1}. They proposed that the first band should have $\sim$ 75% C=C stretching character, whilst the latter should correspond mainly to the C=O stretching modes. Similar deductions were made by Mikami and coworkers (1967) [41], from normal coordinate analysis of Cu(acac)$_2$ and Fe(acac)$_3$. However, Behnke and Nakamoto [42] recommended from the normal coordinate analysis of Pt(acac)Cl$_2^-$ and some of its deuterated analogues, a change in these assignments. The vibrations corresponding to the absorption band of the highest frequency (in the region 1600 - 1250cm^{-1}) were attributed to pure C=0 stretching modes. Musso and Junge [43, 44] from observations of frequency shifts following isotopic substitution in relevant places with ^{13}C and ^{18}O, also supported this new change in assignment. Table 2 shows an agreement between the assignments by Behnke and Nakamoto [42] and those of Junge and Musso [43, 44].

TABLE 2. Assignment of vibrational frequencies (cm^{-1}) of metal acetylacetonates (1600 - 1200 cm^{-1}).

Behnke and Nakamoto[42]	Junge and Musso[43,44]	Assignment
1578	1580	Mainly $\nu_{as}\,\mathrm{C}\overset{---}{\text{——}}\mathrm{O}$
1527	1530	Mainly ν_{as} C-C-C
1430	-	βCH_3
1397	1390	$\nu_s\,\mathrm{C}\overset{\text{▾▾▾}}{\text{——}}\mathrm{O}$
1354	-	βCH_3
1281	1280	$\nu_s\,\mathrm{C}\underline{---}\mathrm{C}\underline{---}\mathrm{C}$

From the IR spectra of most metal β-ketoenolate complexes, $M(RCOCHCOR')_n$ (where $R = CH_3$, C_6H_5, C_4H_3S, C_4H_3O, C_5H_4N, $CF_3=R'$), it is observed that some bands are shifted while others are least affected by changing the metal ion. Bands not sensitive to metals are:

CH_3 degenerate deformation; (1415 - 1385cm^{-1})
CH_3 symmetric deformation; (1370 - 1356cm^{-1})
C - H rocking ; (1028 - 1020cm^{-1})
C - R; (937 - 930cm^{-1}) ; (800 - 770cm^{-1})

Bands between 1600 and 1400 cm^{-1} and 700 - 400 cm^{-1} are found to be sensitive to the nature of the metal while the spectra of the low frequency region < 600cm^{-1} are found to be very helpful in studying the substitution effects.

Belford and coworkers [35] have studied the effect of substitution of CF_3, OC_2H_5, $N(C_2H_5)_2$ for the CH_3 groups of $Cu(acac)_2$ while Dryden and Winston [45] have discussed the relation between $C{=}O$ stretching frequency and the electronic effect of the substituents. Nakamoto and coworkers [46] have found that substitution of CF_3 for CH_3 causes marked shifts of the $C\underline{\text{---}}O$ and $C\underline{\text{---}}C$ stretching bands to higher frequencies and of the M-0 stretching bands to a lower frequency. These results indicate that the strong positive inductive effect of the CF_3 group **strengthens the** former two bonds and weakens the M-0 bond. They have also suggested from the infrared spectra that whereas the CF_3 weakens the M-0 bond, phenyl group substitution strengthens the M-0 bond slightly. The principal electronic effects considered were mesomeric interactions of the phenyl group with the semi-aromatic metal chelate ring. This result is however contradictory to that of an ESR study by Kuska and Rogers [47].

For octahedral coordination in the first row transition metal β-diketonates, the M-0 stretching modes are known [48] to exhibit a variation with the d-orbital population similar to that shown by thermodynamic properties particularly since the masses of the coordinated ions do not markedly differ. In their studies, Hancock and Thornton [48] found the following order of M-0 stretching frequencies:

$$Sc < Ti < V < Cr > Mn > Fe < Co$$

This order is in agreement with the crystal field stabilization (CFSE) data [49]. Moreover it is also known that the CFSE is a function of the magnitude of 10Dq [49] and the mode of occupation of the t_{2g} and e_g orbitals. The majority of octahedral complexes of $3d^4 - 3d^7$ are spin-free except for Co(III) which is invariably spin-paired. Therefore considering a hypothetically complete series of complexes of all the isovalent ions with $3d^0 - 3d^{10}$ configuration, in which the $3d^4 - 3d^7$ ions are spin-free, the calculated CFSE's follow the order:

$$d^0<d^1<d^2<d^3>d^4>d^5<d^7<d^8>d^9>d^{10}$$

The most sensitive M-L stretching modes of the majority of transition metal(II) and -(III) complexes exhibit this order except where Jahn-Teller distortion leads to additional stabilization [50].

Among the first row trivalent transition metals, Mn(III) is unique with respect to Jahn-Teller distortion. Diffraction studies [22] and the complexity of the far - infrared spectrum [40] have been cited as evidence of tetragonal structure. Hancock and Thornton [48] studying acetylacetonates, benzoylacetonates, dibenzoylmethanates, trifluoroacetylacetonates and dipivaloymethanates of the ions, Sc(III), V(III), Cr(III), Mn(III), Fe(III) and Co(III), observed additional bands in the

M-O stretching region occurring in the spectra of Mn(acac)$_3$, Mn(dbm)$_3$ and Mn(bzac)$_3$ but not in those of Mn(dpm)$_3$ and Mn(tfacac)$_3$. They explained this observation by suggesting that, either these latter complexes are not distorted or that there may be a coincidence of the lower frequency band with some other bands in the spectrum.

Nakamoto et al. [46] also proposed that a band occurring near 450cm^{-1} is attributed to M-O stretching vibration; and the force constants they obtained for the various acetylacetonates (1:3 complex) indicate the following sequence:

$$Co(III) > Cr(III) > Fe(III) > Mn(III).$$

Once again the position of Mn(III) in the sequence indicates an appreciable distortion in the Mn(acac)$_3$ complex. Further evidence of the Jahn-Teller effect in manganic acetylacetonate based on IR data has been reported by Forman and Orgel [40].

1.4 Electronic Spectra

Electronic transitions may occur in ultraviolet and or visible and near infrared region of the electromagnetic spectrum. Visible spectroscopy is limited to chelates of the transition metal ions, the lanthanides and the actinides. The bands observed in the visible region are mainly the crystal field bands and depend mainly on the donor atoms of the ligands and on the metal ion under consideration. There are two types of crystal field transitions viz, the more intense spin-allowed transitions and the lower intensity spin-forbidden transitions, which usually appear as shoulders on the spin-allowed transitions. Ultraviolet spectroscopy is also one of the usual tools in structural determinations of all chelates since they all absorb in this region. The ultraviolet spectrum is more complicated and consists of electronic transitions between the ligand and the metal or vice versa (charge transfer), and also transitions within the ligand itself which are usually $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ transitions.

The theoretical and experimental investigations of β-ketoenolate complexes in the near ultraviolet region have been reviewed by Fackler [5]. Several calculations like the Huckel [35, 51 - 53] and self-consistent field [53, 54] types have been done on the acetylacetonate ion π-structure. These have led to the placement of five molecular π levels (Fig. 5), with the general agreement that the lowest spin-allowed transition, $\pi_3 \rightarrow \pi_4^*$, lies in the 30,000 - 37,000cm^{-1} region.

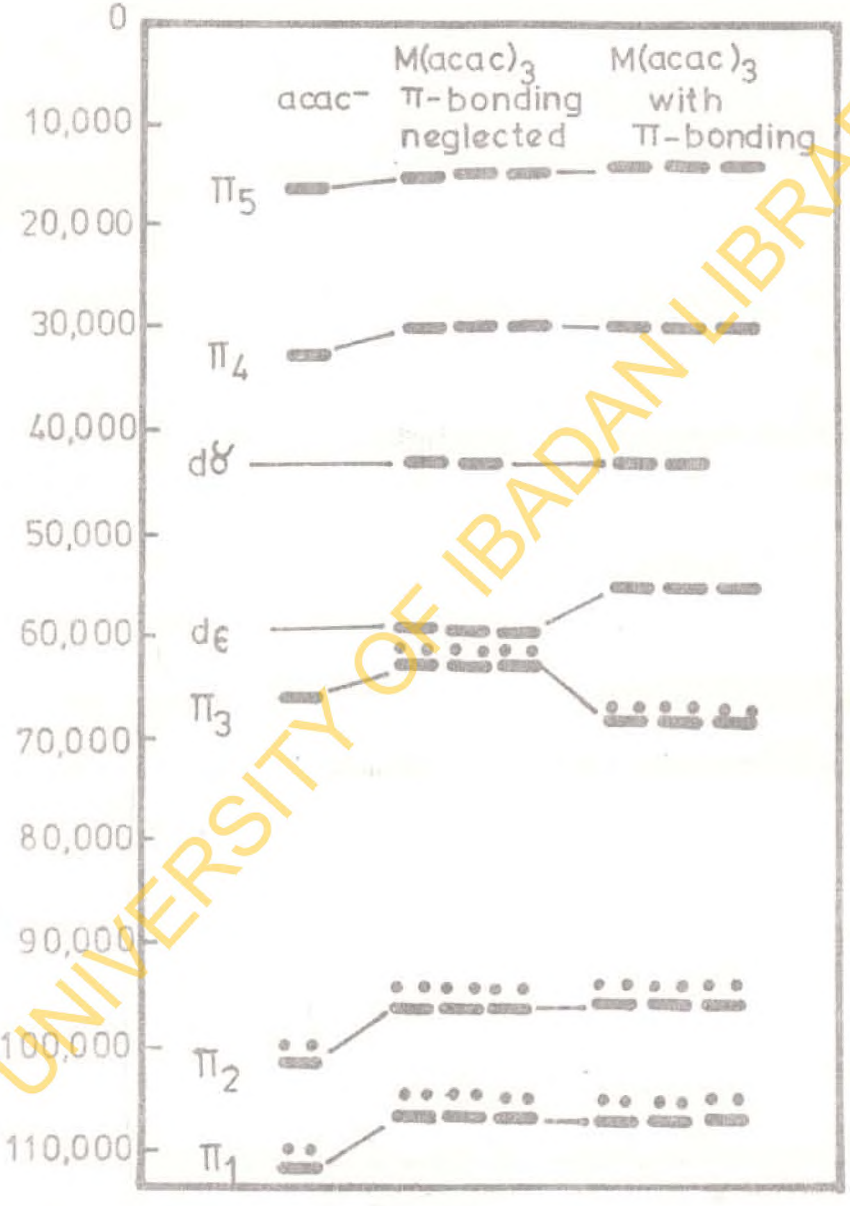


Fig. 5. Molecular orbitals of the acetylacetonate anion and of a trivalent transition metal complex [52]

The second $\pi \rightarrow \pi^*$ spin-allowed transition, less firmly placed, is in the 50,000cm^{-1} region. Ogden and Selbin [55] observed that on replacing the proton of the enol form of a free β-ketoenolate with sodium ion, the $\pi_3 - \pi_4^*$ transition is shifted to a lower energy. This has been attributed to the equivalence of the metal - oxygen bonds in the chelate ring [56] and also to the electrostatic effect of the cation [57]. Many authors [53, 56 - 61] have observed a band in the region 20,000 - 25,000cm^{-1} in most acetylacetonate complexes; and have suggested that it may possibly arise from an $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ spin-forbidden transition within the ligand. As a result of phosphorescent and absorption spectra investigations carried out on a number of β-diketone complexes, Ogden and Selbin [55] firmly assigned this band in the 20,000 - 25,000cm^{-1} region as the spin-forbidden intraligand $\pi - \pi^*$ transition i.e., primarily singlet - triplet within the ligand or doublet-quartet within the complex.

Most β-ketoenolate complexes of transition metal ions also exhibit a band in the 25,000 - 28,000cm^{-1} region. This band has variously been assigned to (i) d-d [62 - 64]; (ii) $\pi - \pi^*$ or $n - \pi^*$ singlet-triplet intraligand transitions

[54, 60] and (iii) metal-to-ligand (3d → π^*) transition [51, 52, 65].

The spectral region 27,000 - 33,000cm^{-1} represents the lowest spin-allowed transition π_3 - π_4^*. This band is very sensitive to the metal-ion nucleus and may move to higher or lower energy with respect to the enolate anion. It has been shown [56] to move to a higher energy when the $d\pi$ orbitals lie between π_3 and π_4 levels thereby increasing the π-interaction($d\pi$-$p\pi$). Furthermore, the transition may be split into several components resulting from a splitting of the excited state by configurational interaction or by the symmetry of the atomic orbitals which are combined in the complex.

Phenyl substituted ligands show bands in the 36,000 - 41,000cm^{-1} region and may be attributed to the primary bands in benzene π system [55, 66]. Other aromatic group substitutions e.g. pyridyl substituted ligands have been shown [67] to behave in a similar manner as phenyl substituted ligands.

The ligand field transitions depend immensely on the spectroscopic term of the metal ion and the magnitude of the ligand field strength of the coordinating ligand.

A survey of the published spectra of chromium(III) complexes [56, 68 - 76] show that, there are usually three strong and intense absorptions around, 17,500cm^{-1}; 23,000cm^{-1} and 30,500cm^{-1}. This is in accordance with a ^4F ground state and ^4P lowest excited state of a $3d^3$ configuration. The first band in the neighbourhood of 17,500cm^{-1} is considered as a direct measure of the crystal field splitting energy parameter 10Dq. In solution however, some of these bands appear highly perturbed.

There are several reports [56, 60, 77-80] appearing in the literature concerning the spectra of six-coordinate, high-spin, manganese(III) complexes and some tentative assignments have been proposed. Several other workers [56, 60, 78, 79] have interpreted their results in terms of an octahedral model and have assigned the absorption at ~ 20,000cm^{-1} as the only spin-allowed crystal field transition, $^5Eg \rightarrow {}^5T_{2g}$. Nyholm et al. [81] have observed splitting of the band near 22,000cm^{-1} with a separation of 2,600cm^{-1}. This splitting has been attributed to the Jahn-Teller distortion of the T_{2g} excited state, i.e., to the transitions $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$. Similar assignments have also been made by

Dingle [82], and Fackler and Chawla [83]. Furthermore, Dingle [80] has studied the spectra of manganese(III) ion in a variety of molecular environments in which two regions of absorptions are observed. One near 20,000cm^{-1} and the other in the region, 5,000 - 15,000cm^{-1}. The higher energy absorption is accounted for by the transition $^5E_g \rightarrow {}^5T_{2g}$ or its components in one or other lower symmetry groups. The lowering of the symmetry could account for the appearance of multiple absorption maxima in some spectra.

Crystal field transitions of iron(III) complexes occur from the ground term $^6A_{1g}$ to higher quartet and doublet terms. The solution spectrum of Fe(acac)$_3$ in acetone shows four bands in the near infrared and visible regions at 9,760 (0.45), 13,160 (0.70); 23,120 (3250) and 28,410cm^{-1} (3420) (extinction coefficient in parenthesis) [20, 60]. Piper and Carlin [60] also studied a pure orthorhombic crystal at 77K and observed that the spectrum displays absorption bands at 9,300 and 12,940 cm^{-1} which they assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions respectively. In chloroform, two weak spin-forbidden bands were observed at 13,800 (725nm) and 10,256cm^{-1} (975nm) [56] and these were assigned to the $^6A_{1g} \rightarrow {}^4T_{2g}$

and the $^6A_{1g} \rightarrow {}^4T_{1g}$ transitions respectively. However, there was in addition, a band at $23{,}200cm^{-1}$ (431nm) whose origin was unknown and consequently no assignment was proposed. Mathews [84], studying the absorption spectrum of tris(thenoyltrifluoroacetonate) iron(III) reported a similar band occuring at $23{,}800cm^{-1}$ and assigned it to the $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}(G)$ transition. This assignment was confirmed by a recent study carried out by Tandon and Gupta [85] on Fe_2O_3.

Crystal field absorption spectra of cobalt(III) complexes consist of transitions from the $^1A_{1g}$ ground state to higher singlet upper states. Singh and Sahai [75] have assigned (this singlet - singlet) transition $^1A_{1g} \rightarrow {}^1T_{2g}$ to the $25{,}000cm^{-1}$ band observed for $Co(acac)_3$ in chloroform solution. In addition to this, they also observed two weak shoulders lying at $12{,}500cm^{-1}$ ($^1A_{1g} \rightarrow {}^3T_{1g}$) and at $9{,}090cm^{-1}$ ($^1A_{1g} \rightarrow {}^3T_{2g}$). These transitions have extinction coefficient < 1.

Aluminium(III) complexes are diamagnetic and basically not being a transition metal, do not show any d-d transitions. Most of the tris(ketoenolate)aluminium(III) complexes known [75] only exhibit transitions typical of the ligand. Thus most of the electronic transitions reported in aluminium(III) complexes occur in the ultraviolet region.

1.5 Magnetic properties

In a hypothetical manner, one can assume the formation of a coordination compound to occur by first, the metal losing electrons, the number being equal to the oxidation state of the cation so formed. This is then followed by the hybridization of the appropriate orbitals on the metal ion so as to facilitate their occupation by electron pairs from the coordinated groups. The disposition of these groups and the hybridized orbitals which they use, define the stereochemistry of the molecule. Consequently the non-bonding electrons of the metal ion, which are assumed to be of secondary importance, as far as bonding is concerned, are then arranged in accordance with Hund's rule: "that the most stable arrangement is one with the maximum number of unpaired electrons" in whatever orbitals remain. These unpaired electrons are in turn associated with paramagnetism of the metal ion.

The study of magnetic properties therefore, can yield valuable information about the bonding and stereochemistry of these transition metal complexes.

According to the theory of Bose-Stoner which was extended by Van Vleck [86], the magnetic moment u_{eff}., of a paramagnetic material should lie between $\sqrt{4S(S+1)}$ and $\sqrt{4S(S+1) + L(L+1)}$ (where S = sum of the spin quantum numbers, $s=\frac{1}{2}$, for individual electrons and L = orbital angular momentum quantum number of the ion). In other words, u_{eff} should lie between the $\mu_{s.o.}$ and u_{S+L} values. The assumption is made for the first row transition elements that the multiplet widths are small compared to kT (where k is the Boltzmann constant and T is the room temperature), whence the "spin-only" formula results providing L=0, or the L(L+1) contribution is almost completely suppressed. In cases where the moment exceeds $\mu_{s.o.}$ value, it is presumed that this is due to the presence of a finite value of L, i.e., of an "orbital contribution".

Orbital angular momentum in d-orbital systems is as a result of the ability to carry an electron in one d-orbital into another equivalent and degenerate d-orbital by a rotation. However, there must not be an electron with the same spin in the second d orbital. By considering how the ground terms of metal ions in octahedral ligand field strengths are most nearly described by $t_{2g}^{n}e_{g}^{m}$ (n = 0 - 6, m = 0 - 4) configurations, we may readily find those systems for which all orbital angular momentum has been destroyed. The e_g^m configurations do not contribute to the angular momentum. The only t_{2g} configurations (apart from t_{2g}^0) for which it is not possible to make the required transformations of d orbitals are t_{2g}^3 (since there is no equivalent, degenerate position of the same spin as any of the three electrons). A similar situation is encountered for t_{2g}^6 configuration. The orbital degeneracies of the terms to which the configurations $t_{2g}^0 e_g^m$, $t_{2g}^3 e_g^m$ and $t_{2g}^6 e_g^m$ correspond are unity or two. Orbital angular momentum is destroyed for A and E ground terms. Conversely for t_{2g}^1, t_{2g}^2 and t_{2g}^5 the orbital transformations can take place. Configurations of the type $t_{2g}^1 e_g^m$, $t_{2g}^4 e_g^m$ and $t_{2g}^5 e_g^m$ which lead to T terms, are associated with orbital angular momentum. Orbital angular momentum remains with T terms. The position is summarised in Table 3.

Table 4 also shows magnetic moments at 300K and at 80K of trivalent metal ions of the first row transition elements that possess A or E ground terms. When there is no orbital angular momentum associated with the ground term, there can

TABLE 3. Ground terms for which orbital angular momentum is or is not Quenched. (Octahedral Complexes).

No. of d electrons	Free-ion ground term	Nearest $t_{2g}^{n}e_{g}^{m}$ configuration	Ground term in complex	Orbital contribution expected
1	^2D	t_{2g}^{1}	$^2T_{2g}$	Yes
2	^3F	t_{2g}^{2}	$^3T_{1g}$	Yes
3	^4F	t_{2g}^{3}	$^4A_{2g}$	No
4	^5D	$t_{2g}^{3}e_{g}^{1}$	$^5E_{g}$	No
		t_{2g}^{4}	$^3T_{1g}$	Yes
5	^6S	$t_{2g}^{3}e_{g}^{2}$	$^6A_{1g}$	No
		t_{2g}^{5}	$^2T_{2g}$	Yes
6	^5D	$t_{2g}^{4}e_{g}^{2}$	$^5T_{2g}$	Yes
		t_{2g}^{6}	$^1A_{1g}$	No
7	^4F	$t_{2g}^{5}e_{g}^{2}$	$^4T_{1g}$	Yes
		$t_{2g}^{6}e_{g}^{1}$	$^2E_{g}$	No
8	^3F	$t_{2g}^{6}e_{g}^{2}$	$^3A_{2g}$	No
9	^2D	$t_{2g}^{6}e_{g}^{3}$	$^2E_{g}$	No

be no spin-orbit coupling splitting of the term. Such systems may be expected to have no energy levels separated from the ground levels by ~ kT. It is therefore predicted that octahedral complexes giving rise to A or E ground terms should have magnetic moments close to the spin-only value, and independent of temperature. Since orbital angular momentum remains in T terms, state separations of the order of kT may occur and consequently, the magnetic moments of transition metal complexes with T terms may depart from the spin-only value and depend on temperature. Representative values are given in Table 5. Here, it is observed that the magnetic moments of compounds with T ground terms depart from the spin-only value, and vary with temperature more than do those with A and E terms.

TABLE 4. Magnetic moment at 300K and at 80K of some trivalent metal ions of the 1st row transition elements that possess A or E ground terms [87]

No. of d Electrons	Compound	Ion	Ground term	$\mu_{eff.}$(300K) B.M.	$\mu_{eff.}$(80K) B.M.	μ_{eff}(S.O.) B.M.	$\mu_{eff}(\lambda)$ B.M.
3	$K(Cr(SO_4)_2\cdot 12H_2O$	Cr^{3+}	$^4A_{2g}$	3.8	3.8	3.88	3.8
4	$Mn(acac)_3$	Mn^{3+}	^5E_g	4.9	4.8	4.90	4.9
5	$(NH_4)Fe(SO_4)_2\cdot 12H_2O$	Fe^{3+}	$^6A_{1g}$	5.9	5.9	5.92	5.9
6	$Co(en)_3Cl_3$	Co^{3+}	$^1A_{1g}$	0.2	0	0	0

TABLE 5. Magnetic moments at 300° and 80°K of trivalent metal ions of the first row transition elements that possess T ground terms. [87].

No. of d electrons	Compound	Ion	Ground Term	μ_{eff}(B.M.) 300K	μ_{eff}(B.M.) 80K	μ_{eff}(S.O.) (B.M.)	$\mu_{eff}(\lambda\lambda)$ (B.M.) 300K	$\mu_{eff}(\lambda\lambda)$ (B.M.) 80K
1	$CsTi(SO_4)_2.12H_2O$	Ti^{3+}	$^2T_{2g}$	1.8	1.5	1.73	1.9	1.2
2	$(NH_4)V(SO_4)_2.12H_2O$	V^{3+}	$^3T_{1g}$	2.7	2.7	2.7	2.7	1.4–1.7
4	$K_3Mn(CN)_6$	Mn^{3+}	$^3T_{1g}$	3.2	3.1	2.83	3.6	2.9
5	$K_3Fe(CN)_6$	Fe^{3+}	$^2T_{2g}$	2.4	2.2	1.73	2.5	2.0
6	K_3CoF_3	Co^{3+}	$^5T_{2g}$	5.5	5.2	4.90	5.6	5.1

Occasionally, the magnetic moments of complexes with A and E ground terms differ appreciably from the spin-only value. The effect is most noticeable toward the right-hand side of the transition series. This is so because, on account of spin-orbit coupling, the "quenching" of orbital angular momentum by the ligand field can never be complete. By coupling the orbital angular momentum to the spin, the spin-orbit coupling prevents the perfect separation of orbitals on the basis of their orbital angular momentum. Taking spin-orbit coupling into account in A and E ground terms systems, the moment is given by

$$\mu_{eff.} = \mu_{eff.}(S.O.)\ (1 - 4\lambda/10D_q) \text{ for } A_{2g} \text{ terms,}$$

$$\mu_{eff.} = \mu_{eff.}(S.O.)\ (1 - 2\lambda/10D_q) \text{ for } E_g \text{ terms}$$

(where $10D_q$ is the energy separating the interacting terms, and λ is the spin-orbit coupling constant for the terms involved).

Thus for a high-spin manganese(III) octahedral complex, the ground term is ^5E_g from the ^5D term of the free ion, and the magnetic moment will lie below the spin-only value (4.90 B.M.) by the factor $(1 - {}^{2\lambda}/10D_q)$ and should be independent of temperature. For hexa-aquomanganese(III) ion the value of $10D_q$ has been reported as 21,000cm^{-1} [80]. The substitution of the values of $\alpha = 2$, $\lambda = 88\text{cm}^{-1}$ and $10D_q = 21{,}000\text{cm}^{-1}$ in $\mu_{eff.} = 4.90\ (1 - 2\lambda/_{10D_q})$ will lead to $\mu = 4.86$ B.M. Spin-free manganese(III) complexes usually have mangetic moments in the range 4.85 - 5.10 B.M. [88].

Table 6 gives a summary of the magnetic moment values at room temperature of some tris(β-ketoenolate) metal(III) complexes of first row transition metals. The variable temperature susceptibility of $Mn(acac)_3$ [89] in the temperature region (300 - 17K) shows that the room temperature magnetic moment is 4.98 B.M., and the Curie - Weiss law holds down to 80K with $\theta = 5.5^{\circ}$. Below 80K susceptibility rises more rapidly than by the Curie-Weiss law.

Chromium(III) in an environment of octahedral symmetry has a $^4A_{2g}$ ground term and the degeneracy of this level is not, in the first approximation, affected by the detailed nature of the ligand field. The magnetic moment is expected to be reduced below the spin-only value for three unpaired electrons by the term $(1 - {}^{4\lambda}/_{10D_q})$. However, the spin-orbit coupling constant of Cr^{3+} is small ($\lambda = 91\text{cm}^{-1}$), and the reduction in moment should be small - some 2%. This difference between the spin only and anticipated moments is not outside the inaccuracy of many of the measurements that have been made [90].

The susceptibility of the $Fe(tftbd)_3$ and $Fe(dbm)_3$ complexes have been measured at several temperatures in the region 86K to room temperature [84]. The susceptibility values for $Fe(dbm)_3$ complex were found [84] to obey the Curie law while those for the $Fe(tftbd)_3$ complex obeyed the Curie-Weiss law with $\theta = 32^{o}$.

Except for a few compounds of cobalt(III), the complexes of trivalent cobalt are of the low-spin type (t_{2g}^{6}) and have a small positive susceptibility of the order of $100x10^{-6}$c.g.s. mol^{-1}. In octahedral spin-paired cobaltic complexes the $^{1}A_{1g}$ term of the t_{2g}^{6} set lies lowest and here the second order Zeeman effect accounts for the small paramagnetism usually observed in these complexes.

TABLE 6. Room temperature magnetic moments for some tris(β-ketoenolate) metal(III) complexes of first row transition metals.

Compound	$\mu_{eff.}$ (B.M.)	T.K.	Reference
$Cr(acac)_3$	3.86	295	[90]
$Mn(acac)_3$	4.89	300	[90]
$Mn(tftbd)_3$	6.16	300	[91]
$Fe(acac)_3$	5.97	300	[92]
$Fe(tfacac)_3$	5.96	300	[92]
$Fe(tftbd)_3$	5.83	293	[84]
$Fe(dbm)_3$	6.21	291	[84]
$Fe(bzac)_3$	5.98	300	[92]
$Fe(bztfac)_3$	5.89	300	[92]

1.6 Applications of β-diketones

Possible applications of β-diketones and their metal chelates exist in the areas of liquid organometallic lasers, NMR shift reagents, unusual phosphors, catalysts for polymerization and extractants for most metals (i.e., in metal analysis and in most analytical procedures).

Metal analysis. The coordinating ability of β-diketones to several metals makes it possible for their uses as extractants in trace analysis of elements. After extraction, the metal constituent may be studied quantitatively by spectrophotometric methods or qualitatively by identification of the metal $(\beta\text{-diketone})_n$ by GC-MS technique. De, Khopkar and Chalmers [93] have given a review on this subject which includes some optimum conditions for extraction of some typical metals using β-diketone systems. This is summarised in Table 7. Although several types of ligands have been examined, the fluorinated 1,3- diketone, Htfacac, is most often used in quantitative analysis. Chromium has been analysed in biological systems as $Cr(tfacac)_3$ [94] and beryllium measured in air as $Be(tfacac)_2$ [94]. The identity of the eluted Cr(tfacac)$_3$ or Be(tfacac)$_2$ is confirmed by GC-MS. The lower limit of detection is of the order of 1×10^{-12}g of beryllium. Terlouw and Heerma [95] have also used 2-thenoyl-trifluoroacetone for the determination of some transition metals (Zn, Ni, Cr) at the nanogram level, using mass spectrometric techniques. Quantitative gas chromatographic schemes also exist for the determination of beryllium in blood, urine and tissue; chromium in serum; aluminium in uranium; aluminium, gallium and indium in aqueous solution; iron in ore; chromium in steel; titanium in bauxite; aluminium, iron, copper in alloys; uranium, tungsten and molybdenum in alloys and ores, etc., [96]. All these are extracted in the form of β-diketonate chelates.

Electron capture gas chromatography has also been used to analyse ultratrace quantities of metals as 1,3-diketonates, $M(RCOCHCOR')_n$ (where M = Be(II), Cr(III), Fe(III), Ni(II), Cu(II), Y(III), Al(III); R = R' = CH_3 or CF_3; n=2 or 3) in aqueous solutions [97, 98, 99], in biological fluids [96] and Be(II) in polluted air [94]. The ECGC has also been further developed by Sievers et al.[100, 101] to the extent that it has become the most rapid and sensitive method for the ultratrace analysis for Be(II) and Cr(III) in terrestrial, meteoritic and in lunar rock and dust samples. Infact, samples returned from the Apollo 11, 12, 14 and 15 sites were analysed using the ECGC method [100].

Organometallic lasers. The principle of stimulation of emission from metastable states has led to the rapid development of powerful light sources which get their name from the process of Light Amplification by the Stimulated Emission of Radiation (LASER). The first laser action of metal β-diketonates was reported by Lempicki and coworkers [102 - 105]. They found that tris(benzoylacetonate) europium (III) dissolved in a mixture of methanol - ethanol (3:1) exhibits laser oscillations when subjected to high-energy flashes, if the solution is contained in an optical cavity of temperatures < 140K. The laser radiation at 612.9nm shows the usual relaxation oscillations and line narrowing associated with stimulated emission. Laser activity of the adduct of the europium tris-benzoylacetone with one molecule of benzoylacetone and one molecule of piperidine, $Eu(bzac)_4$.HP (where HP = piperidine) in methanol - ethanol mixtures, has also been demonstrated [102 - 105]. In all cases, a characteristic intense Eu^{3+} red luminescence (consisting of two strong lines in the 613.0 and 614.0nm region) has been observed.

NMR shift-reagents. In 1969, Hinckley [106] noticed that on adding the pyridine adduct of europium(III) tris-dipivaloylmethanate, $Eu(dpm)_3$, to a carbon tetrachloride solution of cholesterol, characteristic selective downfield shifts in the spectrum of the steroid took place. The europium complex was therefore called a "shift reagent". Potential uses of shift reagents in the assignments of ^{13}C NMR spectra [107] have now been made. For example, lanthanide chelates of optically active camphor derivatives produce different shifts in racemic solutions of optically active compounds, thereby allowing measurements of optical purity of NMR.

Lastly, in search for new complex forming reagents suitable for chromatography, Gil-Av and Schurig [108] prepared a series of $Rh(I)(CO)_2(RCOCHCOR')$(where, RCOCHCOR' anion = acac, tfacac, hfacac) and studied the separation of twenty-seven $C_2 - C_6$ n-alkenes.

TABLE 7. Optimum conditions for extraction of metals using β-diketone systems [93].

Metal	β-Diketone	Solvent	pH	Mode of detection
Al(III)	Hacac	Chloroform	7.5-9.5	GLC
	Htfacac	Carbon tetrachloride	7.0	GLC
	Hdbm	benzene	5-10	Mass spec.
	Htftbd	hexane	5.5	Spectrophotometric at 350nm
	Hbzac	benzene	4.0	GLC
Be(II)	Hacac	Chloroform	5.0	UV at 295nm
	Htfacac	Chloroform	5.5	ECGC
	Htftbd	benzene	~7	GC-MS
Cr(III)	Htfacac	chloroform	6.0	GC-MS
	Htftbd	benzene	6.0	Mass spec.
Cu(II)	Htftbd	benzene	2.4 -6	Mass spec.
	Hacac	benzene	2-5	visible, 570nm
Eu(III)	Htftbd	IBMK	5.5	Fluorimetry
Fe(III)	Hacac	benzene	2.5-7.0	vis, 440nm
	Hbzac	any org. solvent	2-7	vis, 420-440nm
	Hdbm	benzene	2-4	vis, 410nm
In	Hacac	benzene	3-6	Polarography
Ni(II)	Htftbd	acetone-benzene	5.5-8.0	Colorimetric/Mass spec.
Pd(II)	Hacac	any organic solvent	0-8	Polarography
V(III)	Hacac	chloroform	2.0	vis, 450nm
Mn(II)	Htftbd	acetone-benzene	6.7-8.0	vis, 420nm

1.7 Aim of the Work

Though various metal β-diketonates have been reported in the literature, no systematic studies have been made in understanding the effect of variation of metals in a particular oxidation state with specific β-diketones. Moreover, it would also be of interest to examine the relative effects of different β-diketones on the same metal ion; and effects if any, of the various substituents in the β-diketonates on their spectra and magnetic properties. To this end we have selected some trivalent metals of the first row transition metals M(III) = Cr, Mn, Fe, Co; and Al(III) (non-transition metal), using the following ligands.

(i) 2 - Thenoyltrifluoroacetone
(ii) 2 - Thenoylacetone
(iii) 2 - Furoyltrifluoroacetone
(iv) 2 - Furoylacetone
(v) Benzoyltrifluoroacetone
(vi) Benzoylacetone
(vii) Nicotinoyltrifluoroacetone

In this work, the complexes are characterized by studying electronic spectra (reflectance and solution), infrared spectra and magnetic properties.

Furthermore tris-iron chelates of mixed ligands comprising the above group of β-diketones will be examined in order to compare their competitive coordinating abilities.

There is no reason why using the above techniques, the effects of the substituents within and among the several β-diketonates should not be studied extensively.

CHAPTER 2

THEORETICAL

2.1 Electronic spectra [66, 69, 90]

To a first approximation each of several electrons in a partly filled shell may be assigned its own set of one-electron quantum numbers, n, l, m_l and s, m_s. There are always fairly strong interactions among these electrons which make this approximation unrealistic. In general the nature of these interactions is not easy to describe but the behaviour of each real atom often approximates closely to a limiting situation called the L-S or Russell-Saunders coupling scheme. This limiting situation is encountered when we have,

spin-spin coupling > orbit-orbit coupling > spin-orbit coupling

$s_1 \quad s_2 \qquad\qquad l_1 \quad l_2 \qquad\qquad s_1 \quad l_1$

This situation is found to apply to the lighter elements up to the end of the first transition series, and to the lower energy levels of the heavier elements.

For the Russell-Saunders coupling scheme, the quantum numbers necessary to specify the individual electrons are derived from those of the individual electrons in the following way. Capital letters are used to denote the quantum numbers of the entire atom, but the meaning of the symbols is exactly as for the single electron quantum numbers.

$$M_L = \sum_i m_{l_i} \; ; \; L = \text{maximum value of } M_L \qquad \text{.....(2.1)}$$

$$M_S = \sum_i m_{s_i} \; ; \; S = \text{maximum value of } M_S \qquad \text{.....(2.2.)}$$

The summation over i covers all the electrons in the filled shell. Also the quantum numbers equivalent to j and m_j may be referred to,

$$M_J = M_L + M_S \, , \; J = \text{maximum value of } M_J \qquad \text{.....(2.3)}$$

Energy levels of an atom (or free ion) are specified by the above quantum numbers. Due to the combined action of the mutual repulsions between the electrons in the shell and the Pauli exclusion principle, the degenerate set of energy levels that corresponds to a partially filled shell of electrons is split into a number of sets of energy levels, which are called "terms". Terms are specified by two of the above quantum numbers, total spin and the total angular momenta, S and L. The system of nomenclature used is,

$$^{2S+1}L_{J}$$

where the quantity (2S+1) is the spin multiplicity and L given as a capital letter according to the following symbols:

L	: 0	1	2	3	4	5	6
Term symbol	: S	P	D	F	G	H	I

J, the total angular momentum quantum number. J then has the value L-S if the electron shell is less than half-full; and L + S if it is more than half-full. If it is half-full and S has the maximum value, L must be zero and J = S. For convenience, the states which may arise by Russell - Saunders coupling from all d^n configurations are listed in Table 8.

TABLE 8. States for d^{n} systems in Russell-Saunders coupling.

d^{1}, d^{9}	^{2}(D)					
d^{2}, d^{8}	^{1}(S,D,G)	^{3}(P,F)				
d^{3}, d^{7}	^{2}(D)	^{2}(P,D,F,G,H)	^{4}(P,F)			
d^{4}, d^{6}	^{1}(S,D,G)	^{3}(P,F)	^{1}(S,D,F,G,I)	^{3}(P,D,F,G,H)	^{5}(D)	
d^{5}	^{2}(D)	^{2}(P,D,F,G,H)	^{4}(P,F)	^{2}(S,D,F,G,I)	^{4}(D,G)	^{6}(S)
d^{10}, d^{o}	^{1}(S)					

On deciding the ground state term for a particular d^n system, we invoke the Hund's rules:-

(i) The ground state term always has maximum spin multiplicity.

(ii) When comparing two states of the same spin multiplicity, the state with the higher value of L is usually more stable.

(iii) J then has the value L - S if the electron shell is less than half-full and L+S if it is more than half-full.

For example the d^2 configuration has ^3F as the term symbol with ^1D, ^3P, ^1G and ^1S as higher terms (Fig. 6). The ground state symbol is ^3F and it is split by spin-orbit coupling into $^3F_2$, $^3F_3$ and $^3F_4$ states, of which the first is the lowest and the difference between successive pairs are 3λ and 4λ respectively ($E_{(J,J+1)} = \lambda(J+1.)$

In a magnetic field, spectroscopic states are split again to give (2J+1) levels, each separated by $g\beta H$ where g is the Lande splitting factor for the given system, β the Bohr magneton and H the field strength. This is the first order

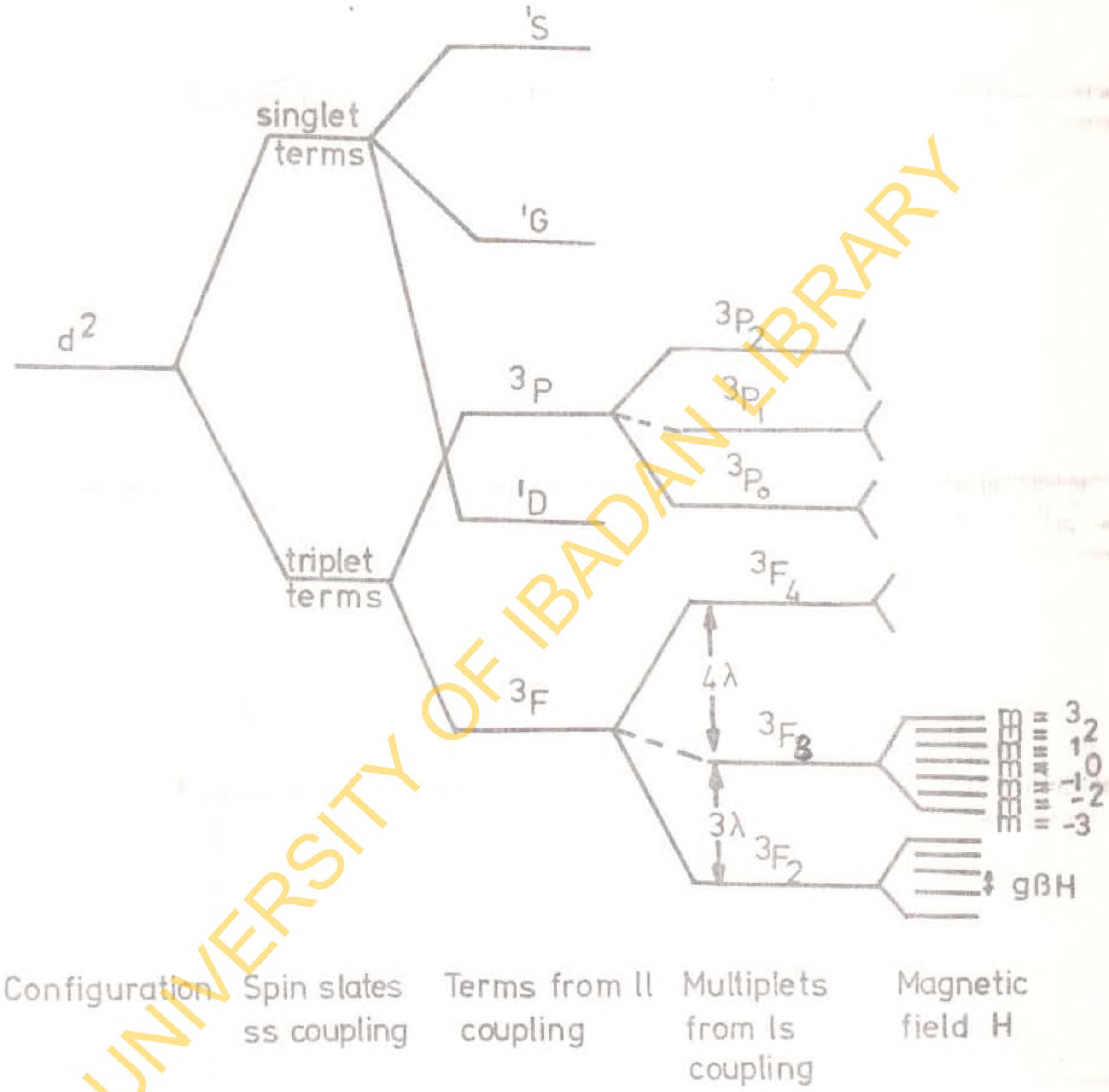


Fig. 6. Splitting of the states of a gaseous d^2 configuration. (not to scale)

Zeeman effect. The g factor is given by the expression,

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)} \qquad \ldots\ldots(2.4)$$

and is a number of the order of unity.

In a strong cubic octahedral field, the ^4F ground state and ^4P lowest excited state of chromium(III) ion split according to the energy level diagram shown in Fig.7. From this energy level diagram, the following electronic transitions are possible:

$^4A_{2g} \rightarrow {}^4T_{2g}(^4F)$ BAND(I)

$^4A_{2g} \rightarrow {}^4T_{1g}(^4F)$ BAND(II)

$^4A_{2g} \rightarrow {}^4T_{1g}(^4P)$ BAND(III)

Manganese(III) ion has a ground term ^5D and in an octahedral setting, the orbital degeneracy is partially removed and the ^5D ground term is split into a lower, doubly-degenerate ^5E_g and a higher, triply-degenerate $^5T_{2g}$ states. Consequently, the only single spin-allowed d-d transition ($^5E_g \rightarrow {}^5T_{2g}$) is expected in the visible region. Crystal field theory predicts that large distortions from octahedral symmetry should occur for such a configuration. Jahn-Teller effect therefore, will lead to a further splitting of the E_g and T_{2g} states, so that even in a complex with six equivalent donor atoms, the regular octahedron configuration is not expected. Rather, one in which the octahedron is elongated or compressed along one of the four-fold axes to give a tetragonally distorted system, is encountered. Assuming an axially elongated octahedral configuration, the energy level diagram shown in Fig. 8 is expected. Thus three visible or near infrared absorption bands are expected, corresponding to the transitions:

$$^5B_{1g} \rightarrow {}^5A_{1g}$$

$$^5B_{1g} \rightarrow {}^5B_{2g}$$

$$^5B_{1g} \rightarrow {}^5E_g$$

If distortion by compression or flattening is assumed, a reversed energy level is expected. Fig. 9 shows this type of splittings in manganese(III) complexes with octahedral, trigonal, tetragonal and rhombic geometries.

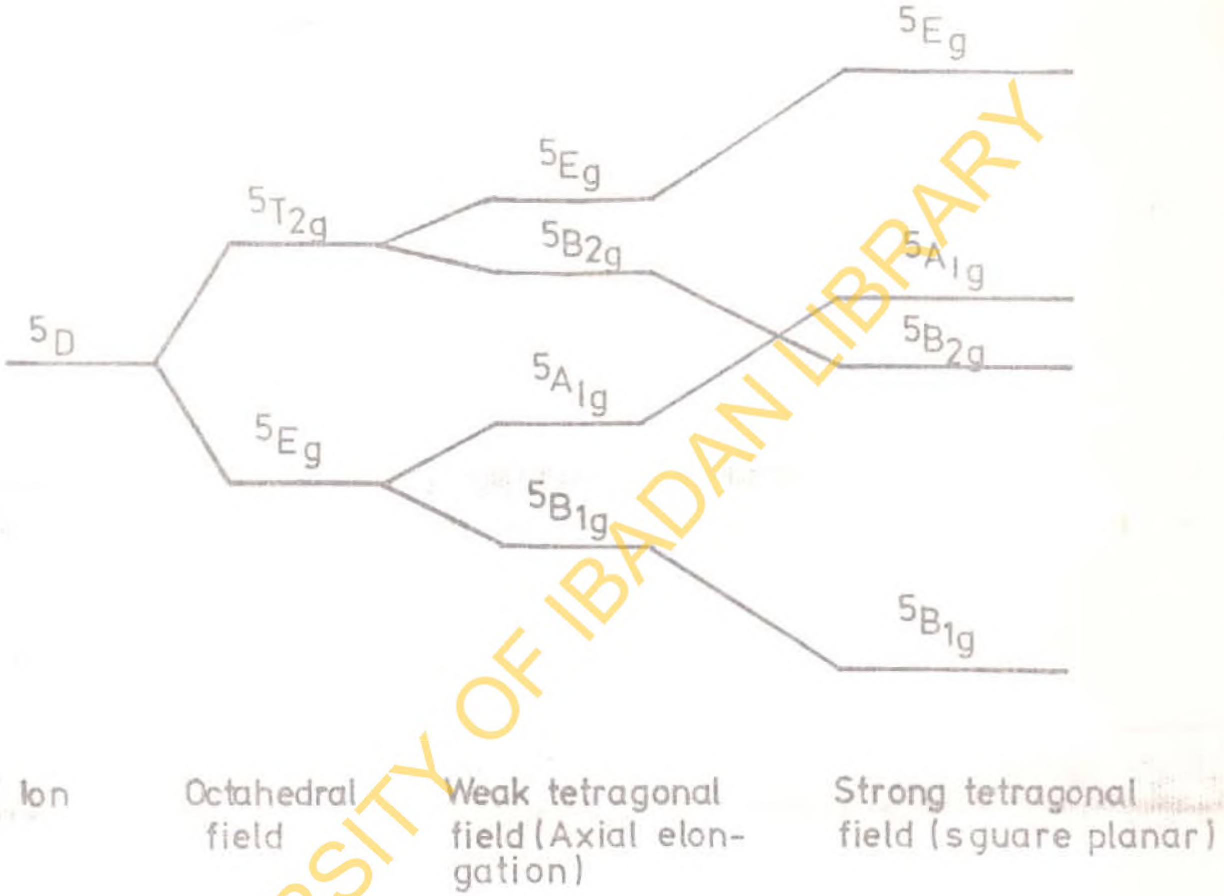


Fig. 8. A simplified energy level diagram of Mn^{3+} ion showing tetragonal distortions.

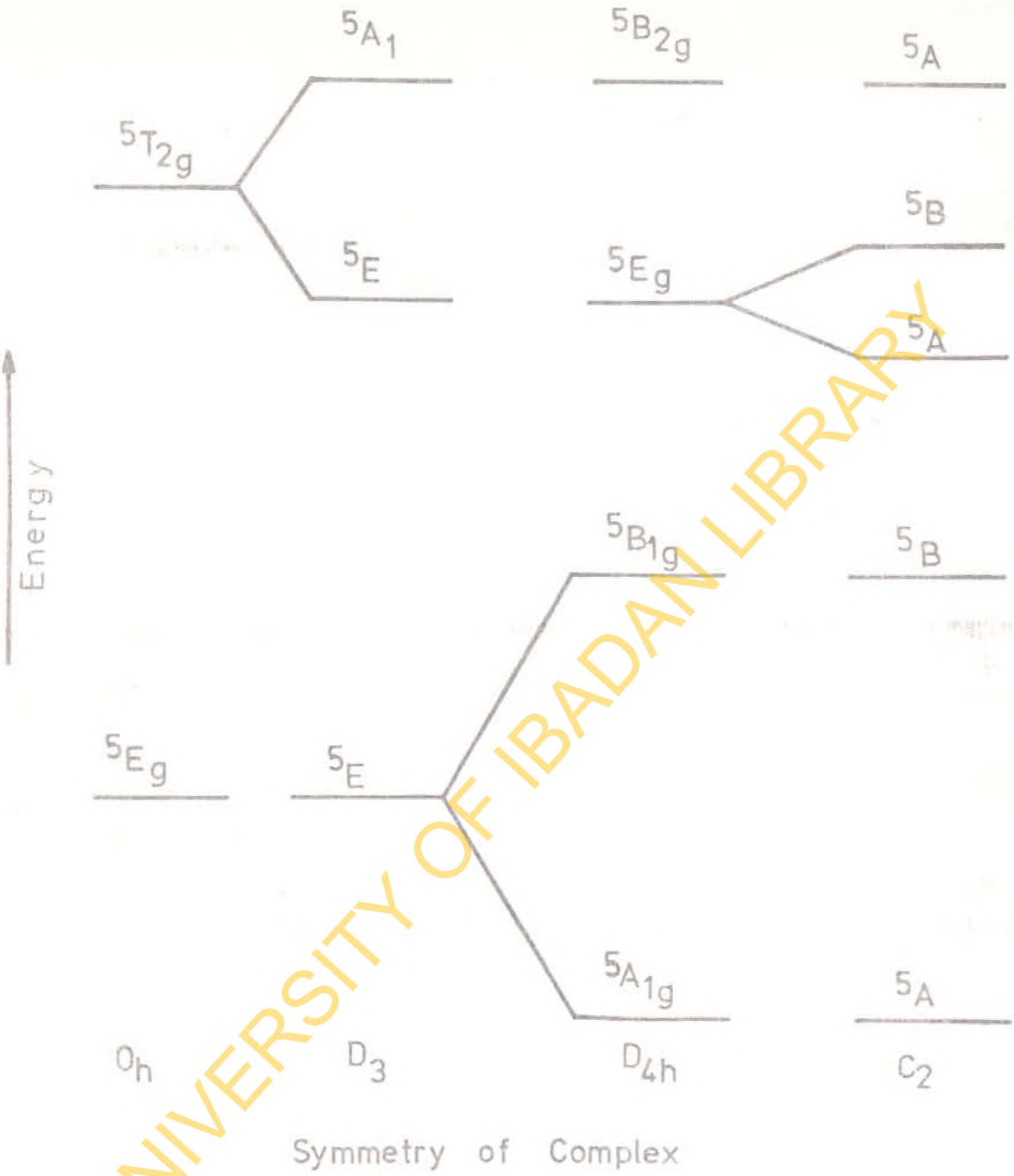


Fig. 9. Schematic term diagrams for the 3d electrons in manganese (III) complexes with octahedral (O_h), trigonal (D_3), tetragonal (D_{4h}) and rhombic (C_2) geometries. (The relative ordering of some of the levels in D_3, D_{4h}, and C_2 symmetries will depend on the specific structure present).

Iron(III) ion has a $t_{2g}^{3}e_{g}^{2}$ electronic configuration which gives rise to only one sextet term in the free ion, i.e., ^{6}S, as well as many quartet and doublet terms (Fig.10). The transitions possible (although spin-forbidden) are:

$^{6}A_{1g} \rightarrow {}^{4}T_{1g}(^{4}G)$

$^{6}A_{1g} \rightarrow {}^{4}T_{2g}(^{4}G)$

$^{6}A_{1g} \rightarrow {}^{4}E_{g}, {}^{4}A_{2g}(^{4}G)$

$^{6}A_{1g} \rightarrow {}^{4}T_{2g}(^{4}D)$

$^{6}A_{1g} \rightarrow {}^{4}E_{g}(^{4}D)$

$^{6}A_{1g} \rightarrow {}^{4}T_{1g}(^{4}P)$

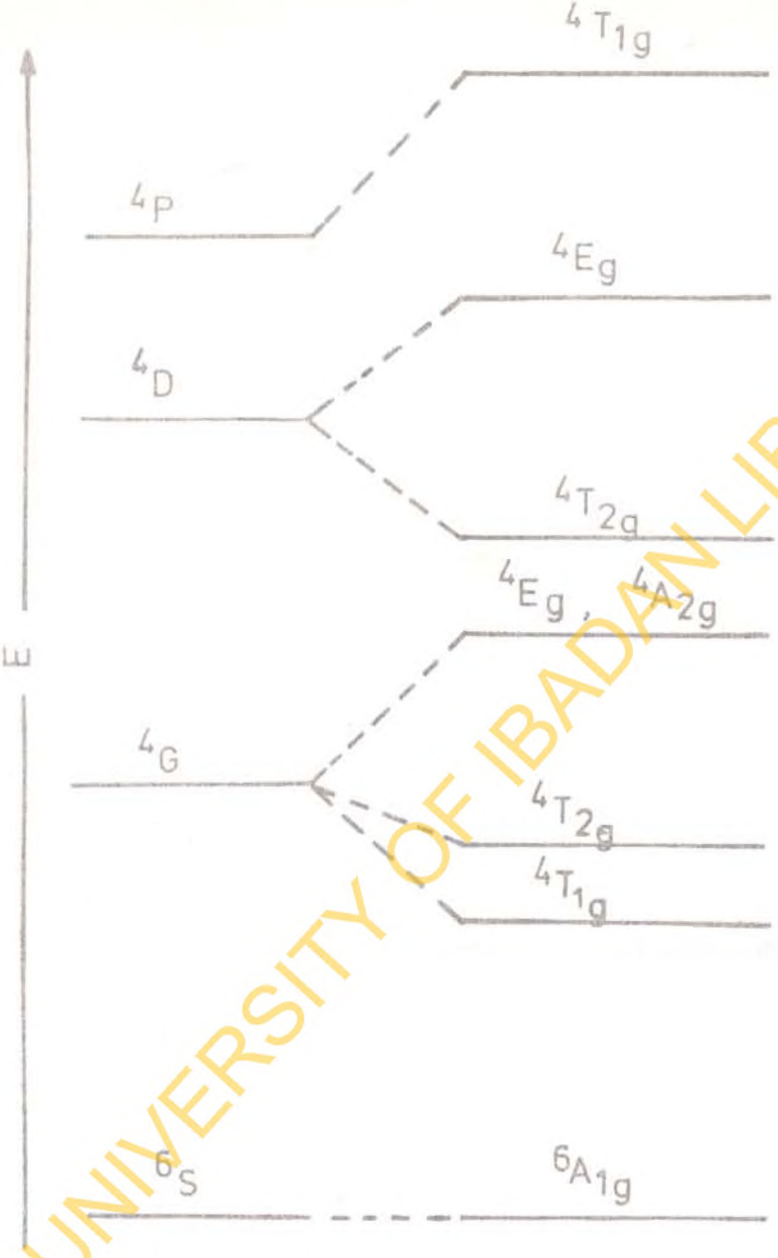


Fig. 10. Splitting of the d^5 ion in the presence of octahedral field (e.g. Fe^{3+}; Mn^{2+})

The visible absorption spectra of cobalt(III) complexes may be expected to consist of transitions from $^1A_{1g}$ ground state to other singlet states. Although the entire energy level pattern for cobalt(III) ion is not known in detail, the two absorption bands usually found in the visible spectra of regular octahedral cobalt(III) complexes represent transitions to the upper singlet states $^1T_{1g}$ and $^1T_{2g}$ ($^1A_{1g} \rightarrow {}^1T_{1g}$; $^1A_{1g} \rightarrow {}^1T_{2g}$).

Selection rules: For a transition to give an optical absorption, $\Delta S=0$. Transitions for which $\Delta S \neq 0$ are said to be spin-forbidden. Other transitions which involve redistribution of electrons in a single quantum shell (e.g., $d \rightarrow d$, $p \rightarrow p$, e.t.c.,) are orbitally forbidden (Laporte rule). For an orbitally allowed transition, $\Delta L = \pm 1$. Transitions of the type $g \rightarrow g$ and $u \rightarrow u$ are described as being parity forbidden. For example in an octahedral complex, there are a number of normal modes of vibrations, some of which are antisymmetric with respect to the inversion centre (u - type vibrations). On mixing the vibrational and electronic parts of the wave function (so-called vibronic coupling), the ground term may become mixed with a g-type vibration and the excited term with a u-type vibration. The transition instead of being g → g becomes partly g → u and is therefore allowed.

Finally there is the phenomenon known as "intensity stealing". When a ligand field transition occurs close to a charge-transfer band, its intensity often increases markedly. This is believed to be due to mixing of the electronic wave functions of the forbidden excited term with the allowed level, resulting in electronic transitions to the excited term becoming more allowed. This gaining of intensity decreases rapidly as the separation between the allowed and forbidden bands increases.

The laxity of the Laporte rule coupled with the "intensity stealing" phenomenon, make it possible for most d → d transitions and spin-forbidden transitions to be observed in the spectra of most transition complexes.

2.2 Magnetochemistry [66, 69, 87, 90, 109]

Magnetochemical measurements are associated with the presence of paramagnetism, which in turn, may be related to the presence of unpaired electrons on the metal ion.

Magnetic susceptibility is defined in the following way. If a substance is placed in a magnetic field of magnitude H, the flux B, within the substance is given by,

$$B = H + \Delta H \qquad \text{.....(2.5)}$$

ΔH is readily related to the intensity of magnetization I of the body. Then,

$$B = H + 4\pi I \qquad \text{.....(2.6)}$$

The ratio B/H, called the magnetic permeability of the material is given by,

$$\begin{aligned} B/H &= 1 + 4\pi(I/H) \\ &= 1 + 4\pi K \qquad \text{.....(2.7)} \end{aligned}$$

where K is called the magnetic susceptibility per unit volume. In practice, susceptibility is usually expressed per unit mass and is given the symbol χ_g .

$$\chi_g = K/\rho \qquad \text{.....(2.8)}$$

where ρ is the density of the material. The molar susceptibility χ_M, is defined as,

$$\chi_M = \chi_g M \qquad \text{.....(2.9)}$$

where χ_M is the susceptibility per mole and M is the molecular weight of the material.

On the basis of I, K and χ, substances may be divided into three categories:

diamagnetic, paramagnetic and ferro - or antiferromagnetic. Substances with negative susceptibilities are said to be diamagnetic and have values of the order of -1 to - 500x10^{-6} c.g.s. units and are usually independent of field strength and temperature. The diamagnetic susceptibility of a molecule may be written as:

$$\chi_{mol} = \sum_{i} ni\chi_i + \sum \varepsilon \qquad .....(2.10)$$

where the molecule contains n_i atoms of atomic susceptibility, χ_i (i.e., per gram atom), ε represents "constitutive" corrections which take account of such factors as the existence of π - bonds. Pascal's constants [109] are used in estimating the diamagnetic contribution to the total susceptibility of a compound.

Paramagnetic compounds have positive susceptibilities and these are of the order of 0-100x10^{-6}c.g.s. units, and are independent of field strength, but dependent on temperature.

If the molar susceptibility of a paramagnetic compound is corrected for the diamagnetism of all except the paramagnetic atom, we obtain the susceptibility per gram atom, χ_A where

$$\chi_A = \chi_M - \chi_{mol} \qquad \ldots\ldots(2.11)$$

χ_{mol} is obtained from equation (2.10).

For an assemblage of non-interacting magnetic dipoles with alignment energy much less than the thermal energy available to the atom, kT, it can further be shown that the magnetic susceptibility should vary inversely with temperature.

$$\chi_A = C/T \qquad \ldots\ldots(2.12)$$

where C is the Curie constant.

In the application of magnetic measurements to chemistry, it is often convenient to deal in terms of a quantity known as the effective magnetic moment, defined by the expression,

$$\mu_{eff.} = \left(\frac{3k}{N\beta^2}\right)^{\frac{1}{2}} (\chi_A T)^{\frac{1}{2}} \qquad \ldots\ldots(2.13)$$

$$= 2.828\ (\chi_A T)^{\frac{1}{2}}$$

where, k is the Boltzmann constant, N is Avogadro number, T the absolute temperature and β, the Bohr magneton defined as,

$$\beta = eh/_{4\pi mc} \qquad \text{.....(2.14)}$$

$$= 9.27 \times 10^{-21} \text{ergs.G}^{-1}$$

e is the electronic charge, h is Planck's constant, m is the rest mass of the electron and c is the velocity of light.

If the Curie law is obeyed, $\mu_{eff,}$ is independent of temperature. In fact, comparatively few systems follow the Curie law. A modification of the Curie law is capable of accounting for the magnetic susceptibility of a great many systems over a considerable range of temperature. This is the Curie-Weiss law.

$$\chi_A = \frac{C}{T+\theta} \qquad \text{.....(2.15)}$$

where θ is the Weiss constant. When the Curie-Weiss law is followed,

$$\mu_{eff,} = 2.828\ [\chi_A(T + \theta]^{\frac{1}{2}} \qquad \text{.....(2.16)}$$

The susceptibility is sometimes expressed as,

$$\chi_A = \frac{N\beta^2\mu^2}{3kT} + N\alpha \qquad \text{......(2.17)}$$

The $N\alpha$ term of the above equation (2.17) arises from the underlying diamagnetism of the ion and is referred to as temperature independent paramagnetism (T.I.P.). The T.I.P. term is defined as

$$N\alpha = \frac{\gamma N\beta^2}{10D_q} \qquad \ldots\ldots(2.18)$$

where γ is 8 or 4 for A or E terms respectively. The T.I.P. is small ~ 100 x 10^{-6} c.g.s. units. In real situations, this is the origin of the paramagnetism of such systems as the Co(III) low-spin complexes in octahedral environment.

Ferromagnetism and antiferromagnetism are special cases of paramagnetism where the magnetic dilution is inadequate, thus making the magnetic dipoles on adjacent paramagnetic centres interact. The two possibilities are, either adjacent dipoles may tend to align themselves parallel to the applied field or antiparallel to the applied field.

The former leads to ferromagnetism and the latter being antiferromagnetism. In systems in which cooperative magnetic alignment takes place, the magnetic alignment energy, may become comparable to, or greater than, the thermal energy kT. Also, the alignment forces on adjacent dipoles may become comparable to, or greater than the alignment force exerted by the applied field. These facts show up in experimental phenomena in the form of a complicated susceptibility dependence on both temperature and applied field strength. For either ferromagnetics or antiferromagnetics, there is a temperature above which the thermal energy is sufficient to start to destroy the cooperative alignment between adjacent dipoles. Such a temperature is known as the Curie temperature, T_c or often in the case of antiferromagnetics, the Neel temperature, T_N (Fig.11a). Above T_c the behaviour approximates that of a normal paramagnetic and at temperatures well above it, a Curie-Weiss law holds and susceptibility is independent of field strength. Below T_c, the susceptibility does not depend on temperature or field strength in a simple manner. At T_c, the susceptibility of a ferromagnet undergoes an abrupt change in slope. For an antiferromagnet, the susceptibility goes through a maximum. Above T_c, systems subject to magnetic exchange obey a Curie-Weiss law.

In general, in magnetically concentrated systems a positive Weiss constant is characteristic of antiferromagnetism, and a

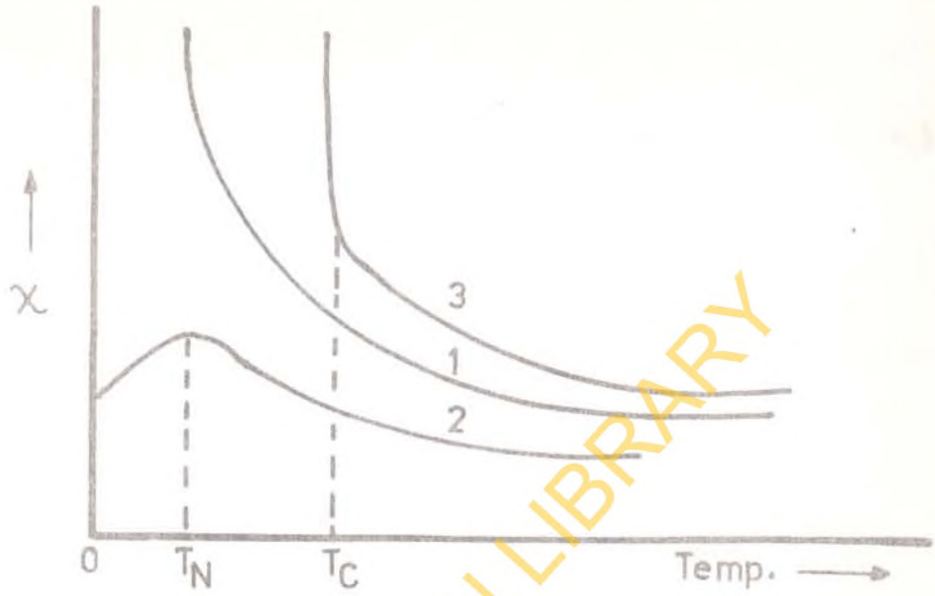


Fig. 11a. The behaviour of typical paramagnetic (I), antiferromagnetic (2), and ferromagnetic substances as a function of temperature.

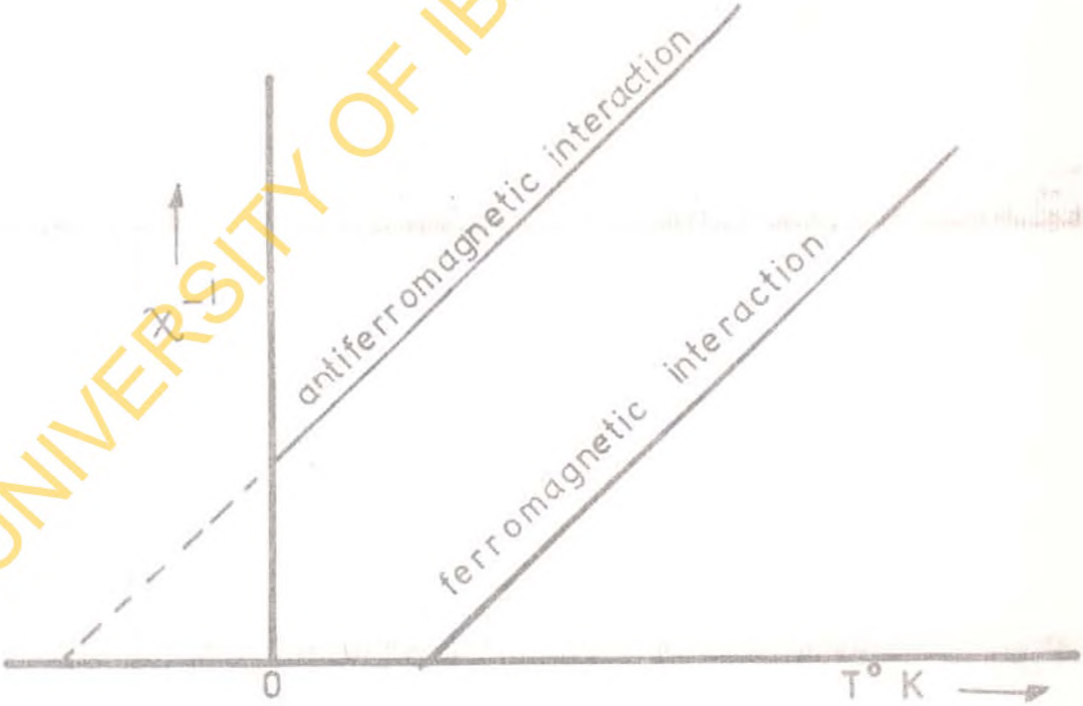


Fig. 11b. Deviations from the Curie law that may be fitted to the Curie-Weiss law.

negative one of ferromagnetism (Fig. 11b).

Many different methods have been used to measure the magnetic properties of materials in solid, liquid and gaseous states among which are the Gouy, Faraday, Quinke and NMR methods. However, the simplest and most common method is the Gouy method [110].

CHAPTER 3

EXPERIMENTAL

3.1. Reagents of interest are:

2-Thenoyltrifluoroacetone	(Htftbd)
2-Thenoylacetone	(Htbd)
2-Furoyltrifluoroacetone	(Htffbd)
2-Furoylacetone	(Hfbd)
Benzoyltrifluoroacetone	(Hbztfac)
Benzoylacetone	(Hbzac)
Nicotinoyltrifluoroacetone	(Htfpybd)

All the above β-diketones were commercially available from Eastman Organic Chemicals Ltd. The organic solvents used were obtained from British Drug Houses Ltd. (BDH). The inorganic chemicals were also commercially available (BDH). All the organic solvents were purified using appropriate methods as described in Vogel [111]. Apart from $Al(NO_3)_3$. $9H_2O$, $CrCl_3.6H_2O$ and $FeCl_3.6H_2O$ which were used as the sources of the aluminium (III) -, chromium (III)- and iron (III) ions respectively, there were no simple metal (III) ions of manganese (III) and cobalt (III) readily available. These last two metal (III) ions were therefore obtained by preparing $Mn(OOCCH_3)_3.2H_2O$ and $Na_3[Co(CO_3)_3].3H_2O$ by established methods [112,113].

3.2 Preparation of complexes

The preparation of Al(III), Cr(III) and Fe(III) complexes was achieved by the general method established by Berg and Truemper [26] whilst the Mn(III) chelates were prepared by an adaptation of a procedure given by Donaruma [114]. The cobalt(III) chelates were isolated starting from sodium tris-carbonate cobalt(III) trihydrate, $Na_3[Co(CO_3)_3].3H_2O$ as the source of cobalt(III) ion [113, 115].

3.2.1 Preparation of aluminium(III), chromium(III) and iron(III) β-diketonates.

The Al(III), Cr(III) and Fe(III) complexes were prepared by mixing stoichiometric amounts of the metal(III) nitrate or chloride where appropriate with the ligand.

The metal(III) salt was made up as a 5wt% aqueous solution and buffered immediately before use by adding 5g. of sodium acetate for every 100ml of solution. The buffered metal(III) ion solution was shaken with an alcoholic solution of the ligand until reaction appeared complete. After precipitation, the chelates were collected by filtration and dried over P_2O_5 in vacuo. Analytical samples were obtained by recrystallization from suitable organic solvents.

3.2.2 Preparation of manganese(III) β-diketonates.

The β-diketone(0.045mole) and manganic acetate dihydrate (0.015 mole) were mixed up until a homogeneous mixture was obtained. The homogeneous mixture was dissolved in 50ml dry methanol and gently refluxed for 30 minutes. After refluxing, about 25 - 30ml of the methanol was distilled off. A further 5 - 10ml of methanol-acetic acid mixture (azeotrope) was also distilled off. The mixture was then cooled down to room temperature and was extracted twice with 15ml portions of dry chloroform. The chloroform extracts were placed in a desiccator and gently pumped out. Fine black powders of manganese(III) β-diketonates were obtained by this method.

3.2.3 Preparation of cobalt(III) β-diketonates

Cobalt(III) β-diketonates were prepared using $Na_3[Co(CO)_3]$. $3H_2O$ as the source of cobalt(III) ion.

3ml of glacial acetic acid was added to a mixture of sodium tris-carbonato cobaltate(III) trihydrate (5.4g, 0.015 mole) and the β-diketone (0.045mole) in 50ml of 60% acetone-water. The mixture was refluxed for 15mins. then the cold mixture was extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution and then water. The organic layer was dried and pumped under vacuum. Analytical samples were obtained by recrystallization from ether.

3.2.4 Preparation of mixed ligand chelates of iron(III) β-diketonates

These chelates were prepared using the method described in section 3.2.1, except that, desired combinations of ligands were used in such a manner as to preserve the 1:3 stoichiometry.

3.3 Microanalysis

The elemental analyses were carried out in the Micro-analytical Laboratories of the University of Ibadan. The composition of the various metal constituents of the complexes was determined by complexometric titrations and other standard analytical methods described in Vogel [116].

3.4 Spectral measurements

The infrared spectra were recorded on a Perkin-Elmer model IR-577 spectrophotometer using KBr discs and nujol mull where appropriate. The calibration of the instrument was checked against a polystyrene film and is believed to be correct to within ± 4cm^{-1} in the 4000 - 2000cm^{-1} range, and ±2cm^{-1} in the spectra range 2000 - 200 cm^{-1}. The diffuse reflectance spectra of the complexes in the range 50,000 - 5,000cm^{-1} were recorded on an Unicam SP 700 spectrophotometer with an SP 735 Diffuse relectance attachment, using LiF as a standard. The electronic spectra of the complexes in chloroform solutions were measured using the SP6 - 400 and SP30UV spectrophotometers.

3.5 Magnetochemical measurements

The magnetic measurements were carried out at room temperature for all the compounds and from 293 - 80K for selected compounds. This was accomplished by use of the Gouy balance.

The principle behind the Gouy method involves suspending a uniform rod of the specimen in a non-homogeneous magnetic field, and measuring by a conventional weighing technique, the force exerted on it [110].

If the field gradient over an element, ∂V, of the specimen is $\partial H/\partial l$, then the force, ∂F exerted is,

$$\partial F = (K_1 - K_2)\partial V \quad H \frac{\partial H}{\partial l} \qquad \text{....(3.1)}$$

where K_1 and K_2 are the susceptibility per unit volume of the specimen and the displaced medium respectively. Integration over the whole length of the specimen from $H = H_1$ at zero length to $H = Ho$ at length l, gives,

$$F = \frac{(K_1 - K_2)V\ (H_1^2 - H_o^2)}{2l} \qquad \text{.....(3.2.)}$$

If F, in dynes, is replaced by wg, (where w is in grams) and $(H_1^2 - H_o^2)$ by H^2 then

$$K_1 = K_2 + \frac{2lgw}{VH^2} \qquad \text{.....(3.3)}$$

but $K = \chi\rho \quad = \quad \frac{\chi W}{V}$

where W is the total weight of the specimen then equation (3.3) becomes,

$$\chi = \frac{K_2V - (\frac{2gl}{H^2})w}{W} \qquad \ldots\ldots(3.4)$$

$$= \frac{A + Bw}{W}$$

Fig.12 shows diagrammatically, the system used for measurements at room temperature only.

The procedure involves measuring the pull on a specimen suspended between two poles of a magnet, usually an electromagnet; and weighing it without the field and then again with the field applied. To be able to allow for the diamagnetism of the glass tube it is necessary first to weigh the empty tube with the field on and off, the difference being W_t (when using an electromagnet, a series of values should be obtained for different fields). When subsequertly the tube is filled with the sample and weighed with and without field, W_{t+s} is obtained. W is then the difference $(W_{t+s} - W_t)$. Since the glass is diamagnetic, W_t is a negative quantity and, for paramagnetic samples, $W > W_{t+s}$ W is obtained as the difference between the weights of the filled and empty tube without field.

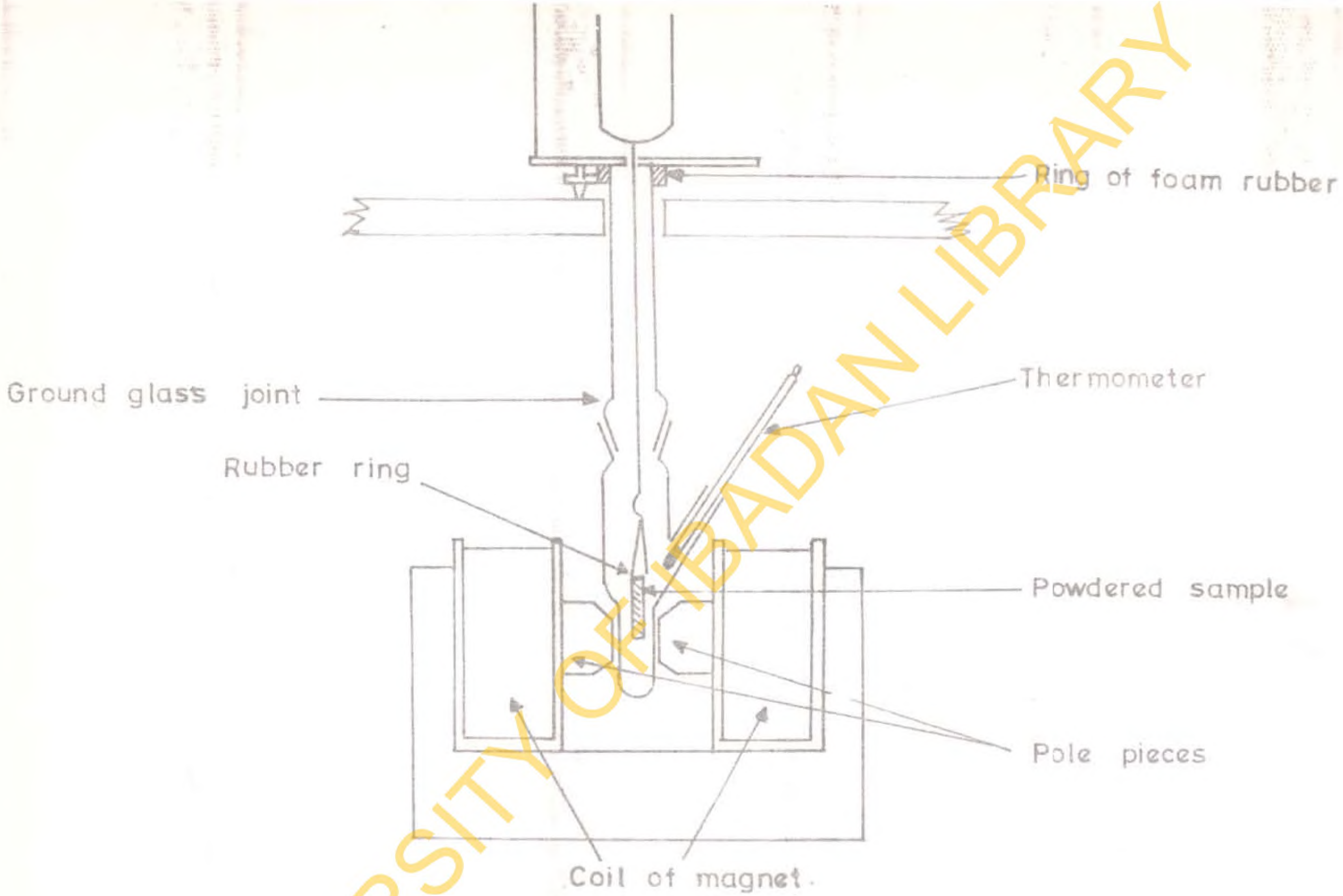


Fig. 12. Schematic diagram of Gouy balance for room temperature measurements.

The constants A and B in equation (3.4) must be obtained by calibration before measurements can be made. This is usually done by using calibrants such as $HgCo(CNS)_4$ and $Ni(en)_3(S_2O_3)$ which have known susceptibilities at 20°C with the appropriate correction factors per degree temperature rise.

Measurements at low temperature can be done using a modification of the room temperature set up. The modification involves surrounding the specimen with a cryostat in order to control the temperature (Fig. 13). Any measurement near, or below, the boiling point of oxygen ($\simeq$ 90K) must be performed in the absence of air. Nitrogen provides a convenient substitute and, if the chamber containing the specimen is previously flushed out with nitrogen, this atmosphere can be maintained by a slow continuous stream of the gas introduced at a distance above the specimen. If this is sufficiently slow, it has no appreciable effect on the weighings. The additional advantage accrues that the K_2V correction is now negligible (κ_2 for nitrogen $\simeq 0.0004 \times 10^{-6}$) and equation (3.4) reduces to

$$\chi = \left(\frac{2gl}{WH^2}\right)w \qquad .....(3.5)$$

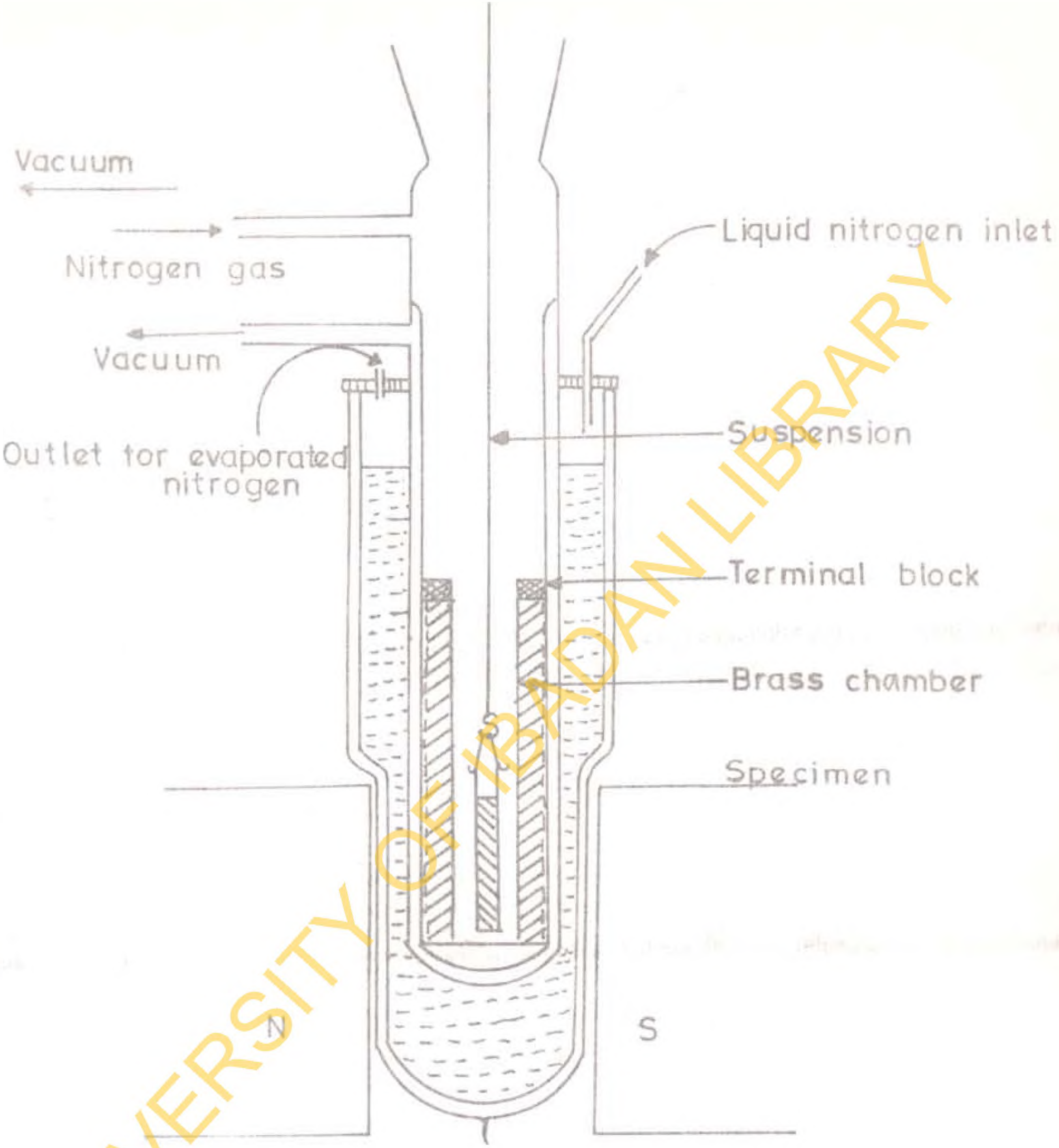


Fig. 13 A cryostat allowing temperature control for a Gouy balance.

CHAPTER 4

RESULTS

4.1 Physical and analytical data

The stoichiometric and chemical composition together with the various decomposition temperatures have been summarised in Table 9.

4.2 Infrared spectra

The infrared spectra of the β-diketones and their trivalent metal complexes investigated, are shown in Figures 14 - 21. Their observed vibrational frequencies together with the proposed assignments of the fundamental modes, in the spectral range 1800 - 200 cm^{-1} are given in Tables 10 - 16.

4.3 Electronic spectra

The diffuse reflectance spectra of the metal β-diketonates at room temperature are shown in Figures 22 - 28. Tentative assignments have been made for the various electronic transitions and these are summarised in Tables 17 - 20. The solution spectra of these compounds in chloroform have also been

TABLE 9 Physical and analytical data of trivalent metal complexes of Htftbd, Htbd, Htfftbd, Hfbd, Hbzac, Hbztfac, Htfpybd and mixed β-diketones.

COMPOUND	FORMULA	COLOUR	Mol wt.	M pt °C or Dec Temp	CALCULATED			FOUND		
					% C	% H	% metal	% C	% H	% metal
Al(tftbd)$_3$	$C_{24}H_{12}F_9O_6S_3Al$	whitish	690.54	203 – 204	41.77	1.76	3.91	41.97	1.80	4.20
Cr(tftbd)$_3$	$C_{24}H_{12}F_9O_6S_3Cr$	dk. brown	715.57	184 – 185	40.30	1.70	7.30	40.10	1.55	6.97
Mn(tftbd)$_3$	$C_{24}H_{12}F_9O_6S_3Mn$	" "	718.50	149 – 150	40.10	1.70	7.65	39.70	1.87	8.05
Fe(tftbd)$_3$	$C_{24}H_{12}F_9O_6S_3Fe$	red	719.41	135 – 136	40.10	1.70	7.80	39.45	1.69	7.10
Co(tftbd)$_3$	$C_{24}H_{12}F_9O_6S_3Fe$	green	722.50	188 – 189	39.92	1.68	8.16	40.03	1.74	7.80
Al(tbd)$_3$	$C_{24}H_{21}O_6S_3Al$	whitish	528.34	221 – 222	54.55	3.97	5.11	54.63	3.90	4.90
Cr(tbd)$_3$	$C_{24}H_{21}O_6S_3Cr$	brown	553.37	238 – 239	52.04	3.79	9.40	51.70	3.90	9.20
Mn(tbd)$_3$	$C_{24}H_{21}O_6S_3Mn$	black	556.30	164 – 165	51.77	3.77	9.88	51.70	3.80	9.80
Fe(tbd)$_3$	$C_{24}H_{21}O_6S_3Fe$	red	557.21	197 – 198	51.69	3.77	10.02	51.40	4.06	9.86
Co(tbd)$_3$	$C_{24}H_{21}O_6S_3Co$	green	560.30	132 – 133	51.40	3.75	10.52	49.67	4.20	9.76
Al(tffbd)$_3$	$C_{24}H_{12}F_9O_9Al$	whitish	642.34	204 – 205	44.88	1.41	4.20	44.98	1.87	4.00
Cr(tffbd)$_3$	$C_{24}H_{12}F_9O_9Cr$	brown	667.37	183 – 184	43.19	1.36	7.79	43.25	1.68	7.60
Mn(tffbd)$_3$	$C_{24}H_{12}F_9O_9Mn$	black	670.30	144 – 145	43.00	1.35	8.20	43.02	2.03	8.16
Fe(tffbd)$_3$	$C_{24}H_{12}F_9O_9Fe$	red	671.21	187 – 188	42.95	1.35	8.32	42.72	1.19	8.25
Co(tffbd)$_3$	$C_{24}H_{12}F_9O_9Co$	green	674.30	142 – 143	42.75	1.35	8.74	43.12	1.81	8.47
Al(fbd)$_3$	$C_{24}H_{21}O_9Al$	whitish	480.41	249 – 250	60.00	4.41	5.62	60.50	4.50	5.60
Cr(fbd)$_3$	$C_{24}H_{21}O_9Cr$	brown	505.44	287 – 288	57.03	4.19	10.29	56.76	4.47	10.01
Mn(fbd)$_3$	$C_{24}H_{21}O_9Mn$	black	508.37	159 – 160	56.70	4.16	10.81	56.44	4.44	10.50
Fe(fbd)$_3$	$C_{24}H_{21}O_9Fe$	red	509.28	233 – 234	56.60	4.16	10.97	56.85	4.65	10.63
Co(fbd)$_3$	$C_{24}H_{21}O_9Co$	green	512.37	174 – 175	56.26	4.13	11.50	56.00	4.23	11.24

Table 9 contd

Table 9 contd

COMPOUND	FORMULA	COLOUR	Mol. wt.	M. pt °C OR Dec. Temp	CALCULATED			FOUND		
					% C	% H	Metal	% C	% H	% Metal
$Al(bzac)_3$	$C_{30}H_{27}O_6Al$	whitish	510.53	224 – 225	70.58	5.33	5.28	70.08	5.73	5.12
$Cr(bzac)_3$	$C_{30}H_{27}O_6Cr$	brown	535.56	214 – 215	67.28	5.08	9.71	67.28	5.14	9.46
$Mn(bzac)_3$	$C_{30}H_{27}O_6Mn$	black	538.49	162 – 163	66.91	5.05	10.20	66.40	5.45	10.01
$Fe(bzac)_3$	$C_{30}H_{27}O_6Fe$	red	539.40	200 – 201	66.80	5.05	10.35	67.01	5.50	10.19
$Co(bzac)_3$	$C_{30}H_{27}O_6Cr$	green	524.49	109 – 110	66.42	5.02	10.86	66.50	5.44	10.60
$Al(bztfac)_3$	$C_{30}H_{18}F_9O_6Al$	whitish	672.43	159 – 160	53.59	2.70	4.01	53.64	2.76	3.83
$Cr(bztfac)_3$	$C_{30}H_{18}F_9O_6Cr$	green	697.45	120 – 121	51.66	2.60	7.46	51.80	2.90	7.19
$Mn(bztfac)_3$	$C_{30}H_{18}F_9O_6Mn$	black	700.39	137 – 138	51.45	2.59	7.84	51.55	2.55	8.01
$Fe(bztfac)_3$	$C_{30}H_{18}F_9O_6Fe$	red	701.29	113 – 114	51.38	2.59	7.96	50.93	2.90	7.76
$Co(bztfac)_3$	$C_{30}H_{18}F_9O_6Co$	green	704.36	162 – 163	51.16	2.58	8.37	51.40	2.41	7.57
$Al(tfpybd)_3$	$C_{27}H_{15}F_9N_3O_6Al$	cream	676.10	175 – 176	49.04	2.38	3.99	49.00	2.30	3.90
$Cr(tfpybd)_3$	$C_{27}H_{15}F_9N_3O_6Al$	green	701.13	234 – 235	46.21	2.30	7.42	46.13	2.29	6.95
$Mn(tfpybd)_3$	$C_{27}H_{15}F_9N_3O_6Mn$	orange	704.06	> 250	46.02	2.29	7.80	46.20	2.28	8.00
$Fe(tfpybd)_3$	$C_{27}H_{15}F_9N_3O_6Fe$	brown	704.97	189 – 190	45.96	2.29	7.92	45.62	2.52	7.85
$Co(tfpybd)_3$	$C_{27}H_{15}F_9N_3O_6Co$	green	708.06	169 – 170	45.76	2.28	8.32	44.23	2.42	7.25
$Fe(tbd)_2(bzac)$	$C_{26}H_{23}O_8Fe$	red	519.31	202 – 203	60.13	4.46	10.75	60.23	4.46	10.72
$Fe(fbd)_2(fbd)$	$C_{24}H_{21}S_2O_7Fe$	"	541.40	218 – 219	53.24	3.91	10.32	52.86	4.20	10.30
$Fe(fbd)_2(tbd)$	$C_{24}H_{21}S\,O_8Fe$	"	525.33	222 – 224	54.87	4.03	10.63	55.30	4.02	10.59
$Fe(bzac)_2(tftbd)$	$C_{28}H_{22}F_3SO_6Fe$	"	599.31	70 – 72	56.12	3.70	9.32	56.79	3.79	9.20
$Fe(tftbd)_2(bzac)$	$C_{26}H_{17}F_6S_2O_6Fe$	"	659.26	78 – 80	47.37	2.60	8.47	47.24	2.53	8.44

investigated and are shown in Figures 29 - 42. The band positions with their molar absorption coefficients, together with their proposed assignments, are given in Tables 21 - 24.

4.3 Magnetic susceptibility data

Table 25 is a summary of the results of magnetic susceptibility measurements at room temperature while Table 26 gives the over-range temperature (293 - 80K) susceptibility measurements of some selected compounds. Figure 43 shows the plots of the reciprocal susceptibility and the effective magnetic moment against temperature for these selected compounds.

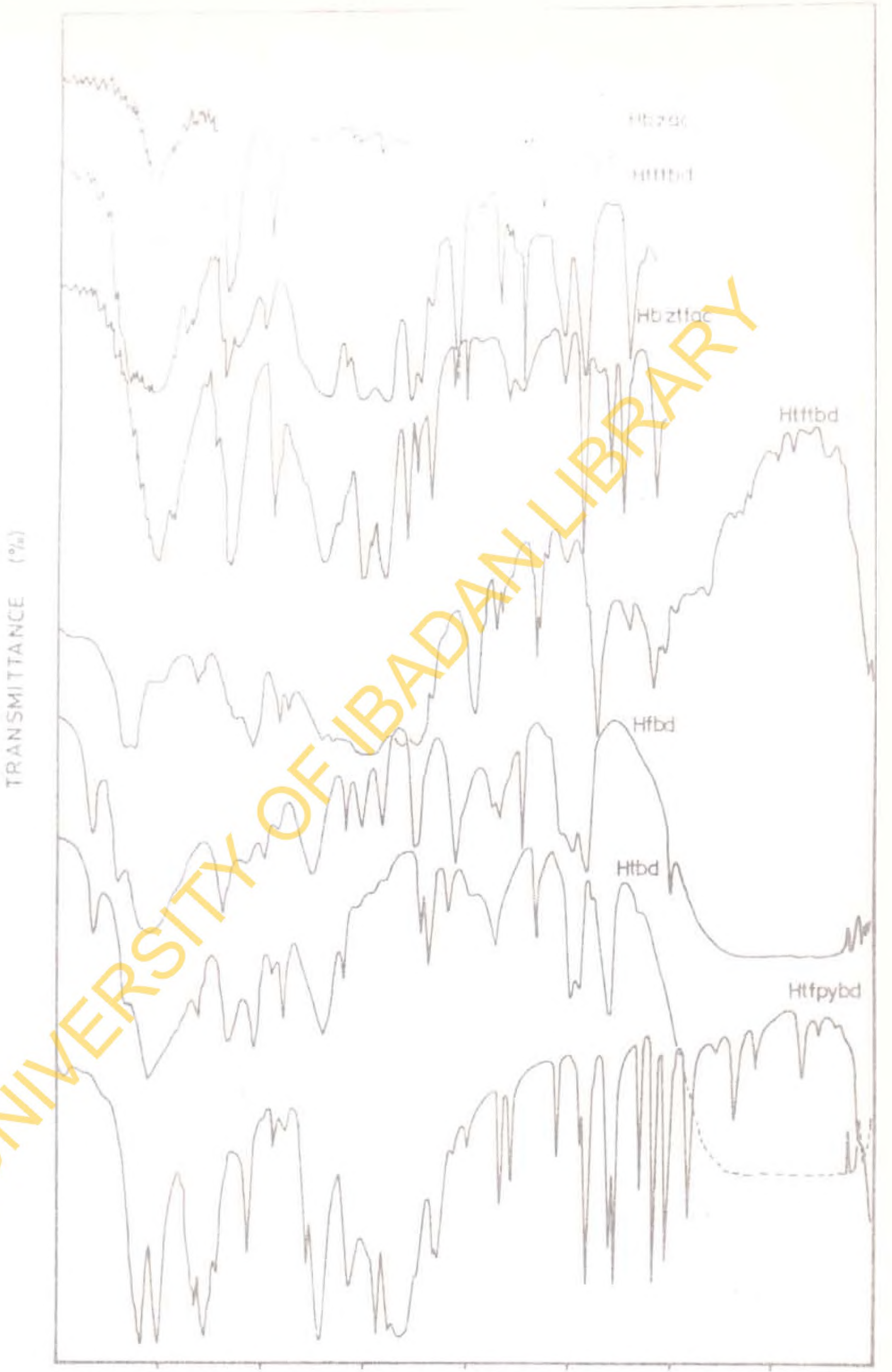


Fig 14 I R Spectra of some β- diketones

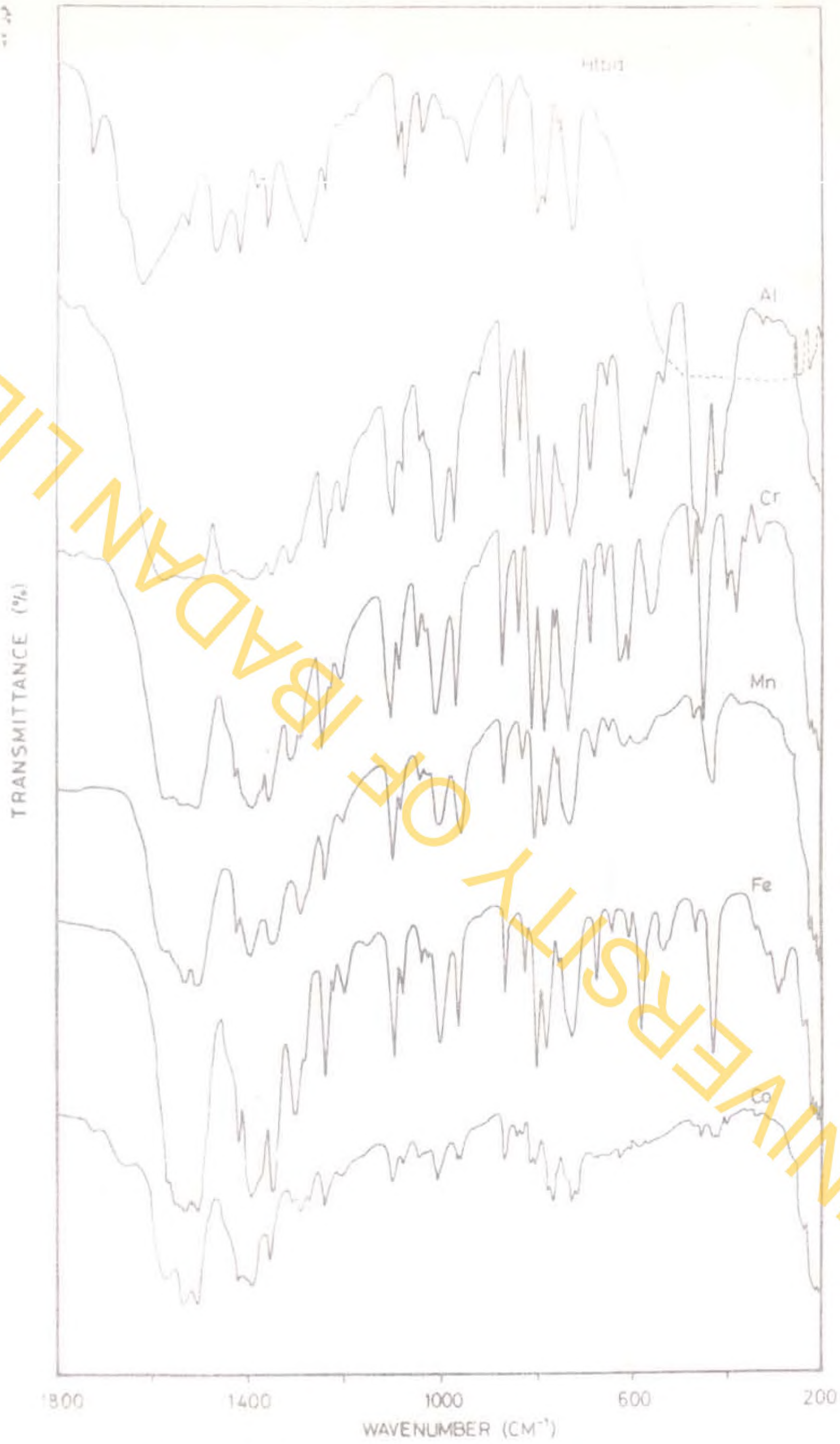


Fig 15 I.R Spectra of Htbd and M(tbd)$_3$ complexes

TABLE 10. Assignment of the observed vibrational frequencies(cm^{-1}) of 1-(2-thienyl)-1,3-butanedione (Htbd) and its trivalent metal complexes

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1620vs	1575s	1570s	1572m	1570m	1568m	νas C---O
1525sh	1535s	1535s	1530s	1535s	1530s	νas C---C---C
1465s	1500s	1500s	1505s	1510s	1508s	
1418s	1450sh	1422sh	1420m	1422m	1420sh	} Thienyl ring stretches
1382w	1400s	1390s	1395s	1395s	1390s	
1360m	1352s	1350s	1350s	1350s	1354m	νC---O + βCH
1280s	1315m	1309m	1286m	1302m	1290m	νs C---O
1240m	1238m	1242s	1230m	1240m	1240s	νs C---C---C
1210w	1200w	1202w	1200w	1200w	1205w	νC=C + νC-R
1090m	1098s	1100s	1098s	1100s	1100m	} βCH (chelate ring)
1075s	1080sh	1080w	1080w	1080w	1078w	
1035m	1042sh	1042w	1044w	1042w	1045w	} βCH (Thienyl)
998sh	1005vs	1005s	1005m	1004m	1005m	
945s	980s	964s	958m	965m	965m	ν C - R
868s	865vs	868s	868m	868m	865s	
=	825m	834m	830m	818m	812m	} νCH (Thienyl)
800s	804vs	804vs	800s	800s	800m	

cont.

TABLE 10 Contd.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
780s	775vs	778vs	780s	780s	764s	γCH (chelate ring)
720vs	730vs	728vs	730s	730s	724s	
665w	684m	682m	678m	678m	670w	Metal - Ligand stretches (combination bands)
-	650w	650w	645w	645w	650w	
600s	600s	580m	580m	580vs	585w	chelate ring deformation + ν_{M-O}
-	-	555m	-	535m	560w	
-	452vs	444vs	438s	430vs	454m	$\nu_{M — O}$ (most sensitive)
-	420s	374s	370w	295w	428m	$\nu_{M — O}$

νas, asymmetric stretch; νs, symmetric stretch;

R, either Thienyl or CH_3; S, strong; vs, very strong;

m, medium; w, weak; sh, shoulder;

β, in-plane-deformations; γ, out-of-plane deformation.

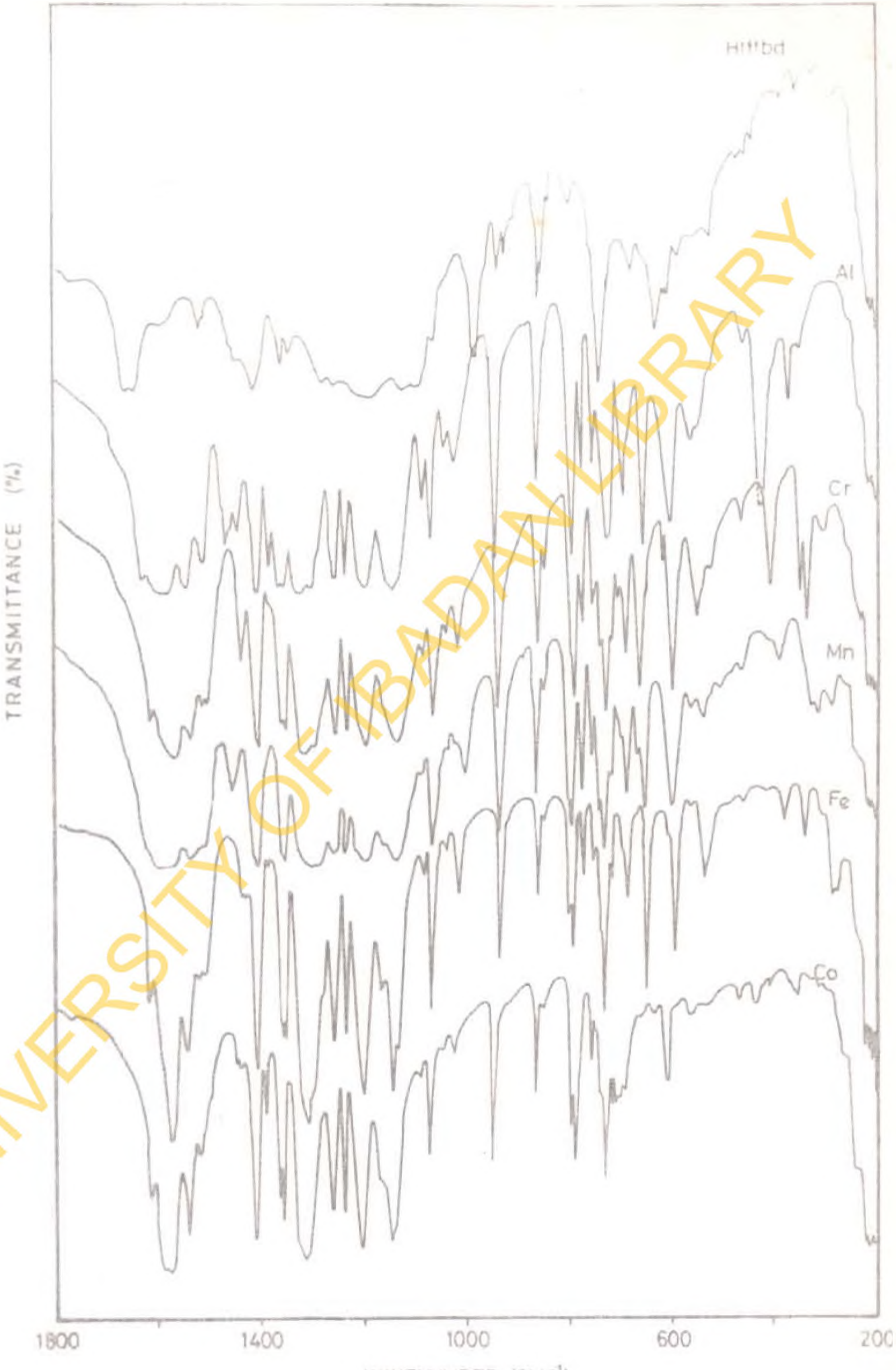


Fig.16. I.R Spectra of Htttbd and M(tttbd)$_3$ complexes

TABLE 11. Assignment of the observed vibrational frequencies(cm^{-1}) of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione(Htftbd) and its trivalent metal complexes.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignments
1655s	1600s	1575s	1595s	1575vs	1580vs	ν_{as} C$\underline{----}$O
1525m	1550s	1542s	1542s	1540s	1540s	ν_{as} C$\underline{--}$C$\underline{---}$C
-	1515w	1515w	-	1520w	1518w	
1450w	1450m	1444m	1460m	1435w	1435w	} Thienyl ring stretches
1420s	1412vs	1410vs	1410vs	1410vs	1420vs	
-	1390m	1390sh	-	1390w	1390w	
1365m	1365m	1360s	1358m	1360s	1355s	νC$\underline{---}$O + δCH
1350w	1330m	1320s	1300m	1310vs	1315vs	ν_s C$\underline{---}$O
1282w	1263s	1264m	1260m	1260m	1260m	ν_s C$\underline{--}$C$\underline{--}$C
1260w	1240s	1240s	1240m	1240m	1240m	νC$=$C + νC - R
1200m	1200s	1205s	1200m	1204m	1202s	νC—CF$_3$ + δCF$_3$
1130w	1150s	1140s	1140m	1145s	1145s	} δCH (chelate ring)
1100m	1090w	1090w	1090w	1088w	1088w	
1070w	1072s	1072s	1060s	1072s	1072s	
-	1045w	1045w	-	1045w	1045w	} δCH (Thienyl)
984s	1028w	1022w	1005m	1020m	1022w	

contd.

TABLE 11. Contd.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignments
940m	950vs	944vs	938vs	942vs	950vs	} νCH (Thienyl)
862vs	867s	868s	868s	865s	865s	
805m	798vs	795vs	800vs	800vs	795vs	} $\nu C{-}CF_3$
765sh	780m	780m	778m	778m	785vs	
740s	758m	758w	758w	758w	758w	νCH (chelate ring)
-	730m	732m	735s	735vs	728vs	} δCF_3
680m	695m	695m	690m	692m	700m	
610w	604s	604vs	600vs	598vs	605s	chelate ring deformations
580w	565w	552m	542m	540m	550w	Thienyl ring deformations
-	465w	468w	465w	465w	465w	chelate ring vibrations + νM - O
-	428vs	410s	392m	382m	435m	νM - O (most sensitive)
-	375s	350m	340m	342m	352m	νM - O
-	350w	338s	318m	310w	310w	νM - O

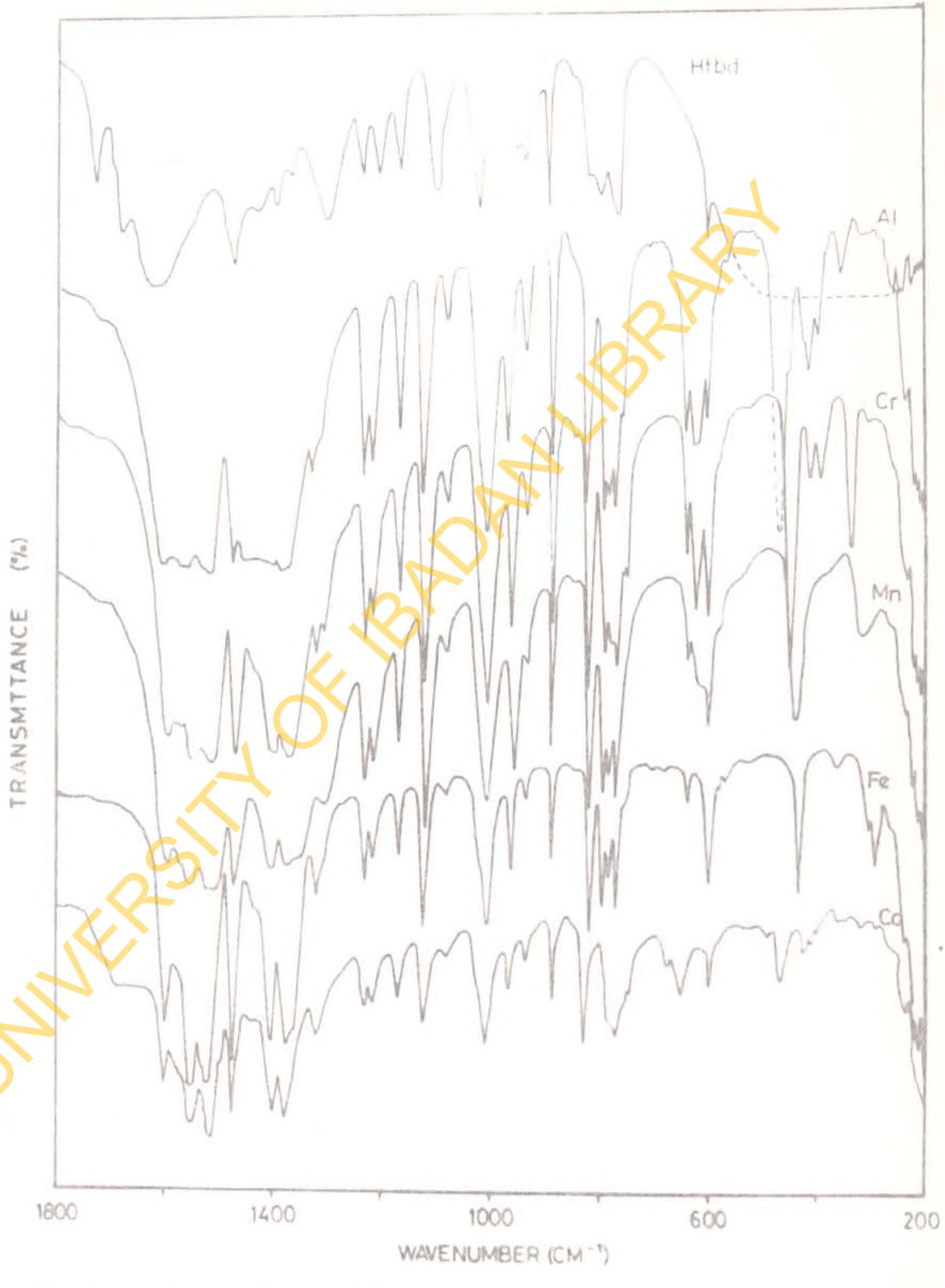


Fig 17 I R Spectra of Htbd and $M(tbd)_3$ complexes

TABLE 12. Assignment of the observed vibrational Frequencies (cm^{-1}) of 1-(2-furyl)-1,3-butanedione (Hfbd) and its trivalent metal complexes.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1730m	1605s	1600s	1595s	1600s	1600m	ν_{as} C---O
1620s	1560s	1550s	1555s	1550vs	1550s	ν_{as} C---C---C
1475m	1520s	1515s	1510s	1520s	1515s	
1430w	1478m	1475s	1470s	1474vs	1485s	Furyl ring stretches
1394w	1380s	1400s	1400m	1400s	1400	
1370w	1330w	1385s	1375m	1374s	1375s	ν_s C---O
1300s	-	1324w	1310w	1320w	1320w	νC = O + βCH
1235m	1235s	1232s	1230s	1232m	1230m	ν_s C---C---C
1205m	1220s	1220m	1220m	1215m	1215m	νC≡C + νC-R
1165m	1170s	1170m	1170m	1170m	1170m	βCH (chelate ring)
1100s	1125s	1124vs	1120vs	1122s	1124s	
-	1085w	1085w	1085w	1080w	1080w	βCH (Furyl)
1020s	1008vs	1010vs	1005vs	1005vs	1010s	
-	970m	984s	956m	964m	965m	νC — R
935m	940m	938m	935w	935w	935w	

contd.

TABLE 12. contd.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
890s	890vs	890vs	890vs	890m	888m	}γCH (Furyl)
-	825vs	824vs	818vs	820vs	830vs	
795s	790vs	790s	792s	795s	785sh	}γCH (chelate ring)
765s	770vs	770vs	770vs	770s	770s	
600m	640s	640m	638w	638w	650m	Chelate ring deformations
-	625vs	624vs	600s	600s	600m	Metal-Ligand Combination bands
-	468vs	450vs	440vs	432vs	470s	ν_{M-O} (most sensitive)
-	415m	415m	-	-	430m	ν_{M-O}
-	400m	395w	380sh	360w	415w	ν_{M-O}
-	358m	340s	320w	298m	350w	ν_{M-O}

ν_{as}, asymmetric stretch; ν_s, symmetric stretch;
R, either Furyl or CH_3; S, strong; VS, very strong;
m, medium; w, weak; sh, shoulder;
β, in-plane deformations; γ, out-of-plane deformations.

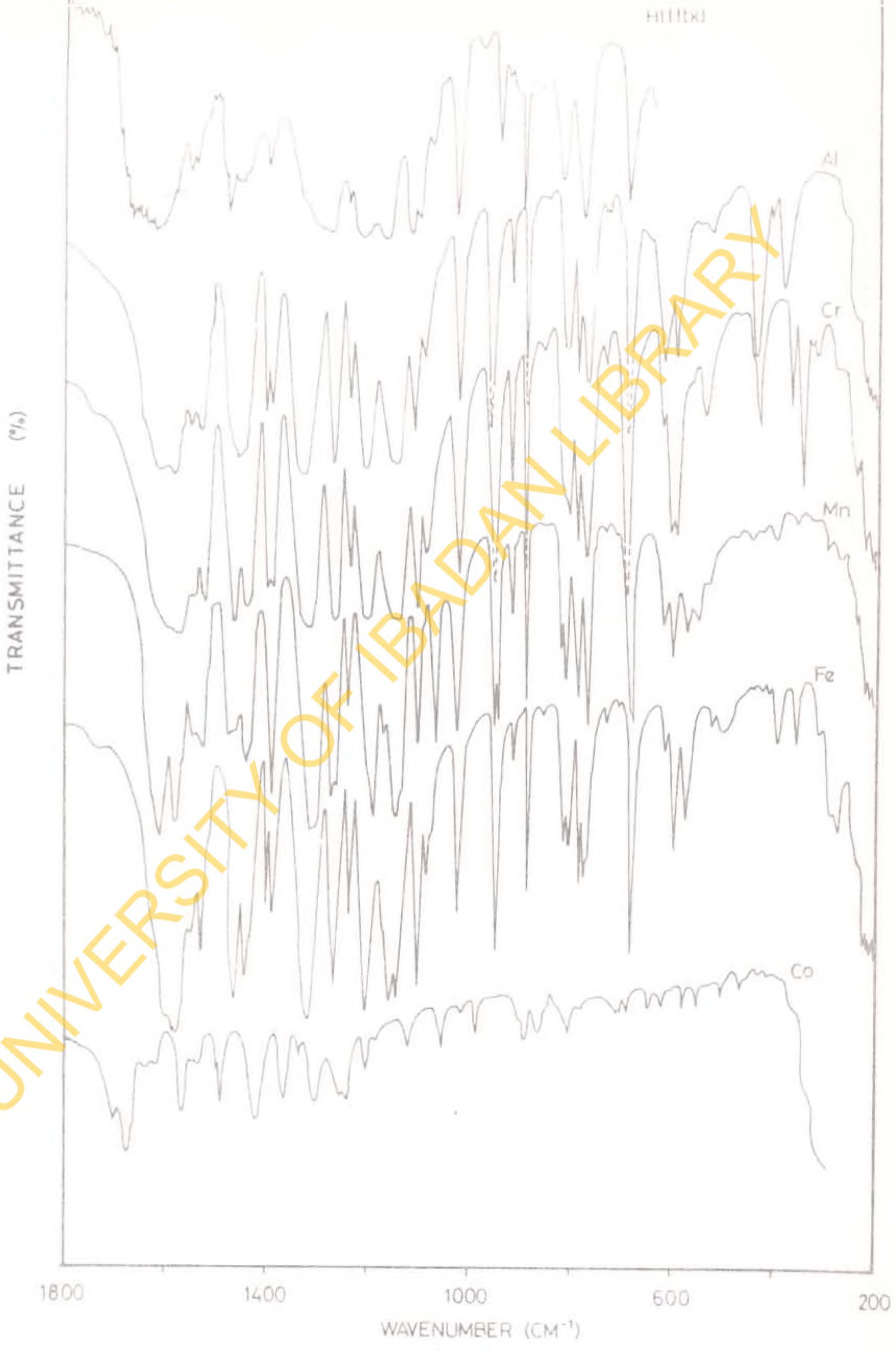


Fig 18 I.R Spectra of Htttbd and M(tttbd)$_3$ complexes

TABLE 13. Assignment of the observed vibrational frequencies(cm^{-1}) of 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione(Htffbd) and its trivalent metal complexes.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1680m	1610m	1600sh	1615s	1600sh	1600sh	ν_{as} C---O
1620s	1585s	1580vs	1582s	1580s	1575s	ν_{as} C---C---C
1550m	1550w	1525m	1530m	1530m	1540w	Furyl ring stretches
1475m	1505w	1460vs	1472m	1465s	1465s	
1450m	1460vs	1445vs	1440s	1445m	1435m	
1395w	1405s	1400vs	1392vs	1400s	1390s	ν_s C---O
1320sh	1330vs	1320vs	1315vs	1320vs	1320vs	$\nu_{C=O}$ + β C H
1275s	1270s	1270s	1275s	1270vs	1268s	ν_s C---C---C
1235w	1240m	1240m	1242m	1240m	1240m	$\nu_{C=C}$ + ν_{C-R}
1210m	1205s	1210s	1192vs	1205vs	1205s	ν_{C-CF_3} + β CF_3
1160m	1150s	1150m	1150s	1150vs	1145s	β CH (chelate ring)
1110s	1110s	1105	1105s	1104vs	1105s	
1095m	1095w	1088w	1070s	1085w	1090w	βCH (Furyl)
1020vs	1022vs	1025vs	1028s	1025s	1022m	

contd.

TABLE 13. Contd.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
972w	960vs	955vs	950vs	950vs	958s	γCH
945s	920m	920m	920m	920s	920w	
890vs	890vs	890vs	890vs	890vs	890vs	δCF_3
810s	810s	802s	812s	810s	805sh	
720vs	788s	790s	785s	788s	795s	$\nu C - CF_3$
630s	768s	770s	768vs	780s	770m	
-	687vs	690vs	680vs	682vs	708m	Chelate ring deformations
-	618s	605vs	615m	610m	615m	+ $\nu_M - O$
-	595s	600vs	598m	600vs	595m	
-	525w	535m	570m	578m	550w	$\nu_M - O$
-	435vs	428s	394m	390m	450m	$\nu_M - O$ (most sensitive)
-	380s	365	350w	358m	405m	$\nu_M - O$

ν_{as}, asymmetric stretch; ν_s, symmetric stretch;

R, either Furyl or CF_3; s, strong; vs, very strong;

m, medium; w, weak; sh, shoulder;

β, in-plane deformations; γ, out-of-plane deformations.

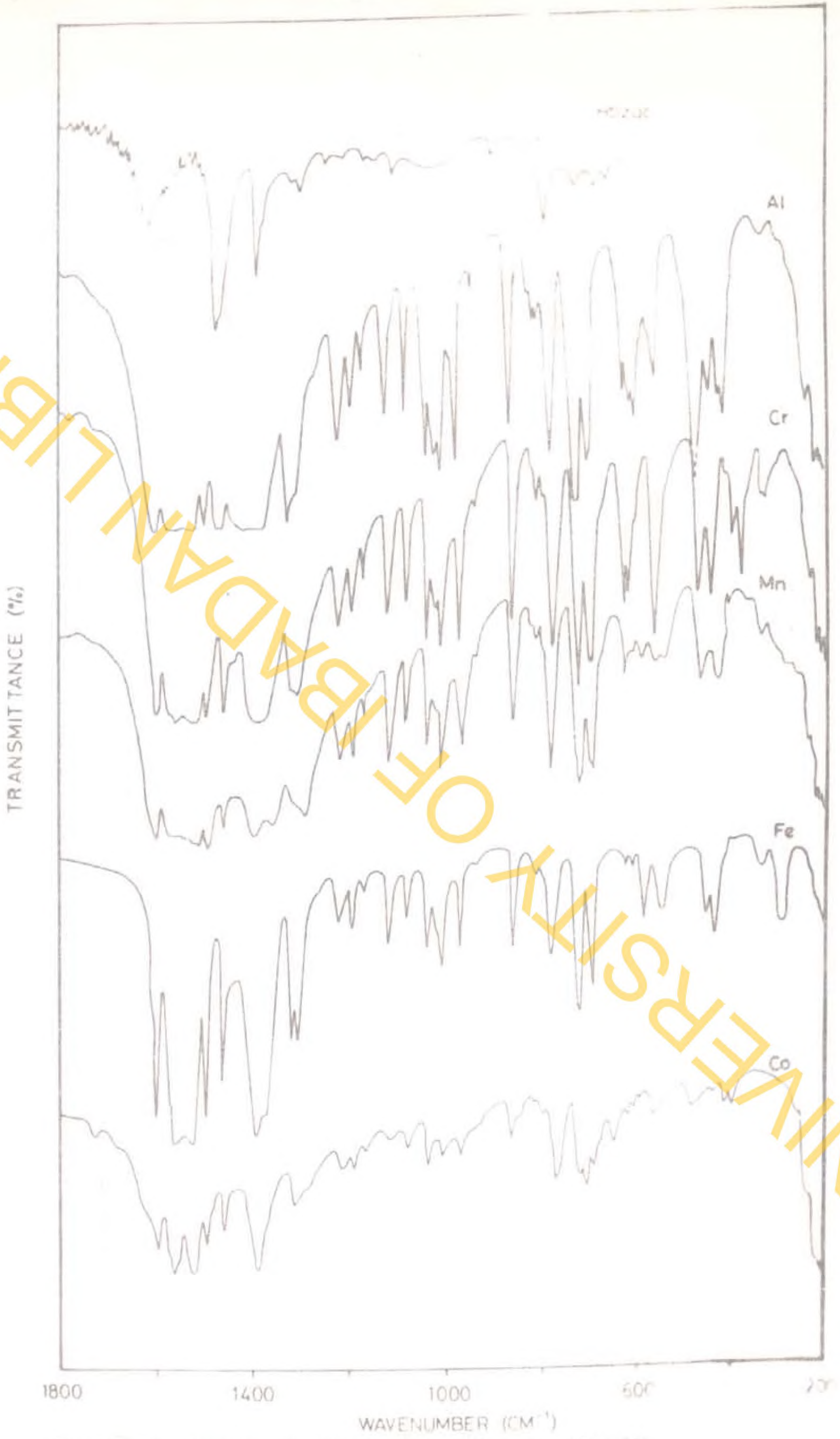


Fig 19 I.R Spectra of Hbz-ir [illegible]

TABLE 14. Assignment of the observed vibrational frequencies(cm^{-1}) of 1-phenyl-1,3-butanedione (Hbzac) and its trivalent metal complexes

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1590m	1600s	1595s	1595s	1595s	1592m	$\nu_{as}\ \mathrm{C\underline{---}O}$
1550s	1570m	1555m	1560m	1555s	1560s	$\nu_{as}\ \mathrm{C\underline{---}C\underline{---}C}$
1515w	1530m	1520m	1510m	1520s	1520s	Phenyl ring stretches
-	1495m	1492m	1490m	1492s	1492m	
1453s	1465m	1455m	1455m	1455s	1455m	
1348s	1400m	1380s	1390s	1385vs	1385vs	$\nu_{\mathrm{C=O}} + \delta\mathrm{CH}$
1266m	1320s	1300s	1290m	1312s 1300s - dbt	1310s	$\nu_s\ \mathrm{C\underline{---}O}$
1235m	1215s	1215m	1212m	1215m	1210m	$\nu_s\ \mathrm{C\underline{---}C\underline{---}C}$
1166w	1186m	1188m	1188m	1185m	1185m	$\nu_{\mathrm{C=C}} + \nu_{\mathrm{C-R}}$
1156w	1165w	1162w	1160w	1162w	1165w	δCH (chelate ring)
1110w	1120s	1115s	1110s	1112m	1115w	
1064w	1078s	1078s	1078m	1076m	1075m	δCH (phenyl ring)
1042m	1035s	1034s	1034m	1034m	1032s	
1000s	1008s	1005s	1005s	1005s	1005m	γCH (phenyl ring)
970s	975vs	965s	960s	965m	965m	

contd.

TABLE 14. Contd.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
930m	935w	935w	932w	932w	930w	
830m	860vs	858vs	855vs	855s	862s	
758s	775vs	772vs	775vs	775s	770vs	ν_{CH} (chelate ring)
722m	720vs	715vs	718vs	715vs	705s	
702m	700s	695s	690s	688vs	690m	
690m	625m	624s	620m	620m	648m	Metal - Ligand (combination bands)
-	600s	615s	586w	582m	-	
-	558m	560vs	560m	545m	565m	ν_{M} — O
-	475vs	466vs	465vs	450m	488s	ν_{M} — O (most sensitive)
-	445m	440vs	430vs	432vs	415m	ν_{M} — O
-	415s	398m	335w	335w	398m	ν_{M} — O
-	-	378s	-	-	-	ν_{Cr} — O/

ν_{as}, asymmetric stretch; ν_{s}, symmetric stretch;
R, either phenyl or CH_3; s, strong; vs, very strong;
m, medium; w, weak; sh, shoulder; δ, in-plane deformation
γ, out-of-plane deformation.

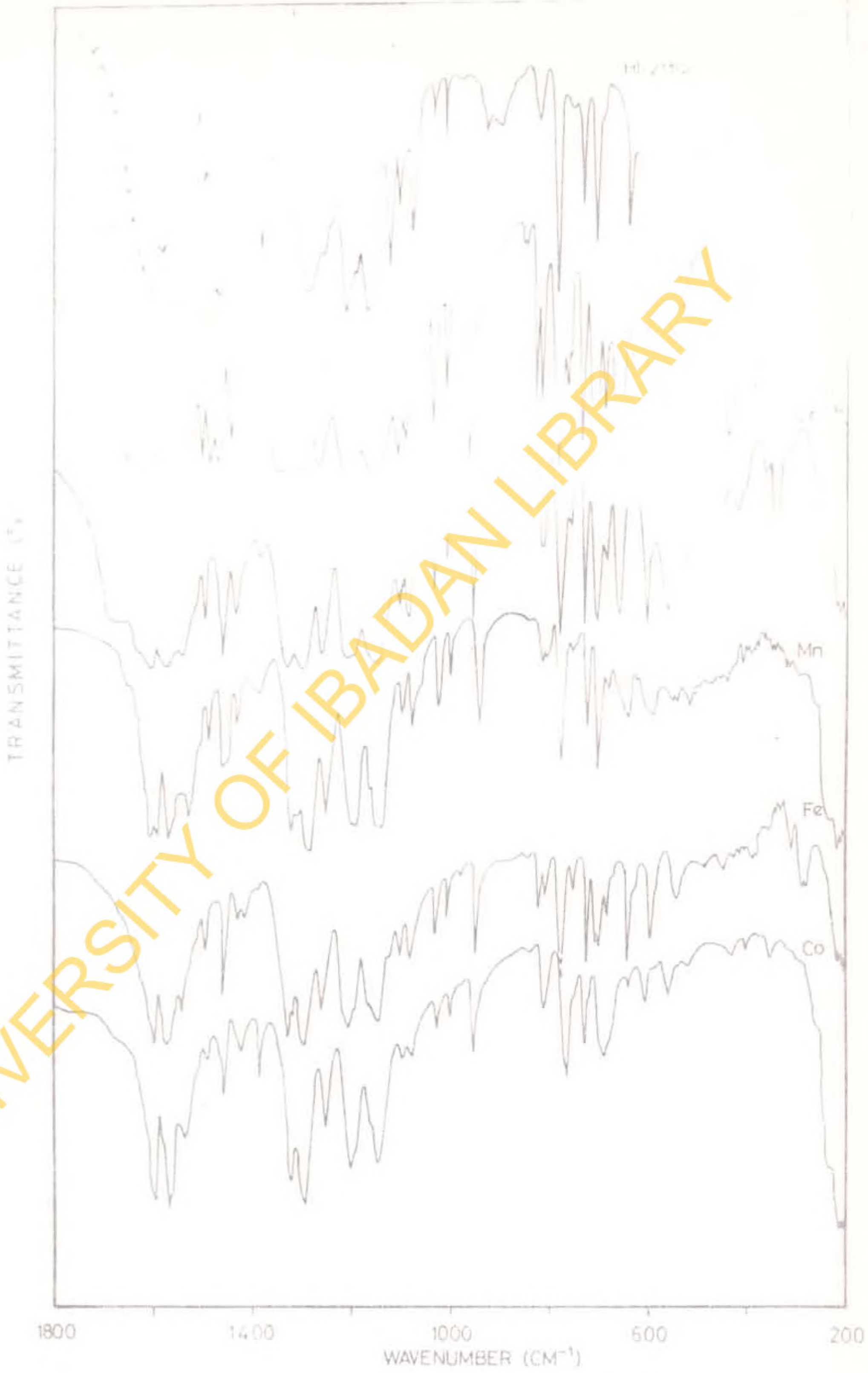


Fig 20 I.R. Spectra of Hbzttac and M(bzttac)$_3$ complexes

TABLE 15. Assignment of the observed vibrational frequencies(cm^{-1}) of 4,4,4-trifluoro-1-phenyl-1,3-butanedione(Hbztfac) and its trivalent metal complexes.

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1610s	1610s	1602s	1600s	1600s	1598s	$\nu_{as}\ \mathrm{C\overset{\cdots}{-}O}$
1580m	1580s	1574s	1570s	1575s	1570s	$\nu_{as}\ \mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}C}$
1515sh	1555m	1540m	1535s	1540m	1540m	Phenyl ring stretches
1498sh	1500m	1500m	1490s	1500m	1495w	
1470vs	1485s	1460s	1470s	1460s	1460m	
1465sh	1465s	1432m	1435s	1430m	1425m	
1380s	1442m	1386w	1385w	1420m	1390m	$\nu\mathrm{C{=}O} + \pi\mathrm{CH}$
1325sh	1340s	1330s	1323s	1330m	1325s	$\nu_{s}\ \mathrm{C\overset{\cdots}{-}O}$
1284s	1300s	1300s	1285s	1300s	1298vs	$\nu_{s}\ \mathrm{C\overset{\cdots}{-}C\overset{\cdots}{-}C}$
1210s	1260m	1260m	1250s	1260m	1255m	$\nu\mathrm{C{=}C} + \nu\mathrm{C{-}R}$
1165s	1200s	1205s	1200s	1205s	1200s	$\nu\mathrm{C{-}CF_3} + \pi\mathrm{CF_3}$
1120s	1150s	1150s	1190s	1150s	1150s	πCH (chelate ring)
1100m	1105m	1100w	1140s	1105w	1100w	βCH (phenyl ring)
1075s	1088w	1085m	1078m	1085m	1080w	
1030m	1030s	1032m	1028s	1032m	1030m	γCH
1002s	1005m	1008m	1003	1008m	1005w	

contd.

TABLE 15. Contd.

Ligand	Al	Cr.	Mn	Fe	Co	Approximate Assignment
920m	960vs	954vs	945s	950s	958m	δCF_3
890m	845w	848w	840w	824m	840w	
812m	820s 810s dbt	815s	815m	810w	815m	
779vs	775vs	775vs	775s	780s	768s	$\nu_{C—F}$
748w	758sh	755w	750m	755w	750sh	$\nu_{C—CF_3}$
722vs	730vs	730vs	723s	728s	730m	
700s	700vs	702s	700m	705s	690s	chelate ring deformations
682sh	680m	685sh	680sh	685m	-	
620vs	655m	660s	643m	642s	642w	
-	615s	602s	595m	600m	608m	$\nu_{M—O}$
-	560m	558m	550w	545m	570m	$\nu_{M—O}$ (most sensitive)
-	430vs	460w	450m	450w	405w	$\nu_{M—O}$
-	380vs	340s	390w	390m	355m	$\nu_{M—O}$

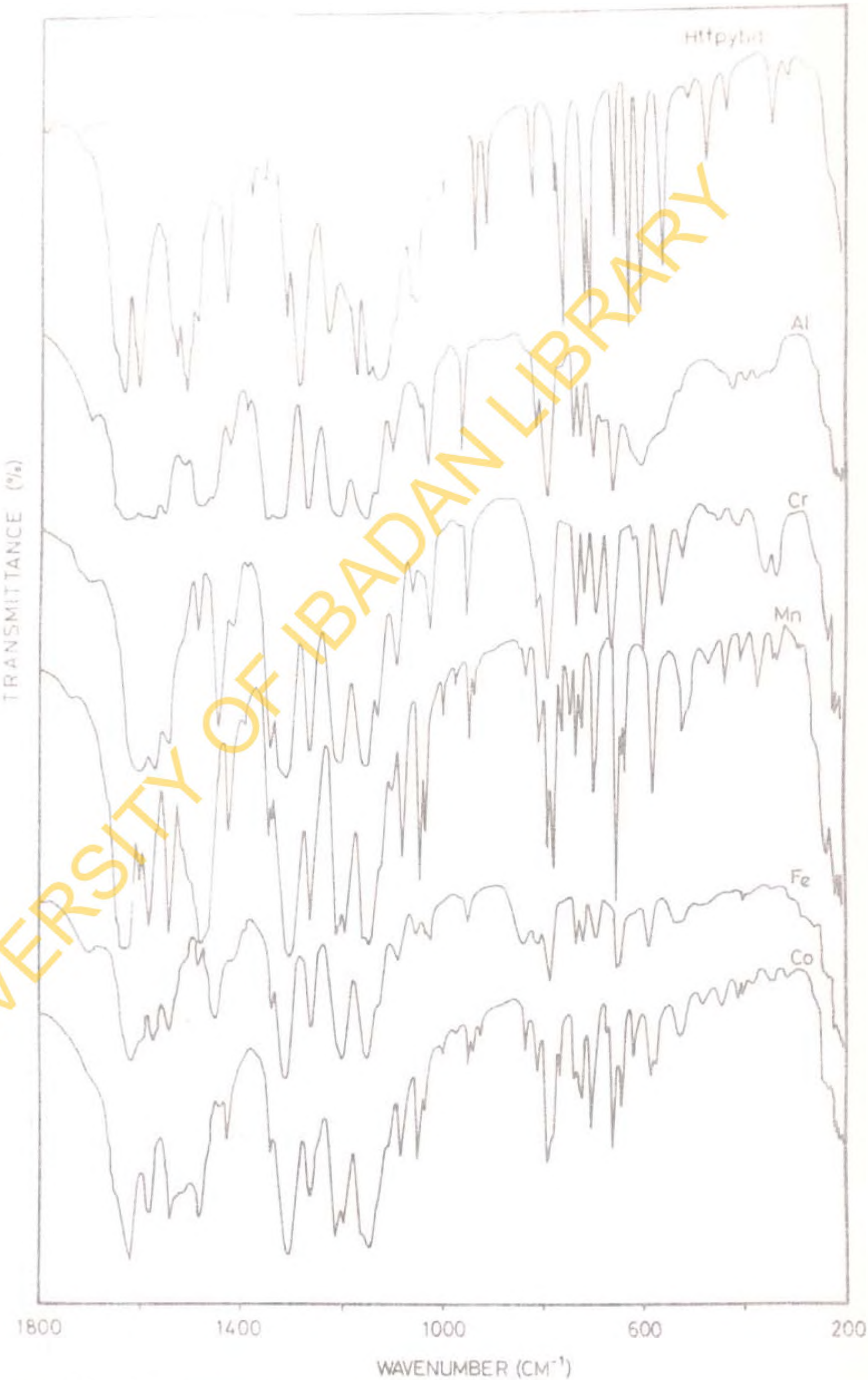


Fig. 21 I.R Spectra of Httpybd and M(ttpybd)$_3$ complexes

TABLE 16. Assignment of the observed vibrational frequencies(cm^{-1}) of 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione(Htf$_{p}$ybd) and its trivalent metal complexes

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
1645s	1620m	1600s	1630s	1615s	1618s	$\nu_{as}\ C\underline{---}O$
1615s	1580m	1570s	1580m	1575m	1580m	$\nu_{as}\ C\underline{---}C\underline{---}C$
1540m	1550m	1545m	1542s	1542m	1542m	Pyridyl ring stretches
1524s	1515w	1485m	1480s	1485w	1480m	
1444s	1475s	1446vs	1425m	1450s	1428m	
1390w	1390w	1390w	1390w	1390w	1390w	
1322m	1320s	1315vs	1305vs	1310s	1305vs	$\nu_{s}\ C\underline{---}O$
1300vs	1265s	1265s	1265m	1260m	1262m	$\nu_{s}\ C\underline{---}C\underline{---}C$
1230s	1205s	1210s	1205s	1200s	1210s	$\nu_{O-C} + \nu_{C-R}$
1185m	1150s	1155s	1148vs	1150s	1145s	βCH
1140s	1100m	1130w	1105w	1125sh	-	
1068m	1080m	1085m	1082s	1090w	1082m	γCH
1010w	962s	1028m	1048s	1025w	1050m	
948m	940w	955s	1038s	950m	1035sh	
925m	830sh	818sh	950m	840m	950m	$3CF_3$
835m	815m	-	810m	812m	835w	

contd.

TABLE 16. Contd

Ligand	Al	Cr	Mn	Fe	Co	Approximate Assignment
790w	790s	795vs	795s	788s	790vs	ν_{C-CF_3}
775vs	760m	740m	740m	736m	740sh	
730s	728m	724m	730m	724m	725m	ν_{C-R}
720vs	702m	700m	705s	700m	705s	
670m	664s	670s	658vs	656s	660s	chelate ring deformations + ν_{M-O}
645vs	608m	605vs	642m	620w	645m	
620vs	570sh	570m	585vs	594m	590m	chelate ring vibrations
575s	530w	530w	525m	535m	530m	
485m	425m	460w	480w	480w	450m	
-	398m	420m	442m	405w	415m	ν_{M-O}
-	375m	365m	380m	390w	405m	ν_{M-O}
-	350m	342m	340m	330w	350m	ν_{M-O} (most sensitive)

ν_{as}, asymmetric stretch; ν_s, symmetric stretch; s, strong; vs, very strong; m, medium; w, weak; sh, shoulder; R, pyridyl or CF_3; 9, in-plane deformation; ν, out-of-plane deformations.

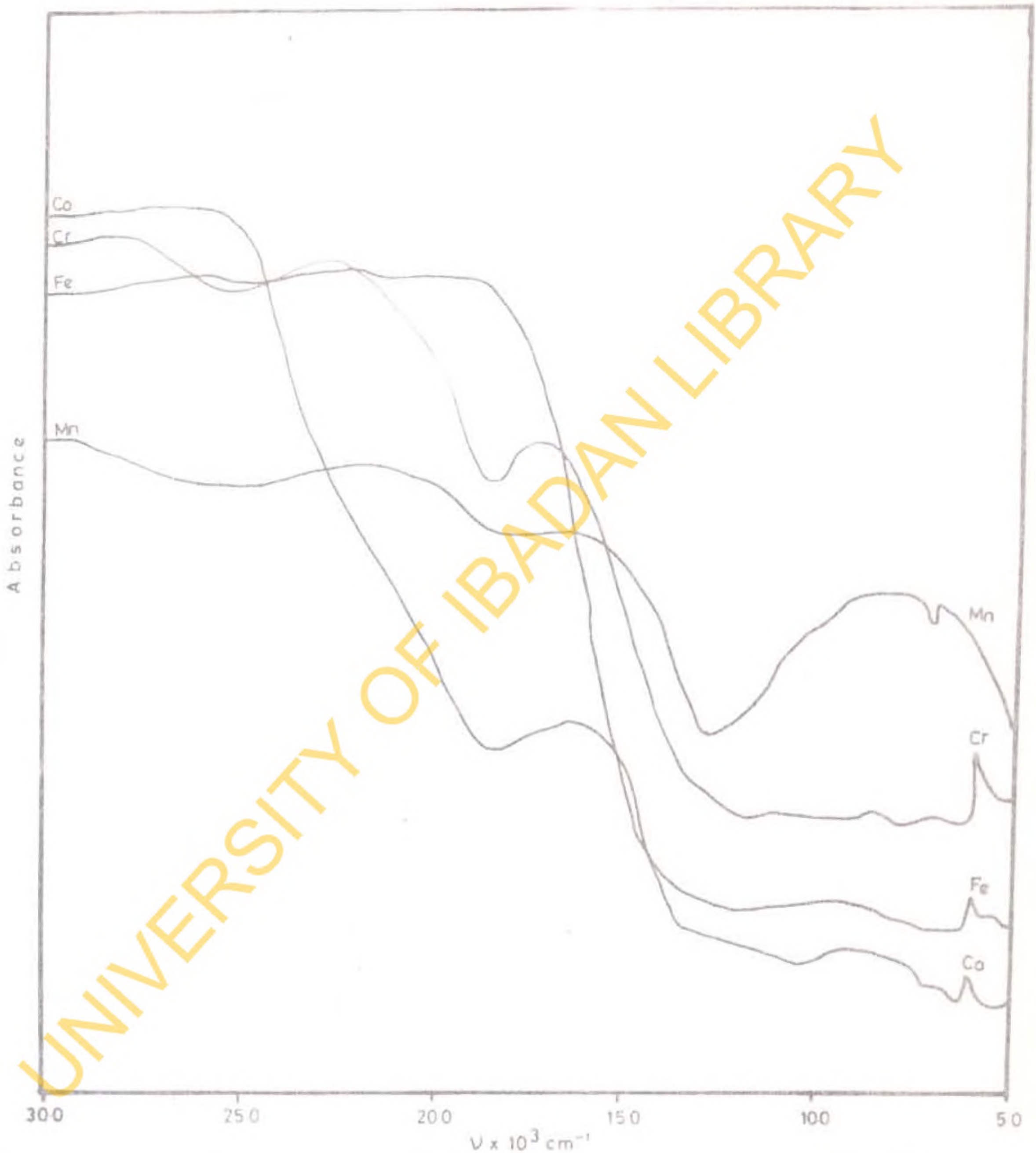


Fig 22 Reflectance spectra of $Cr(tbd)_3$, $Mn(tbd)_3$, $Fe(tbd)_3$ and $Co(tbd)_3$ in the visible region

Fig 23 Reflectance spectra of $Cr(tftbd)_3$, $Mn(tftbd)_3$, $Fe(tftbd)_3$ and $Co(tftbd)_3$ in the visible region

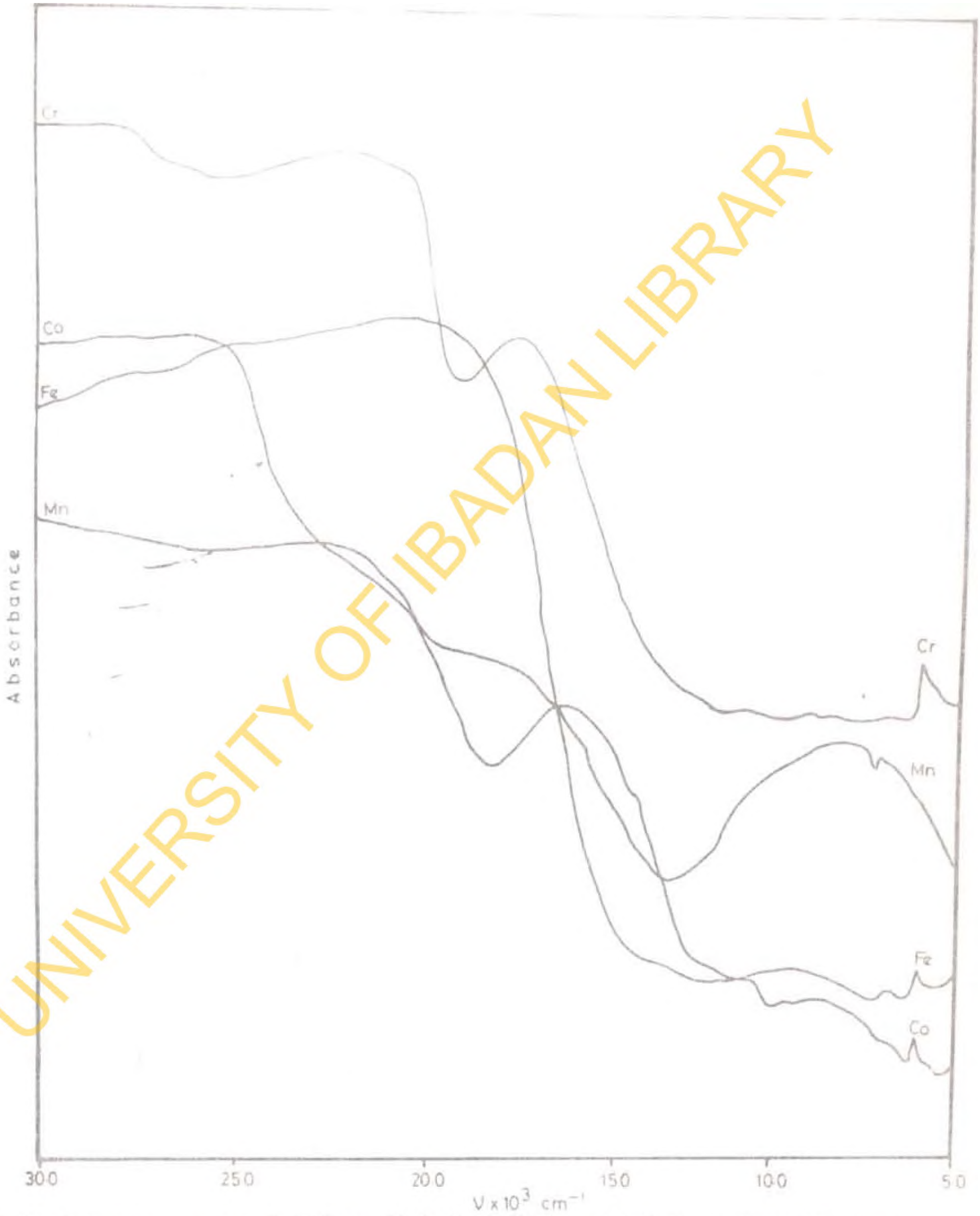


Fig 24 Reflectance spectra of $Cr(tbd)_3$, $Mn(tbd)_3$, $Fe(tbd)_3$ and $Co(tbd)_3$ in the visible region

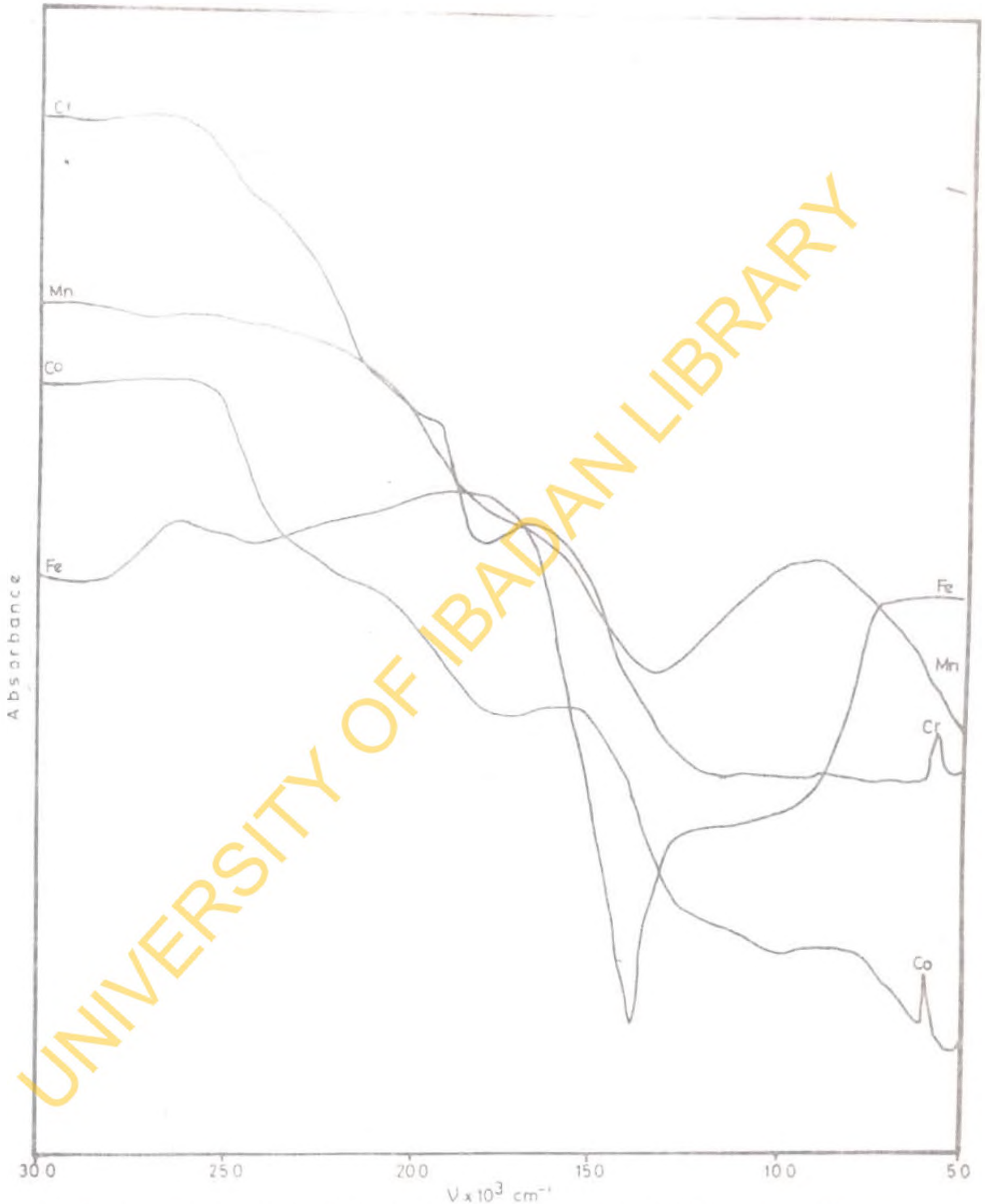


Fig 25 Reflectance spectra of Cr(tftbd)$_3$, Mn(tftbd)$_3$, Fe(tftbd)$_3$ and Co(tftbd)$_3$ in the visible region

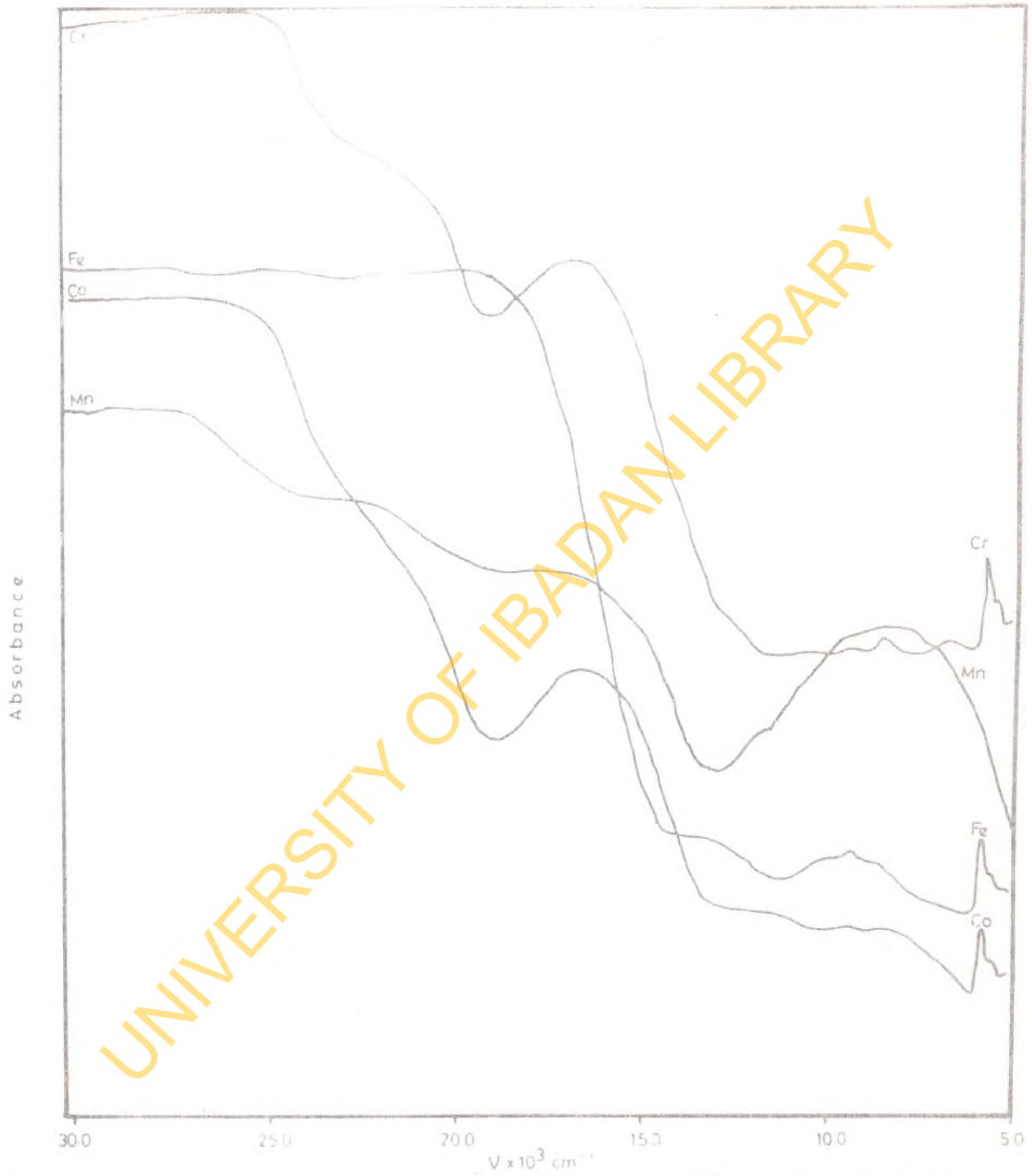


Fig 26 Reflectance spectra of $Cr(bzac)_3$, $Mn(bzac)_3$, $Fe(bzac)_3$ and $Co(bzac)_3$ in the visible region

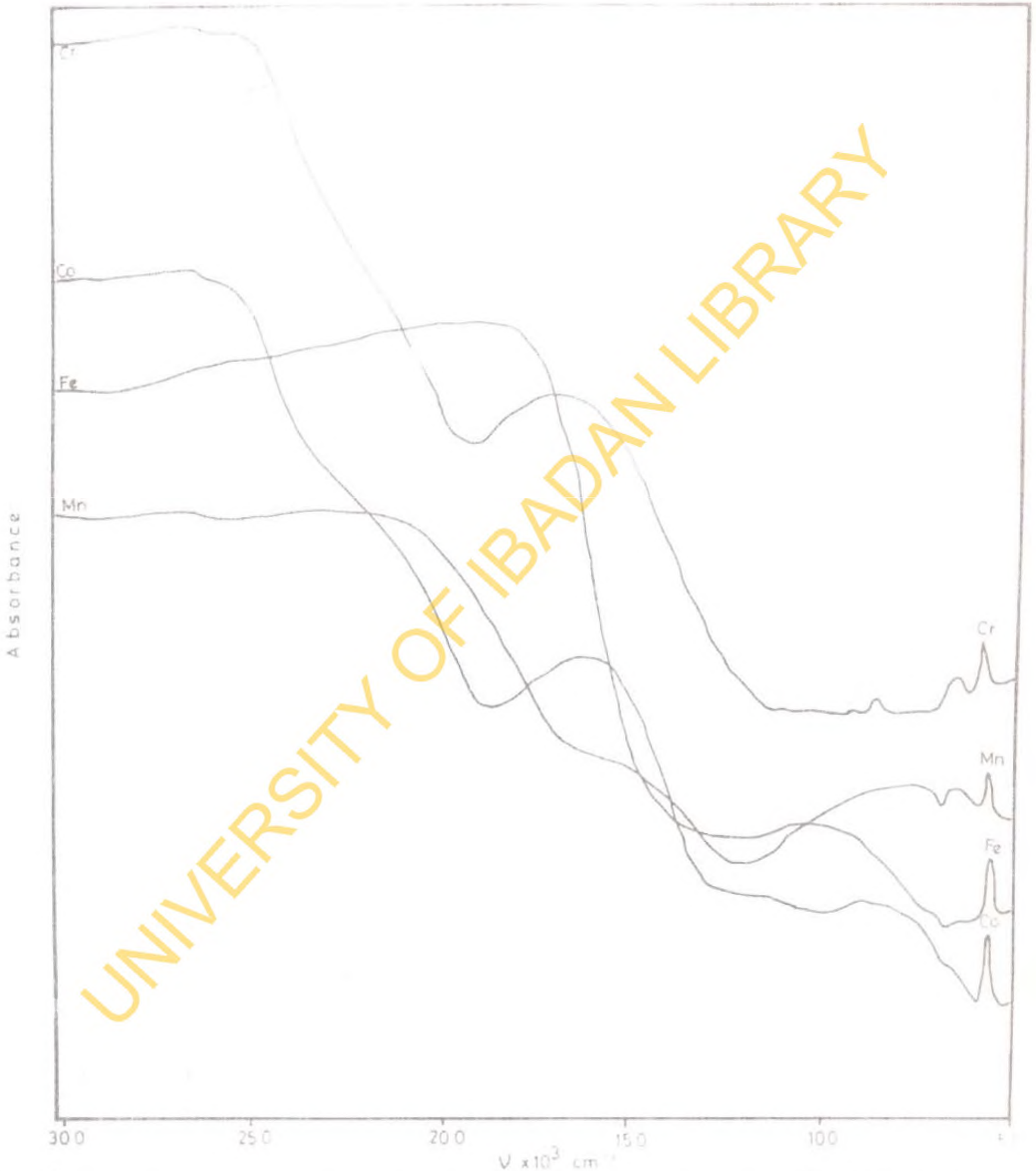


Fig 27 Reflectance spectra of Cr(bzttac)$_3$, Mn(bzttac)$_3$, Fe(bzttac)$_3$, Co(tttbd)$_3$ in the visible region

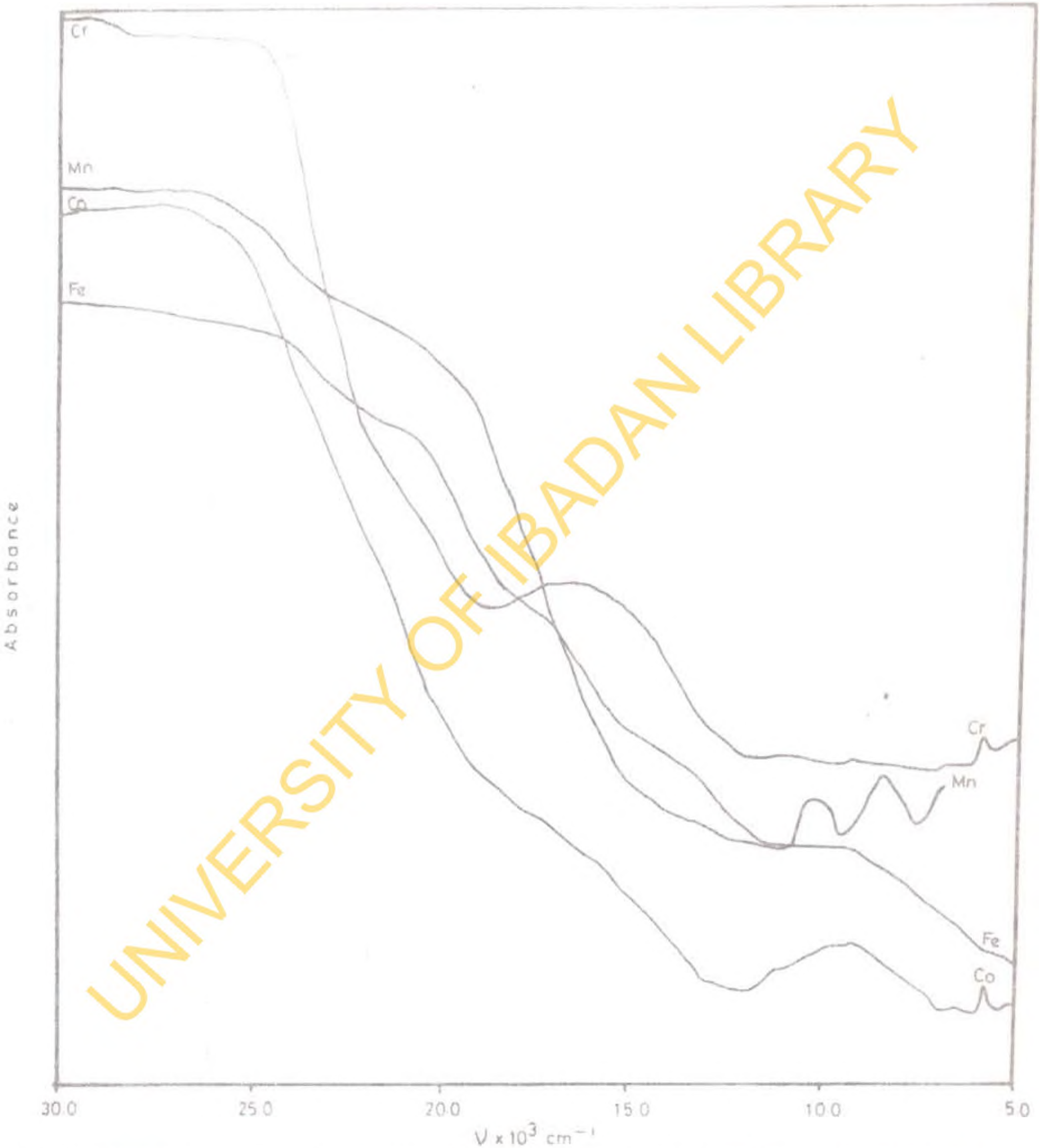


Fig 28 Reflectance spectra of $Cr(tfpybd)_3$, $Mn(tfpybd)_3$, $Fe(tfpybd)_3$ and $Co(tfpybd)_3$ in the visible region

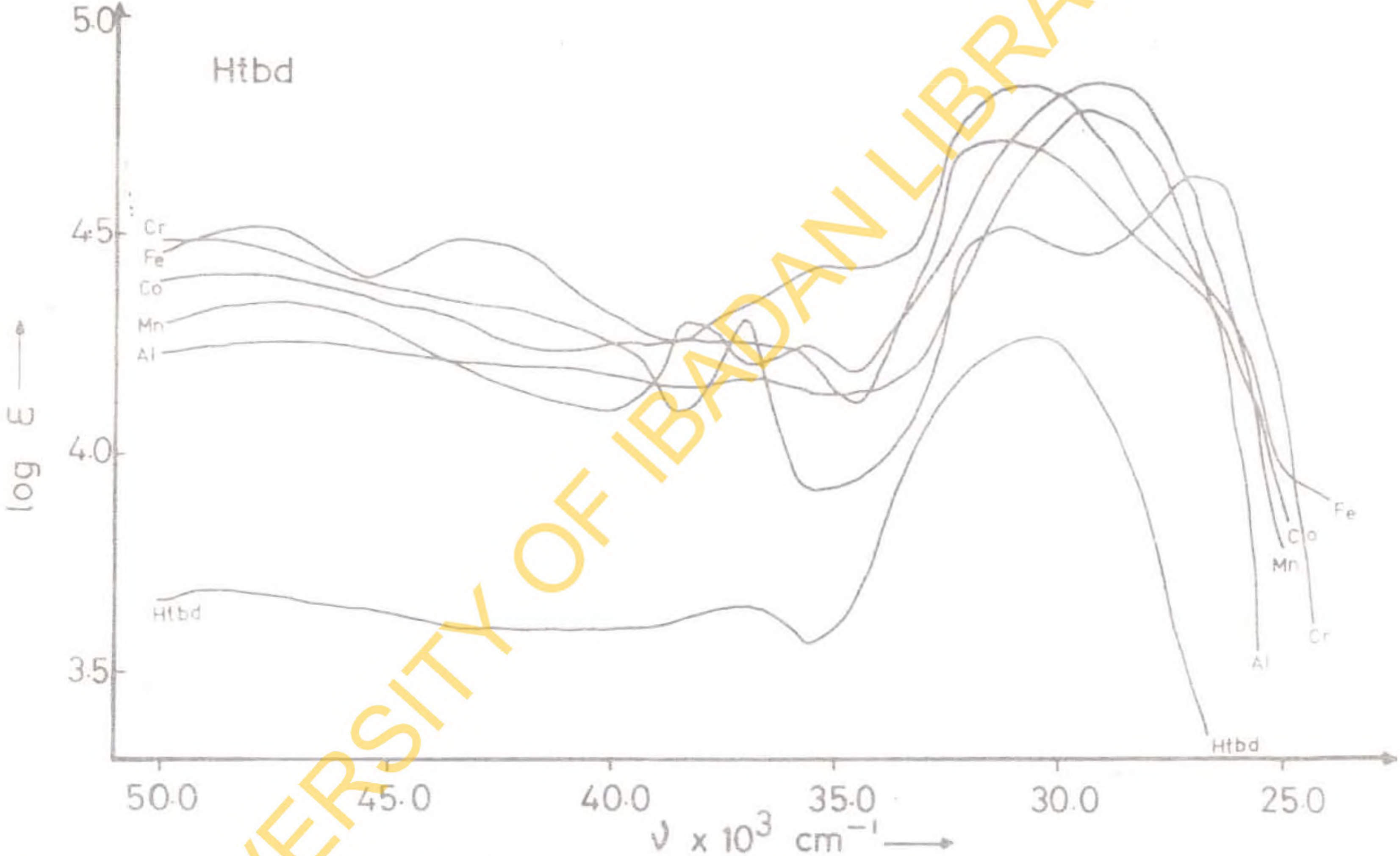


Fig 29 U.V. spectra of Htbd and the corresponding trivalent metal complexes in chloroform solution.

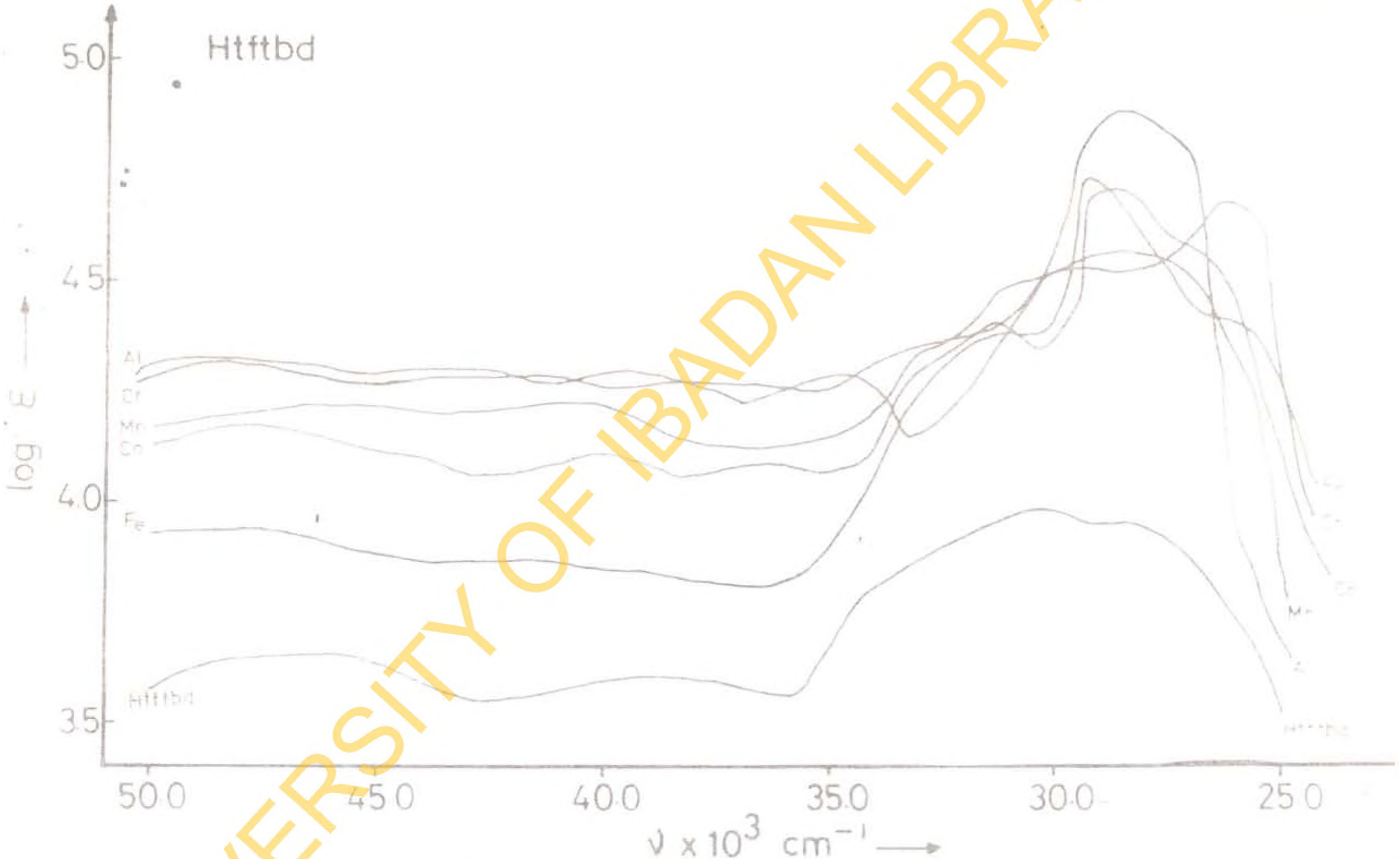


Fig.30 U.V. spectra of Htftbd and Al(tftbd)$_3$, Cr(tftbd)$_3$, Mn(tftbd)$_3$ and Co(tftbd) complexes in chloroform solution.

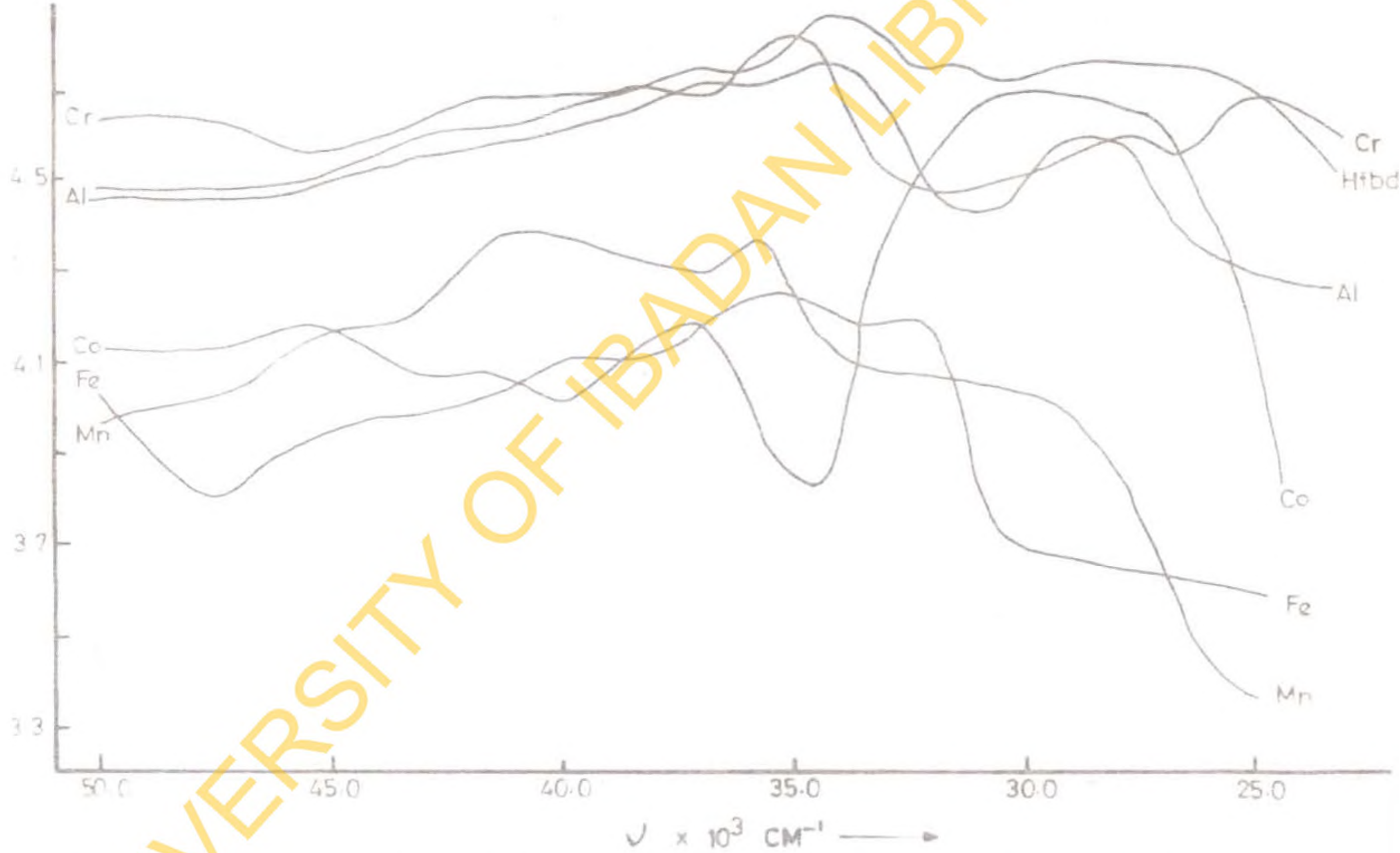


Fig. 31 U.V. Spectra of Hfbd and its trivalent metal complexes in chloroform solution.

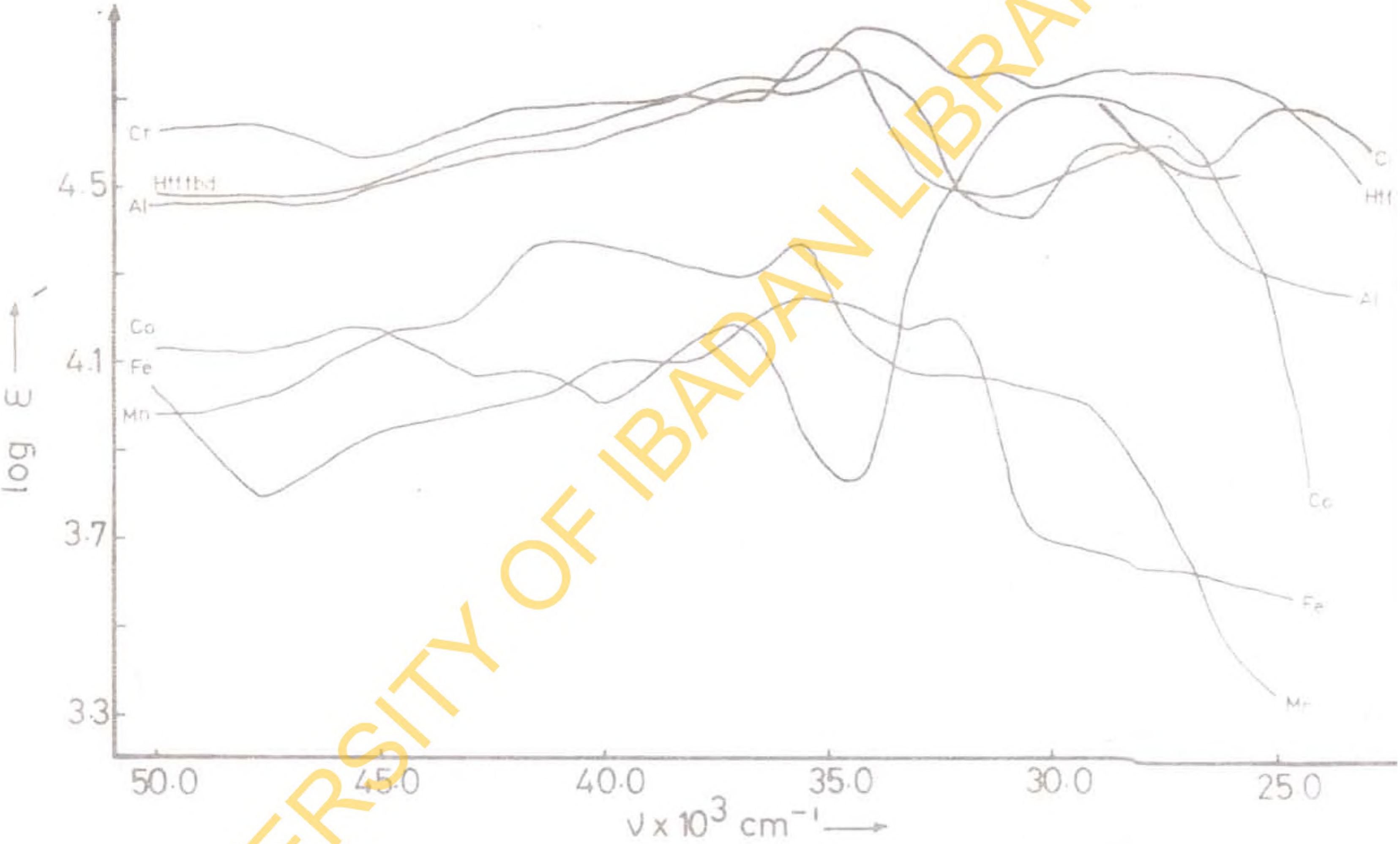


Fig. 32 U.V. spectra of Htffbd and its trivalent metal complexes in chloroform solution.

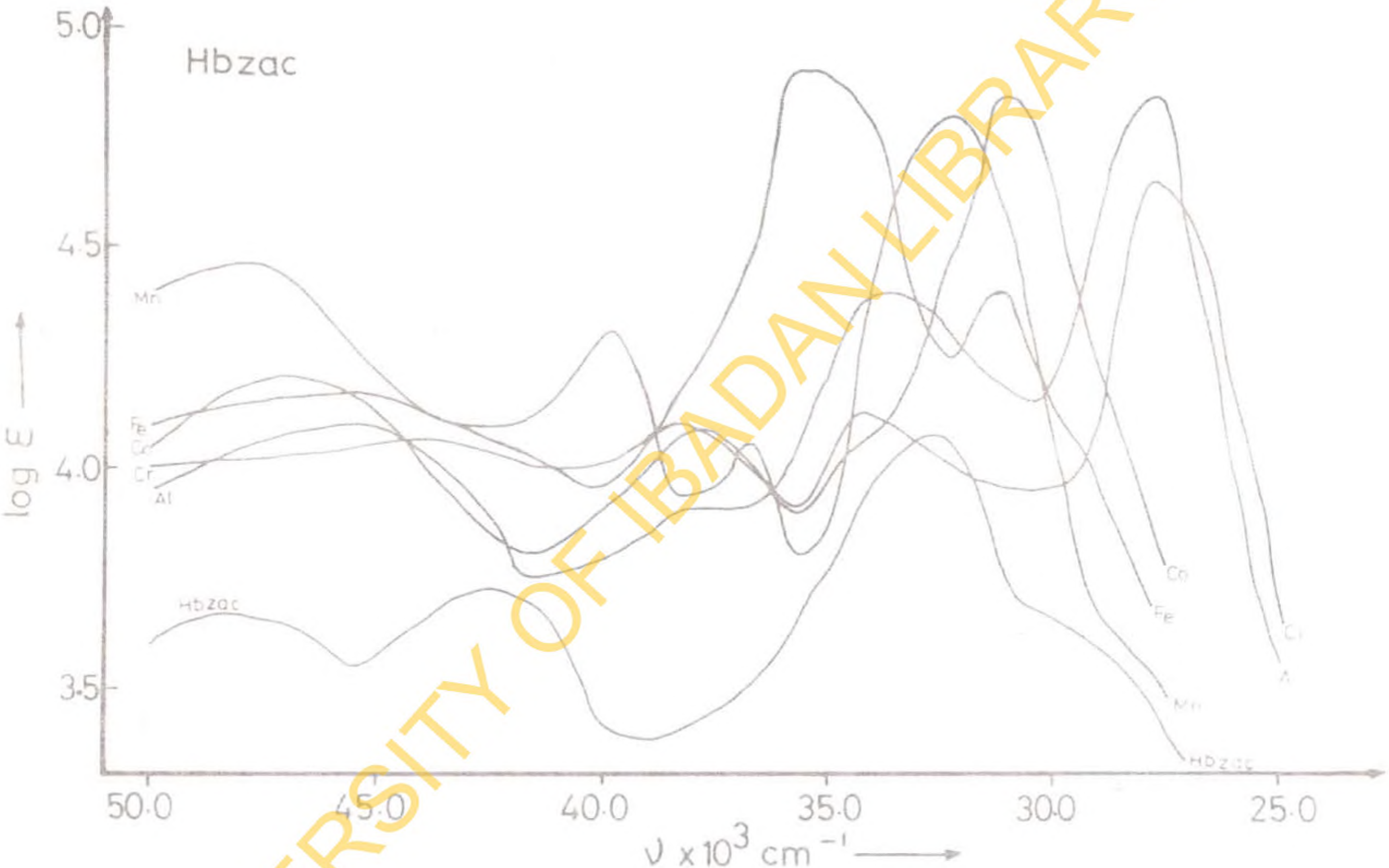


Fig. 33 U.V. spectra of Hbzac and the corresponding trivalent metal complexes in chloroform solution.

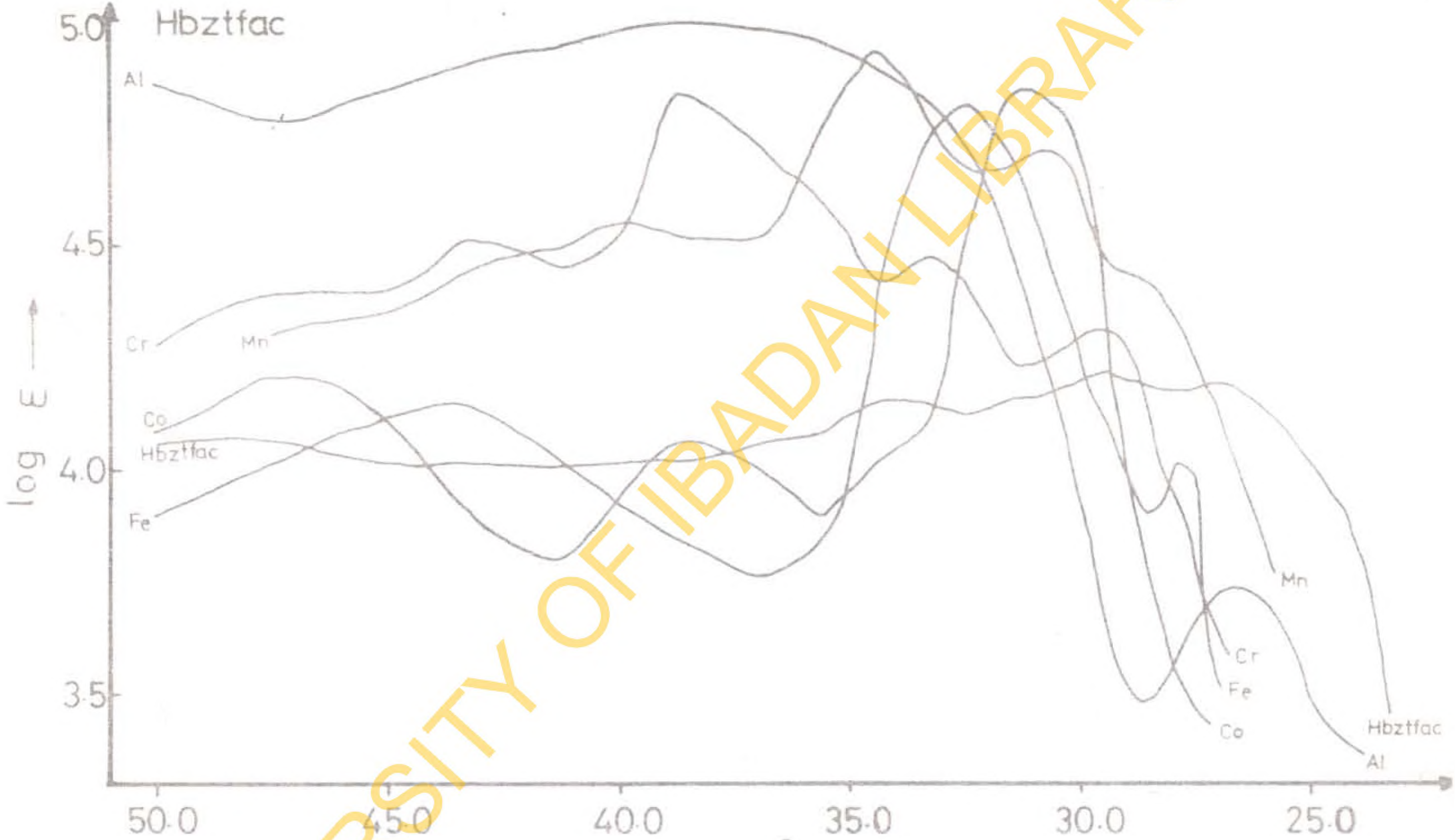


Fig.3- U.V. spectra of Hbztfac and its trivalent complexes in chloroform solution

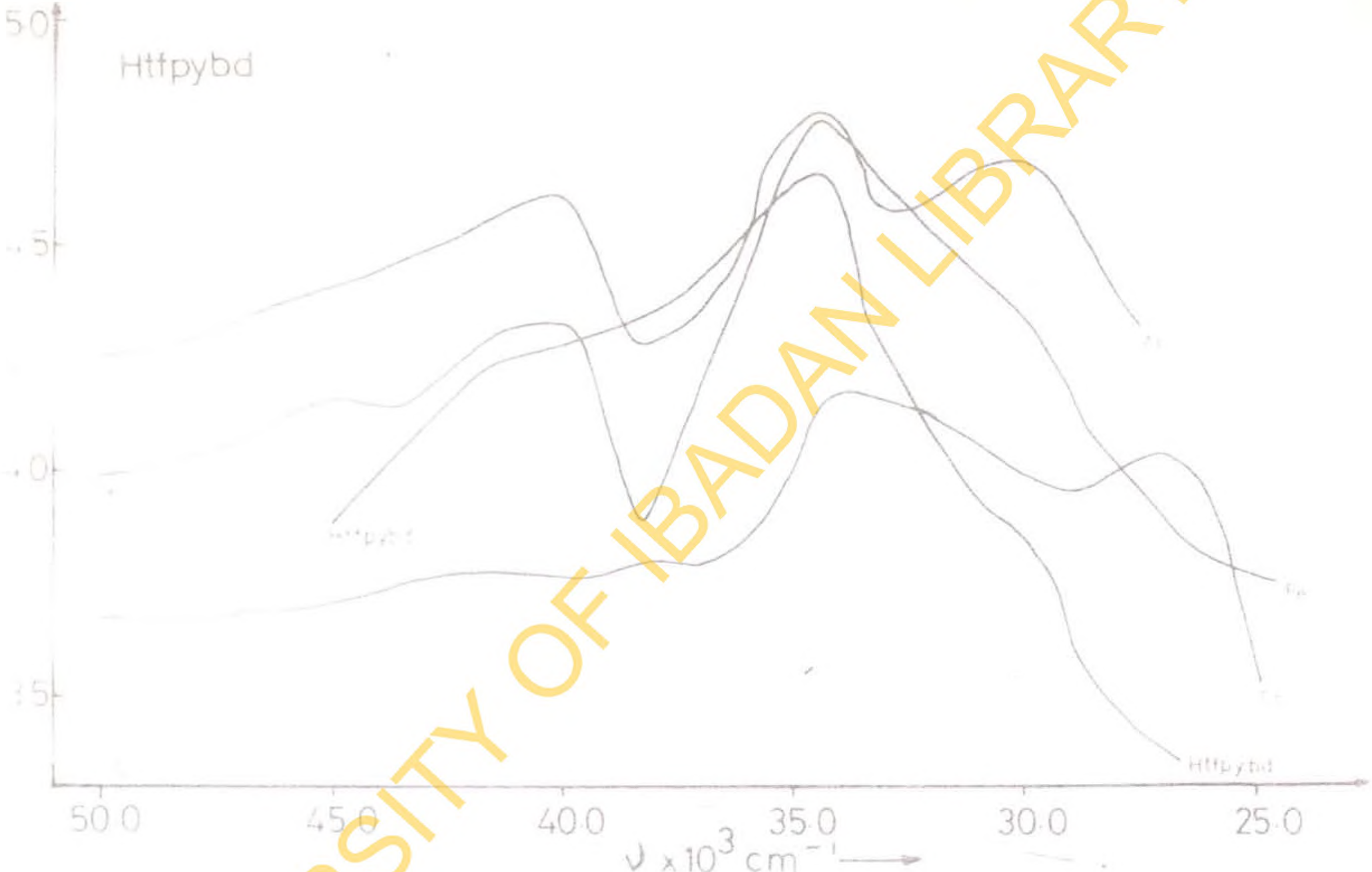


Fig. [illegible] UV spectra of Httpybd and its trivalent metal complexes in chloroform solution.

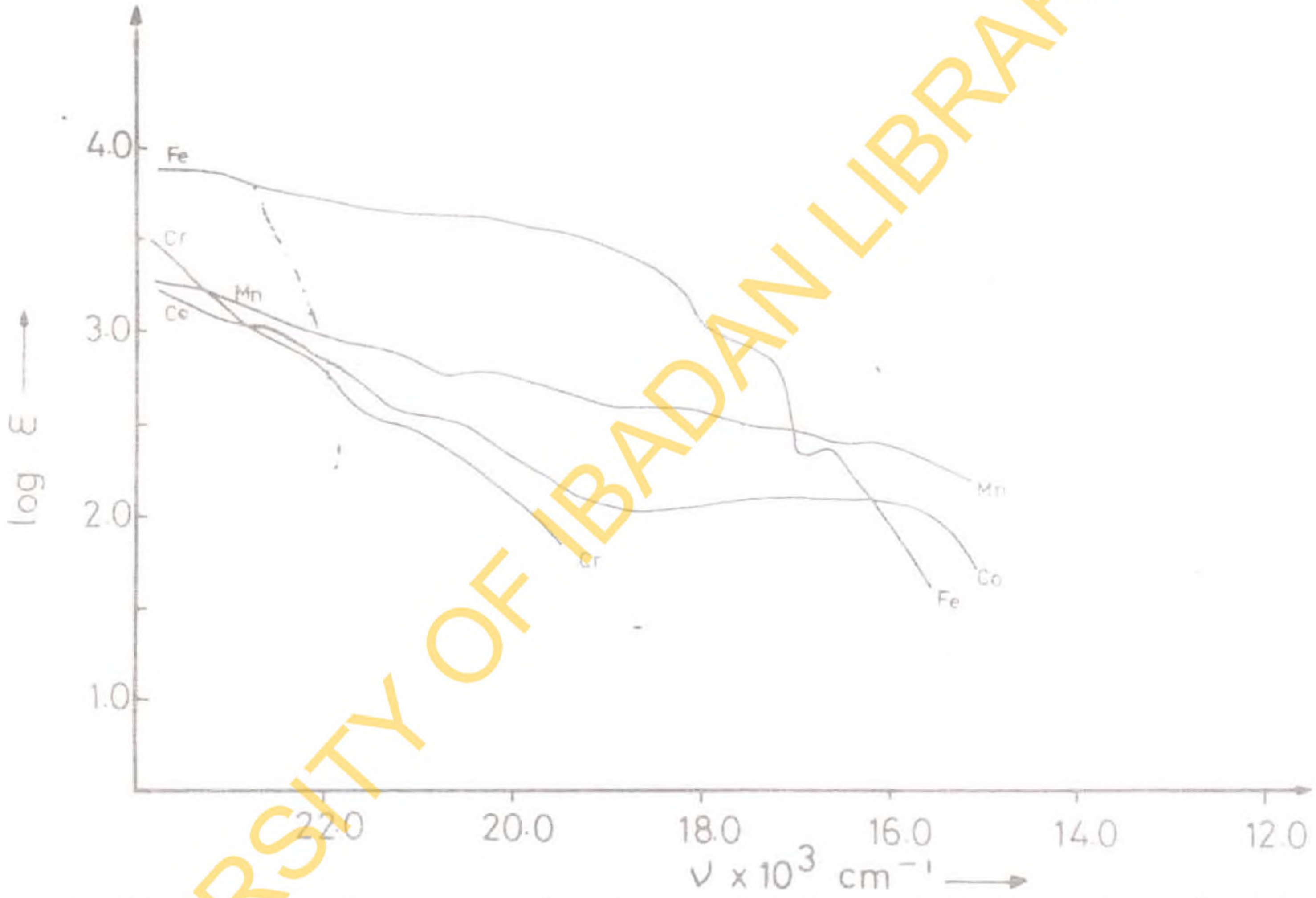


Fig 36 Visible spectra of $Cr(tbd)_3$, $Mn(tbd)_3$, $Fe(tbd)_3$ and $Co(tbd)_3$ in chloroform solution

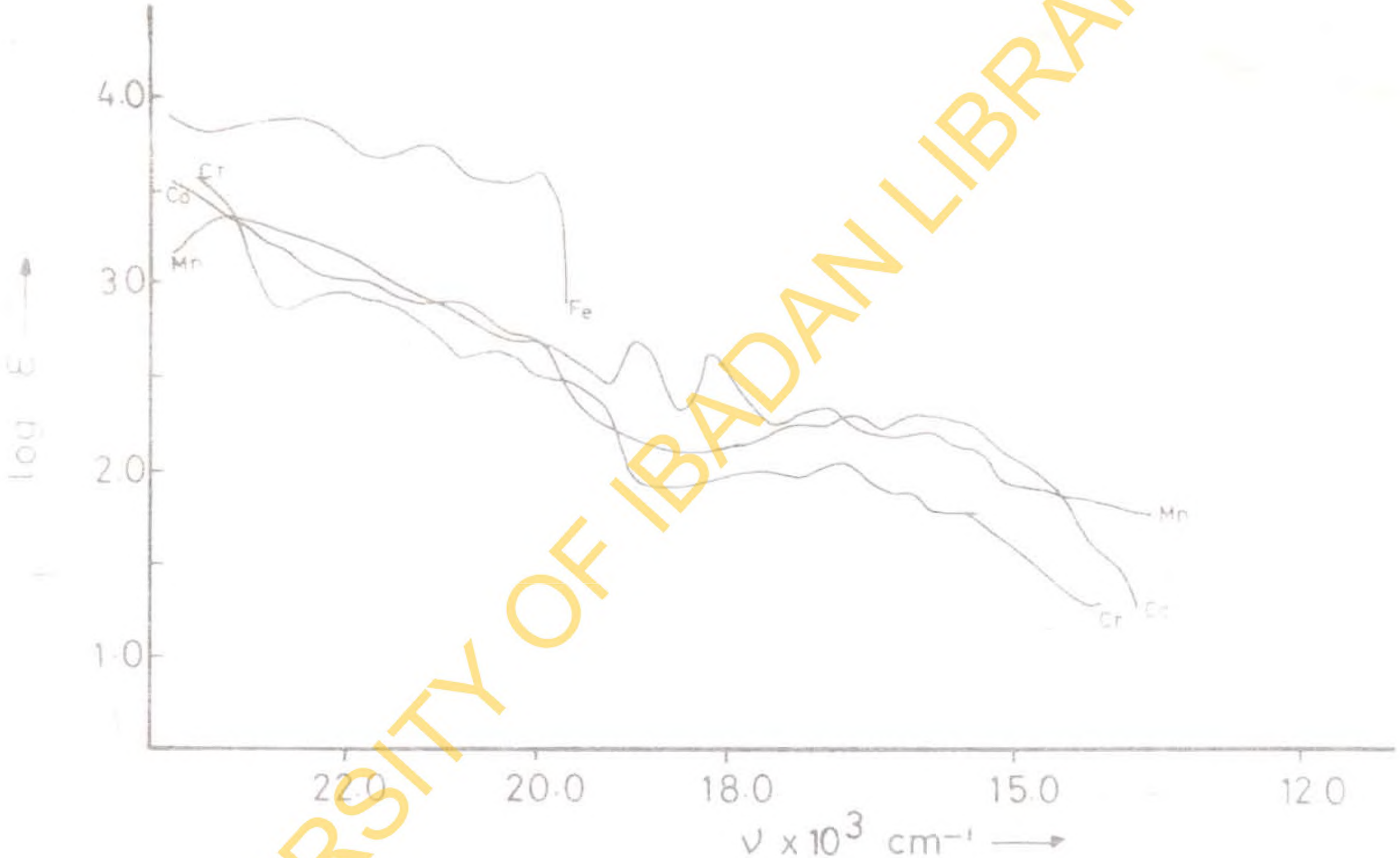


Fig. 37 Visible spectra of Cr(tftbd)$_3$, Mn(tftbd)$_3$, Fe(tftbd)$_3$ and Co(tftbd)$_3$ in chloroform solution.

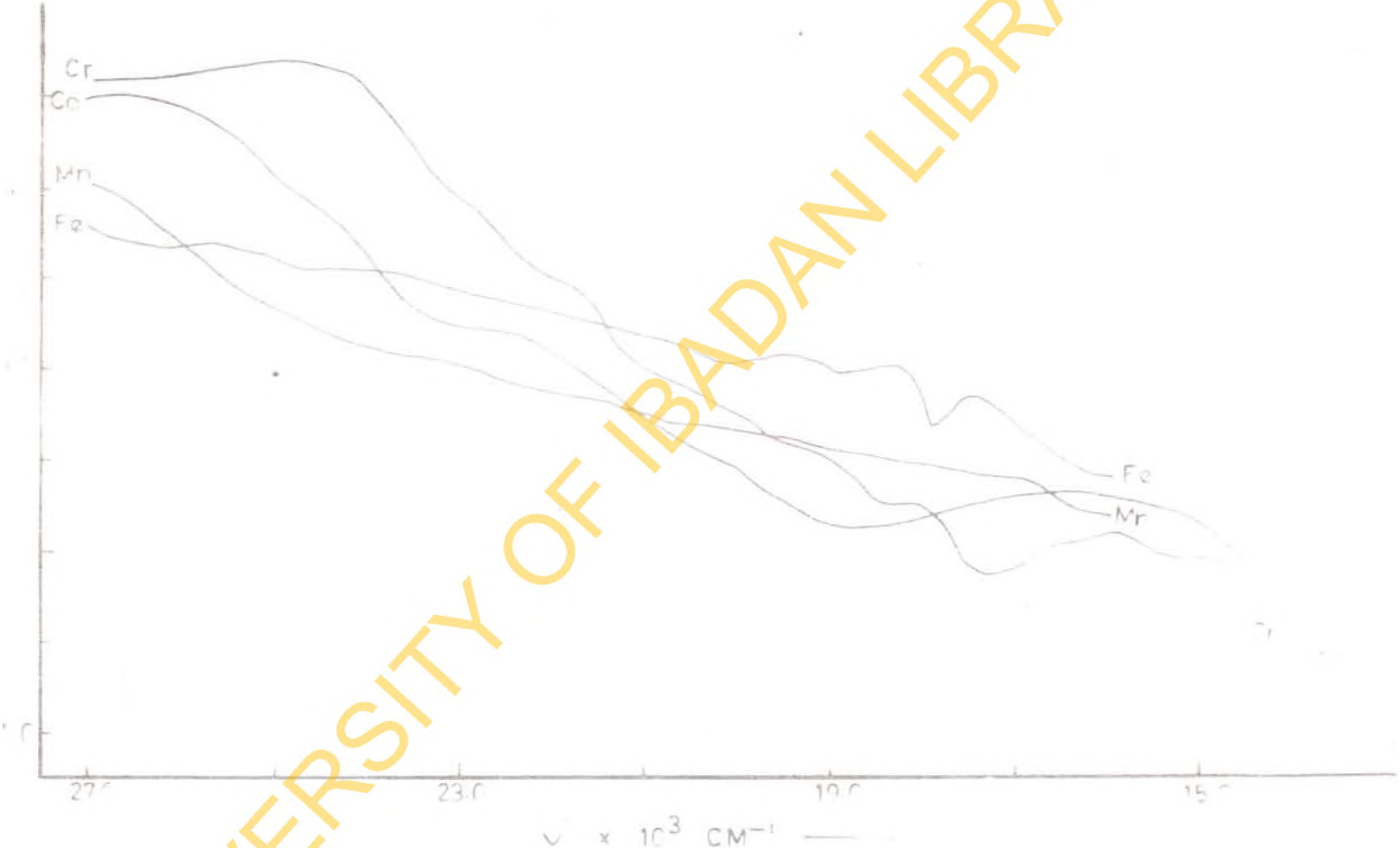


Fig. 38. Visible spectra of $Cr(fbd)_3$, $Mn(fbd)_3$, $Fe(fbd)_3$ and $Co(fbd)_3$ in chloroform solution.

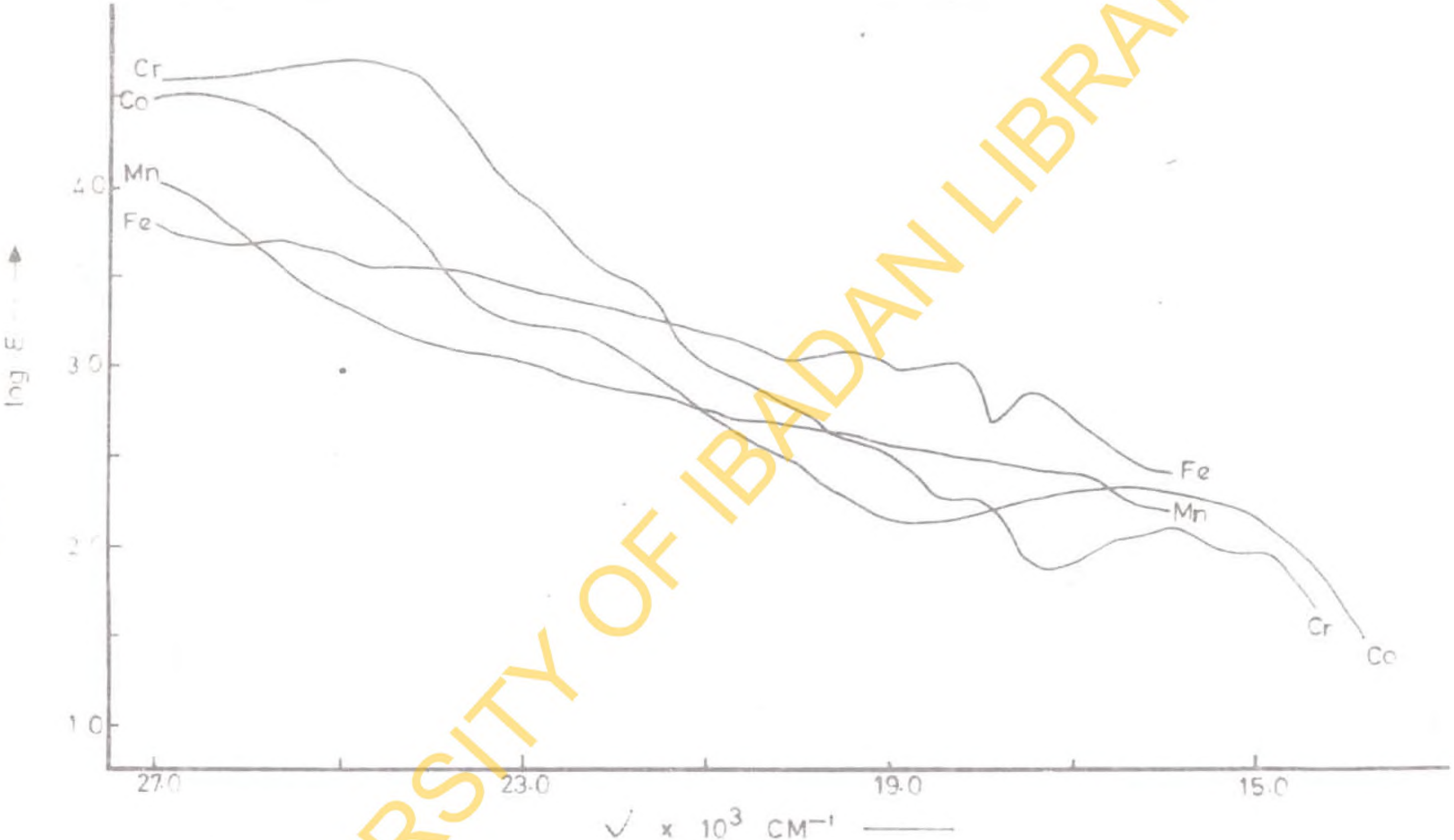


Fig. 38. Visible spectra of $Cr(fbd)_3$, $Mn(fbd)_3$, $Fe(fbd)_3$ and $Co(fbd)_3$ in chloroform solution.

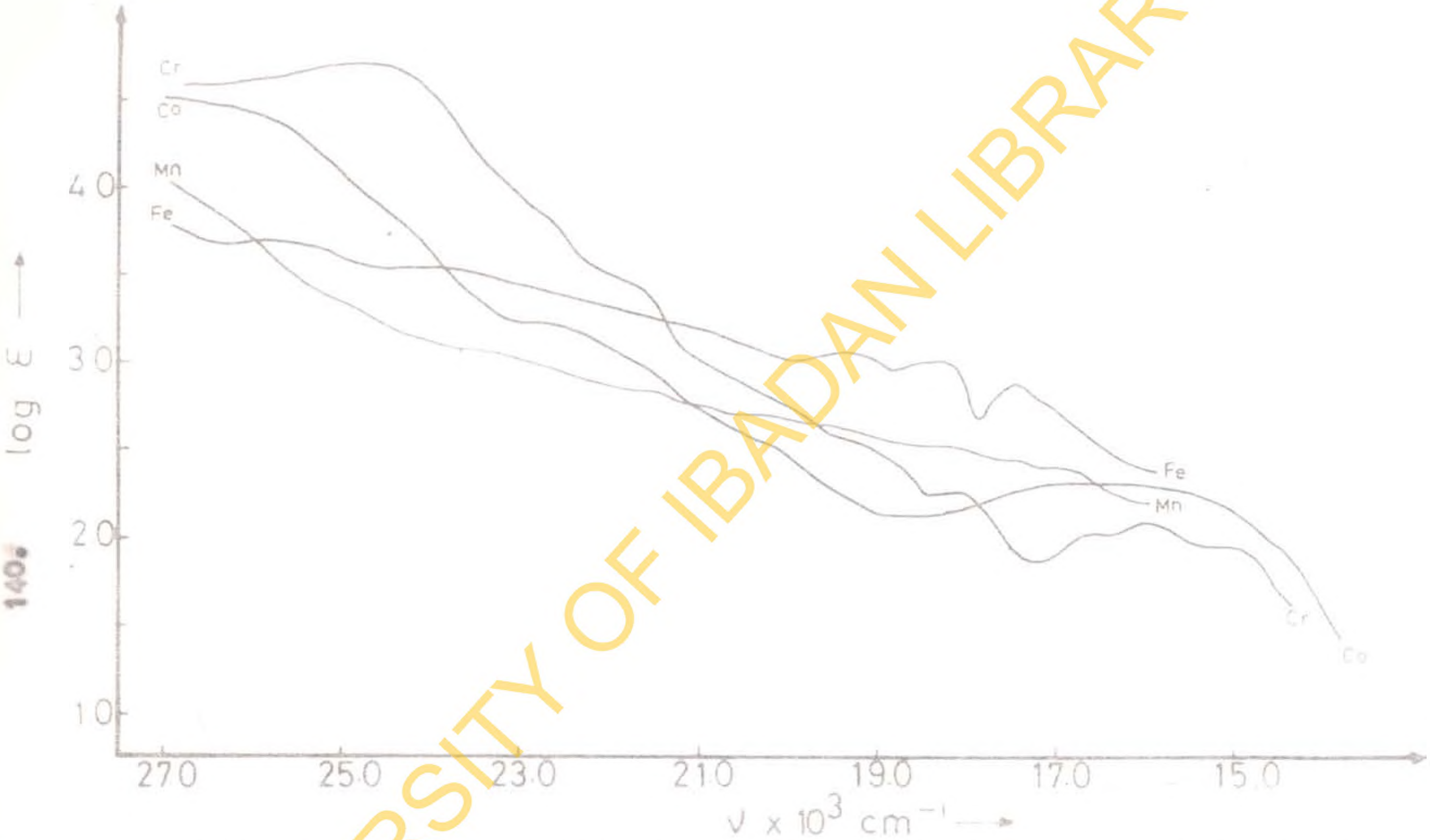


Fig. 32 Visible spectra of $Cr(tftbd)_3$, $Mn(tftbd)_3$, $Fe(tftbd)_3$ and $Co(tftbd)_3$ in chloroform solution

Fig 40 Visible spectra of $Cr(bzac)_3$, $Mn(bzac)_3$, $Fe(bzac)_3$ and $Co(bzac)_3$ in chloroform.

Fig 4.2 Visible spectra of $Cr(tfpybd)_3$ and $Fe(tfpybd)_3$

TABLE 17. Diffuse reflectance spectra of trivalent metal complexes of 1-(2-thienyl)-1,3-butanedione (Htbd) and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione(Htftbd) in the region 50000-5000 cm^{-1} and their proposed assignments.

M(III)	$M(tbd)_3$ $\nu_{cm^{-1}}$	$M(tftbd)_3$ $\nu_{cm^{-1}}$	Assignments
Al(III)	45600 br	45600 br	$\pi_3 - \pi_5^*$
	37600 br	37500 br	$\pi - \pi^*$ (Intraligand; S.A.)
	32500 br	31800 br	$\pi_3 - \pi_4^*$
	27000 brsh	27300 brsh	$\pi - \pi^*$ (Thienyl)
	25400 sh	25600 sh	$\pi - \pi^*$ (spin forbidden)
Cr(III)	45200 vbr	45200 vbr	$\pi_3 - \pi_5^*$
	37800 br	37000 br	$\pi - \pi^*$ (Intraligand; S.A.)
	33400 br	33300 br	$\pi_3 - \pi_4^*$
	30200 br	30000 br	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	27600	27500	$\pi - \pi^*$ (Thienyl)
	-	26200 sh	
	23400	23400	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	21000 sh	21200 sh	$\pi - \pi^*$ (spin forbidden)
	-	20300	

contd.

TABLE 17. Contd.

M(III)	M(tbd)$_3$ $\nu_{cm^{-1}}$	M(tftbd)$_3$ $\nu_{cm^{-1}}$	Assignments
	17500	17500	$^4A_{2g} \rightarrow {}^4T_{2g}$(F)
Mn(III)	45200 br	45200 br	$\pi_3 - \pi_5^*$
	38200 vbr	37800 vbr	$\pi - \pi^*$ (Intraligand; S.A.)
	34300 br	32000 br	$\pi_3 - \pi_4^*$
	29300 sh	29300 sh	$\pi - \pi^*$ (Thienyl)
	24200	23400	$\pi - \pi^*$ (spin forbidden)
	21300 br	21500 br	$^5A_{1g} \rightarrow {}^5B_{2g}$
	16800	16800	$^5A_{1g} \rightarrow {}^5E_g$
	9800	9000	$^5A_{1g} \rightarrow {}^5B_{1g}$
Fe(III)	45200 br	45300 br	$\pi_3 - \pi_5^*$
	37600 vbr	37400 vbr	$\pi - \pi^*$ (Intraligand; S.A.)
	33800 br	34800 br	$\pi_3 - \pi_4^*$
	27000	26000	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$; π-π^* (Thienyl)
	23400 sh	22800 sh	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	20000	18800	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$

contd.

TABLE 17. Contd.

M(III)	$M(tbd)_3$ $\nu_{cm^{-1}}$	$M(tftbd)_3$ $\nu_{cm^{-1}}$	Assignments
	12300 sh	12800 sh	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
	9600	9500	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
Co(III)	45600 br	45500 br	$\pi_3 - \pi_5^*$
	37600 vbr	37000 vbr	$\pi - \pi^*$ (Intraligand; S.A.)
	32400 br	32200 br	$\pi_3 - \pi_4^*$
	26000 br	26600 br	$\pi - \pi^*$ (Thienyl)
	22000 sh	21400 sh	d → d
	16400	16500	$^1A_{1g} \rightarrow {}^1T_{1g}$
	11400 sh	11400 sh	$^1A_{1g}(S) \rightarrow {}^3T_{2g}(F)$
	9200	8600	$^1A_{1g}(S) \rightarrow {}^3T_{1g}(F)$

Abbreviations: br, broad; sh, shoulder; v, very;
S.A., spin-allowed.

TABLE 18. Diffuse reflectance spectra of trivalent metal complexes of 1-(2-furyl)-1,3-butanedione(Hfbd) and 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione(Htffbd) in the region 50000 - 5000 cm^{-1} and their proposed assignments.

M(III)	M(fbd)$_3$ $\bar{\nu}$ cm^{-1}	M(tffbd)$_3$ $\bar{\nu}$ cm^{-1}	Assignments
Al(III)	45400 br	45400 br	$\pi_3 - \pi_5^*$
	37600 br	37200 br	$\pi - \pi^*$ (Intraligand; S.A.)
	33300 br	32400 br	$\pi_3 - \pi_4^*$
	28000 brsh	-	$\pi - \pi^*$ (Furyl)
Cr(III)	45300 vbr	45300 vbr	$\pi_3 - \pi_5^*$
	37600 br	37200 br	$\pi - \pi^*$ (Intraligand; S.A.)
	34400 br	33300 br	$\pi_3 - \pi_4^*$
	30600 br	30400 br	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	28400 sh	27700 sh	$\pi - \pi^*$ (Furyl)
	23600	23400	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	21800 sh	21300 sh	$\pi - \pi^*$ (spin forbidden)
	20400	20000	
	17600	17400	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$

contd.

TABLE 18. Contd.

M(III)	M(fbd)$_3$ $\bar{\nu}_{cm^{-1}}$	M(tffbd)$_3$ $\bar{\nu}_{cm^{-1}}$	Assignments
Mn(III)	45000 br	45000 br	$\pi_3 - \pi_5^*$
	37400 br	37300 br	$\pi - \pi^*$ (Intraligand; S.A.)
	30000 br	30400 br	$\pi_3 - \pi_4^*$
	28500 sh	28200 sh	$\pi - \pi^*$ (Furyl)
	26000	25400	
	21400 br	22000 br	$^5A_{1g} \rightarrow {}^5B_{2g}$
	16800	16400	$^5A_{1g} \rightarrow {}^5E_g$
	8500	9600	$^5A_{1g} \rightarrow {}^5B_{1g}$
Fe(III)	45300 br	45800 br	$\pi_3 - \pi_5^*$
	37600 br	36600 br	$\pi - \pi^*$ (Intraligand; S.A.)
	35000 vbr	34400 vbr	$\pi_3 - \pi_4^*$
	27400 sh	26600 sh	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$; π-π^* (Furyl)
	24200 sh	23200 sh	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$
	19600	19200	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$

contd.

TABLE 18. Contd.

M(III)	M(fbd)$_3$ $\bar{\nu}_{cm}{}^{-1}$	M(tffbd)$_3$ $\bar{\nu}_{cm}{}^{-1}$	Assignments
	12800 sh	11600 sh	$\left.\right\}{}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
	9600	-	
Co(III)	45600 br	45300 br	$\pi_3 - \pi_5^*$
	37400 br	36700 vbr	$\pi - \pi^*$ (Intraligand; S.A.)
	32000 br	31800 br	$\pi_3 - \pi_4^*$
	26600 br	26200 br	$\pi - \pi^*$ (Furyl)
	21200 sh	20600 sh	d → d
	16400	16300	${}^1A_{1g} \rightarrow {}^1T_{1g}$
	11200 sh	11300 sh	${}^1A_{1g}(S) \rightarrow {}^3T_{2g}(F)$
	8400	8600	${}^1A_{1g}(S) \rightarrow {}^3T_{1g}(F)$

Abbreviations: br, broad; v, very; sh, shoulder;

S.A., spin-allowed.

TABLE 19. Diffuse reflectance spectra of trivalent metal complexes of 1-phenyl-1,3-butanedione(Hbzac) and 4,4,4-trifluoro-1-phenyl-1,3-butanenedione(Hbztfac) in the region 50000 - 5000 cm^{-1} and their proposed assignments.

M(III)	$M(bzac)_3$ $\bar{\nu}_{cm^{-1}}$	$M(bztfac)_3$ $\bar{\nu}_{cm^{-1}}$	Assignment
Al(III)	45300 br	45400 br	$\pi_3 - \pi_5^*$
	37800 vbr	37600 vbr	ph $\pi - \pi^*$;
	34600 br	35000 br	$\pi_3 - \pi_4^*$
	28600 sh	28800 sh	$n - \pi^*$
Cr(III)	45300 br	45200 br	$\pi_3 - \pi_5^*$
	37400 vbr	37600 vbr	ph $\pi - \pi^*$; $\pi - d$
	31800 vbr	31600 br	$\pi_3 - \pi_4^*$
	30000 br	30100 br	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	26800	26800	C. T.
	21500 sh	22200 sh	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	17600	17400	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$

contd.

TABLE 19. Contd.

M(III)	M(bzac)$_3$ $\bar{\nu}_{cm^{-1}}$	M(bztfac)$_3$ $\bar{\nu}_{cm^{-1}}$	Assignment
Mn(III)	45100 br	45200 br	$\pi_3 - \pi_5^*$
	37700 vbr	38000 vbr	ph $\pi - \pi^*$; $\pi - d$
	35200 br	35000 br	$\pi_3 - \pi_4^*$
	28200	28200	C. T.
	21800 br	22000 br	$^5A_{1g} \rightarrow {}^5B_{2g}$
	16600	16400	$^5A_{1g} \rightarrow {}^5E_g$
	8500	9000	$^5A_{1g} \rightarrow {}^5B_{1g}$
Fe(III)	45400 br	45300 br	$\pi_3 - \pi_5^*$
	35800 vbr	36800 vbr	ph $\pi - \pi^*$; $\pi - d$
	29400 vbr	27800 vbr	$\pi_3 - \pi_4^*$; C. T.
	25400 brsh	24800 brsh	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$
	22800 sh	21200 sh	$^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$
	19800	20400	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$
	13000 sh	10600	$\left.\right\} {}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
	9600	-	

contd.

TABLE 19. Contd.

M(III)	M(bzac)$_3$ $\bar{\nu}_{cm^{-1}}$	M(bztfac)$_3$ $\bar{\nu}_{cm^{-1}}$	Assignment
Co(III)	45400 br	45300 br	$\pi_3 - \pi_5^*$
	37600 vbr	37000 vbr	ph $\pi - \pi^*$; π - d
	33200 vbr	33800 vbr	$\pi_3 - \pi_4^*$
	25600	26300	C. T.
	22000 sh	22000 sh	d → d
	16500	16500	$^1A_{1g} \rightarrow {}^1T_{1g}$
	11300 sh	12000 sh	$^1A_{1g}(S) \rightarrow {}^3T_{2g}(G)$
	8600	8800	$^1A_{1g}(S) \rightarrow {}^3T_{1g}(G)$

Abbreviations: v, very; br, broad; sh, shoulder;
C. T., charge transfer; ph, phenyl ring.

TABLE 20. Diffuse reflectance spectra of trivalent metal complexes of 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione(Htfpybd) in the region 50000 - 5000 cm^{-1} and their proposed assignments.

Compound	$\bar{\nu}_{cm^{-1}}$	Assignments
$Al(tfpybd)_3$	45200 br	$\pi_3 - \pi_5^*$
	37600 vbr	Py $\pi - \pi^*$;
	34000 vbr	$\pi_3 - \pi_4^*$
	28400 brsh	$n - \pi^*$ (pyridyl)
$Cr(tfpybd)_3$	45100 br	$\pi_3 - \pi_5^*$
	36800 vbr	Py $\pi - \pi^*$; $\pi - d$
	31300 vbr	$\pi_3 - \pi_4^*$
	30000	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	25600 brsh	C. T.
	20800 sh	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	17400 br	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$
$Mn(tfpybd)_3$	45400 br	$\pi_3 - \pi_5^*$
	37400 vbr	Py $\pi - \pi^*$; $\pi - d$
	33600 br	$\pi_3 - \pi_4^*$
	27400 brsh	C. T.
	22600 sh	$^5A_{1g} \rightarrow {}^5B_{2g}$
	14800 sh	$^5A_{1g} \rightarrow {}^5E_g$
	11000	$\left.\right\} {}^5A_{1g} \rightarrow {}^5B_{1g}$
	9000	

contd.

TABLE 20. Contd.

Compound	$\bar{\nu}_{cm^{-1}}$	Assignments
$Fe(tfpybd)_3$	45300 br	$\pi_3 - \pi_5^*$
	37400 vbr	Py $\pi - \pi^*$; π - d
	33000 vbr	$\pi_3 - \pi_4^*$
	26800 brsh	C.T.
	25000	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$
	21000 sh	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	16800 sh	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$
	13600 sh	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
$Co(tfpybd)_3$	45400 br	$\pi_3 - \pi_5^*$
	37200 vbr	Py $\pi - \pi^*$; π - d
	31600 vbr	$\pi_3 - \pi_4^*$
	27400	C. T.
	22000	d → d
	16600	$^1A_{1g} \rightarrow {}^1T_{1g}$
	10000	$^1A_{1g}(S) \rightarrow {}^3T_{1g}(G)$

Abbreviations: v, very; br, broad; sh, shoulder;
C.T., charge transfer; Py, pyridine.

TABLE 21. Electronic spectral data of Htbd and Htftbd and their trivalent metal complexes in chloroform.

Compound	$\bar{\nu}_{max} \times 10^3 cm^{-1}$; log ε		Assignment
	Htbd	Htftbd	
Ligand	47.62 ; 3.67	45.45 ; 3.65	$\pi_3 - \pi_5^*$
	37.04 ; 3.66	38.46 ; 3.60	$\pi - \pi^*$ (Intraligand; S.A.)
	33.33 ; 4.00	34.48 ; 3.79	$\pi_3 - \pi_4^*$
	30.49 ; 4.27	30.30 ; 3.98	$\pi - \pi^*$ (Thienyl)
	-	28.57 ; 3.95	$\pi - \pi^*$ (spin forbidden)
Al(III)	46.51 ; 4.22	47.62 ; 4.31	$\pi_3 - \pi_5^*$
	40.82 ; 4.20	42.02 ; 4.28	$\pi - \pi^*$ (Intraligand; S.A.)
	37.04 ; 4.16	38.46 ; 4.27	
	32.25 ; 4.38	34.84 ; 4.27	$\pi_3 - \pi_4^*$
	28.99 ; 4.79	28.57 ; 4.88	$\pi - \pi^*$ (Thienyl)
Cr(III)	48.78 ; 4.49	46.51 ; 4.30	$\pi_3 - \pi_5^*$
	40.00 ; 4.30	40.00 ; 4.28	$\pi - \pi^*$ (Intraligand; S.A.)
	37.04 ; 4.30	35.71 ; 4.40	
	33.56 ; 4.00	34.48 ; 4.35	$\pi_3 - \pi_4^*$
	31.25 ; 4.52	30.77 ; 4.50	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	27.03 ; 4.62	25.97 ; 4.65	$\pi - \pi^*$ (Thienyl)
	23.81 ; 3.48	22.99 ; 3.45	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	20.83 ; 2.27	20.41 ; 2.68	$\pi - \pi^*$ (spin forbidden)
	17.79 ; 2.12	17.86 ; 2.05	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$

contd.

TABLE 21. Contd.

Compound	$\tilde{\nu}_{max}$ x $10^3 cm^{-1}$; $\log\varepsilon$		Assignment
	Htbd	Htftbd	
Mn(III)	48.78 ; 4.34	46.45 ; 4.20	$\pi_3 - \pi_5^*$
	40.00 ; 4.30	40.00 ; 4.23	$\pi - \pi^*$ (Intraligand; S.A.)
	37.04 ; 4.05	-	
	30.77 ; 4.80	28.57 ; 4.55	$\pi_3 - \pi_4^*$
	25.00 ; 3.72	-	
	23.26 ; 3.20	23.26 ; 3.35	$\pi - \pi^*$ (spin forbidden)
	21.28 ; 2.90	20.41 ; 2.90	$^5A_{1g} \rightarrow {}^5B_{2g}$
	20.41 ; 2.81	18.52 ; 2.70	$^5A_{1g} \rightarrow {}^5E_g$
Fe(III)	40.00 ; 4.25	41.32 ; 3.87	$\pi - \pi^*$ (Intraligand; S.A.)
	37.04 ; 4.42	31.25 ; 4.38	
	30.77 ; 4.84	29.41 ; 4.73	$\pi_3 - \pi_4^*$
	26.67 ; 4.42	27.80 ; 4.57	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	-	25.38 ; 4.36	C. T.
	23.81 ; 3.92	22.73 ; 3.89	$^6A_{1g}(S) \rightarrow {}^4T_{2g}$ (G)
	20.83 ; 3.69	21.28 ; 3.76	
	17.24 ; 2.83	-	
Co(III)	40.00 ; 4.27	41.67 ; 3.60	$\pi - \pi^*$ (Intraligand; S.A.)
	37.04 ; 4.20	32.26 ; 3.35	
	31.25 ; 4.72	29.41 ; 4.60	$\pi_3 - \pi_4^*$
	27.03 ; 4.40	27.78 ; 4.42	$\pi - \pi^*$ (Thienyl)
	22.73 ; 3.05	22.22 ; 3.20	C. T.
	20.83 ; 2.54	20.41 ; 2.70	d → d
	17.09 ; 2.12	16.39 ; 2.30	$^1A_{1g} \rightarrow {}^1T_{1g}$

Abbreviations: S.A., spin - allowed; C.T., charge transfer.

TABLE 22. Electronic spectral data of Hfbd and Htffbd and their trivalent metal complexes in chloroform.

Compound	$\bar{\nu}_{max} \times 10^3 cm^{-1}$; log ε		Assignment
	Hfbd	Htffbd	
Ligand	46.51 ; 3.19	45.45 ; 4.57	$\pi_3 - \pi_5^*$
	37.74 ; 3.20	38.46 ; 4.70	$\pi - \pi^*$ (Intraligand; S.A.)
	34.48 ; 4.25	33.90 ; 4.87	$\pi_3 - \pi_4^*$
	31.25 ; 5.00	31.25 ; 4.67	$\pi - \pi^*$ (Furyl)
	27.03 ; 4.95	27.55 ; 4.68	
Al(III)	47.62 ; 4.54	45.45 ; 4.56	$\pi_3 - \pi_5^*$
	36.36 ; 4.80	35.71 ; 4.77	$\pi - \pi^*$ (Intraligand; S.A.)
	33.90 ; 4.81	33.33 ; 4.75	$\pi_3 - \pi_4^*$
	27.78 ; 4.80	28.57 ; 4.60	$\pi - \pi^*$ (Furyl)
Cr(III)	47.62 ; 4.65	45.30 ; 4.52	$\pi_3 - \pi_5^*$
	40.00 ; 4.70	40.82 ; 4.54	$\pi - \pi^*$ (Intraligand)
	36.36 ; 4.82	35.08 ; 4.55	$\pi_3 - \pi_4^*$
	28.57 ; 4.60	27.78 ; 4.52	$\pi - \pi^*$ (Furyl)
	23.40 ; 4.72	24.69 ; 4.54	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	21.00 ; 2.73	21.28 ; 3.52	$\pi - \pi^*$ (spin forbidden); C.T.
	20.30 ; 2.50	19.23 ; 2.56	
	17.60 ; 2.09	17.68 ; 2.25	${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$
Mn(III)	45.45 ; 4.19	43.50 ; 4.20	$\pi_3 - \pi_5^*$
	40.82 ; 4.20	40.82 ; 4.35	$\pi - \pi^*$ Intraligand
	35.97 ; 4.67	35.71 ; 4.30	$\pi_3 - \pi_4^*$
	31.25 ; 4.50	30.77 ; 4.10	

contd.

TABLE 22. Contd.

Compound	$\bar{\nu}_{max} \times 10^3 cm^{-1}$; log ϵ		Assignment
	Hfbd	Htffbd	
	27.03 ; 3.26	27.40 ; 4.00	$\pi - \pi^*$ (Furyl)
	23.53 ; 2.87	24.39 ; 3.45	
	21.50 ; 2.30	22.22 ; 2.95	$^5A_{1g} \rightarrow {}^5B_{2g}$
	-	18.87 ; 2.80	$^5A_{1g} \rightarrow {}^5E_g$
Fe(III)	44.44 ; 4.49	44.44 ; 4.00	$\pi_3 - \pi_5^*$
	40.00 ; 4.24	40.00 ; 4.10	$\pi - \pi^*$ (Intraligand)
	37.04 ; 4.42	35.09 ; 4.25	$\pi_3 - \pi_4^*$
	30.78 ; 4.85	31.75 ; 4.20	$\pi - \pi^*$ (Furyl)
	26.67 ; 4.42	26.32 ; 3.80	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$
	23.53 ; 3.92	22.47 ; 3.50	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	20.41 ; 3.69	18.18 ; 3.05	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$
	16.67 ; 2.38	17.39 ; 2.80	
Co(III)	40.00 ; 4.37	41.67 ; 4.20	$\pi - \pi^*$ (Intraligand)
	37.04 ; 4.25	37.04 ; 4.15	
	32.79 ; 4.21	31.25 ; 4.60	$\pi_3 - \pi_4^*$
	26.67 ; 4.70	28.57 ; 4.50	$\pi - \pi^*$ (Furyl)
	23.53 ; 4.38	22.73 ; 3.20	C. T.
	20.41 ; 2.54	20.83 ; 2.60	d → d
	16.95 ; 2.12	16.81 ; 2.35	$^1A_{1g} \rightarrow {}^1T_{1g}$

TABLE 23. Electronic Spectral data of Hbzac and Hbztfac and their trivalent metal complexes in chloroform.

Compound	ν_{max} x $10^3 cm^{-1}$; log ϵ		Assignment
	Hbzac	Hbztfac	
Ligand	47.62 ; 3.65	47.62 ; 3.85	$\pi_3 - \pi_5^*$
	40.82 ; 3.70	38.46 ; 3.90	ph - $\pi - \pi^*$
	32.79 ; 4.80	31.45 ; 4.18	$\pi_3 - \pi_4^*$
	28.57 ; 4.10	29.41 ; 4.17	$n - \pi^*$
Al(III)	45.45 ; 4.10	46.51 ; 4.85	$\pi_3 - \pi_5^*$
	38.17 ; 3.90	38.17 ; 5.00	ph. $\pi - \pi^*$
	33.90 ; 4.40	31.25 ; 4.10	$\pi_3 - \pi_4^*$
	27.78 ; 4.60	26.67 ; 3.74	$n - \pi^*$
Cr(III)	44.44 ; 4.05	45.45 ; 4.40	$\pi_3 - \pi_5^*$
	38.46 ; 4.10	41.67 ; 4.50	ph. $\pi - \pi^*$; $\pi - d$
	33.90 ; 4.10	34.48 ; 4.85	$\pi_3 - \pi_4^*$
	32.26 ; 4.00	29.85 ; 4.48	${}^4A_{2g} - {}^4T_{1g(P)}$
	27.62 ; 4.65	27.40 ; 4.30	C. T.
	21.74 ; 3.15	22.73 ; 2.75	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	17.86 ; 2.50		${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$

TABLE 23. Contd.

Compound	ν_{max} x $10^3 cm^{-1}$; log ε		Assignment
	Hbzac	Hbztfac	
Mn(III)	40.00 ; 4.30	40.00 ; 4.55	ph. $\pi - \pi^*$; π - d
	37.04 ; 4.30	34.48 ; 4.90	$\pi_3 - \pi_4^*$
	31.65 ; 4.55	30.30 ; 4.70	n - π^*
	25.00 ; 3.50	28.57 ; 4.42	C. T.
	23.53 ; 2.55	22.73 ; 3.20	$\pi - \pi^*$ (Spin forbidden)
		21.74 ; 3.08	$^5A_{1g} \rightarrow {}^5B_{2g}$
	19.31 ; 2.40	19.23 ; 2.73	
Fe(III)	45.66 ; 4.20	45.45 ; 4.10	$\pi_3 - \pi_5^*$
	38.17 ; 4.40	38.46 ; 4.15	ph. $\pi - \pi^*$; π - d
	34.72 ; 4.95	32.26 ; 4.80	$\pi_3 - \pi_4^*$
	31.25 ; 4.40		
	29.41 ; 4.00	27.78 ; 4.00	C. T.
	26.32 ; 3.55	25.64 ; 3.50	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$
	21.74 ; 2.30	21.98 ; 2.40	$^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	19.53 ; 1.75	20.41 ; 1.50	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$

Contd.

TABLE 23. Contd.

Compound	ν_{max} x 10^3 cm^{-1} ; log ε		Assignment
	Hbzac	Hbztfac	
Co(III)	44.84 ; 4.20	46.51 ; 4.30	$\pi_3 - \pi_5^*$
	37.74 ; 4.05	41.67 ; 4.45	ph $\pi - \pi^*$; $\pi - d$
	30.77 ; 4.85	34.48 ; 4.80	$\pi_3 - \pi_4^*$
		29.41 ; 4.40	} C. T.
	25.91 ; 3.20		
	23.81 ; 2.45	23.81 ; 3.05	
	21.74 ; 2.55	22.22 ; 2.70	$d \rightarrow d$
		20.83 ; 2.35	
		18.18 ; 2.00	
	17.24 ; 2.10	17.24 ; 2.10	${}^1A_{1g} \rightarrow {}^1T_{1g}$

TABLE 24. Electronic Spectral data of Htfpybd and its trivalent metal complexes in chloroform

Compound	$\bar{\nu}_{max} \times 10^3$ cm^{-1}	log ϵ	Assignment
Htfpybd	41.67	4.23	py, $\pi - \pi^*$
	34.48	4.67	$\pi_3 - \pi_4^*$
	29.94	3.96	$n - \pi^*$ (Pyridyl)
	27.78	3.45	$\pi - \pi^*$ (Spin forbidden)
Al(tfpybd)$_3$	40.00	4.61	py $\pi - \pi^*$
	34.48	4.80	$\pi_3 - \pi_4^*$
	30.03	4.70	$n - \pi^*$
	24.39	2.27	$\pi - \pi^*$ (Spin forbidden)
	22.73	2.09	
Cr(tfpybd)$_3$	42.55	3.78	$\pi_3 - \pi_5^*$
	38.46	3.80	py $\pi - \pi^*$
	33.33	4.17	$\pi_3 - \pi_4^*$
	27.03	4.03	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	25.00	3.54	C. T.
	23.81	2.98	$\pi - \pi^*$ (Spin forbidden)
	20.83	2.20	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$

Contd.

TABLE 24. Contd.

Compound	$\bar{\nu}_{max}$ x 10^3 cm^{-1}	$\log_{\epsilon}$	Assignment
$Fe(tfpybd)_3$	45.45	4.14	$\pi_3 - \pi_5^*$
	40.00	4.33	py $\pi - \pi^*$
	34.00	4.81	$\pi_3 - \pi_4^*$
	31.25	4.50	$n - \pi^*$
	29.41	4.25	C. T.
	24.39	3.69	${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$
	22.73	3.44	${}^6A_{1g}(S) \rightarrow {}^4E_g, {}^4A_{1g}(G)$
	20.00	3.25	$\pi - \pi^*$ (Spin forbidden)
	18.52	2.91	${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$

TABLE 25: Room temperature magnetic measurement data at a field ~ 5000 Gauss.

Compound	(-ve)DMC x 10^{-6} erg. gauss^{-2} mole^{-1}	χ_A x 10^{-6} erg. gauss^{-2} mole^{-1}	μeff. (293K) B. M.
Al(tbd)$_3$	206.7	7.2	0.13
Cr(tbd)$_3$	206.7	5838.3	3.69
Mn(tbd)$_3$	206.7	10609.1	4.99
Fe(tbd)$_3$	206.7	14470.9	5.82
Co(tbd)$_3$	206.7	444.0	1.02
Al(tftbd)$_3$	237.0	102.5	0.49
Cr(tftbd)$_3$	237.0	6026.7	3.76
Mn(tftbd)$_3$	237.0	11020.9	5.08
Fe(tftbd)$_3$	237.0	14355.9	5.80
Co(tftbd)$_3$	237.0	169.4	0.63
Al(fbd)$_3$	185.7	0.2	0.02
Cr(fbd)$_3$	185.7	6374.9	3.87
Mn(fbd)$_3$	185.7	10372.4	4.99
Fe(fbd)$_3$	185.7	14554.0	5.84
Co(fbd)$_3$	185.7	286.9	0.82
Al(tffbd)$_3$	205.8	49.3	0.34
Cr(tffbd)$_3$	205.8	6821.3	3.99
Mn(tffbd)$_3$	205.8	10557.1	4.98
Fe(tffbd)$_3$	205.8	14855.2	5.90
Co(tffbd)$_3$	205.8	259.6	0.78
Al(bzac)$_3$	197.7	30.3	0.27
Cr(bzac)$_3$	197.7	6410.6	3.88
Mn(bzac)$_3$	197.7	11086.4	5.09
Fe(bzac)$_3$	197.7	14699.7	5.87
Co(bzac)$_3$	197.7	197.3	0.68

Contd.

TABLE 25.Contd.

Compound	(-ve) DMC x 10^{-6} erg. guass^{-2} mole^{-1}	χ_A x 10^{-6} erg. guass^{-2} mole^{-1}	$\mu_{eff.}$ (293K) B. M.
$Al(bztfac)_3$	228.0	13.5	0.18
$Cr(bztfac)_3$	228.0	7527.9	4.20
$Mn(bztfac)_3$	228.0	10668.8	5.00
$Fe(bztfac)_3$	228.0	12539.7	5.42
$Co(bztfac)_3$	228.0	345.7	0.90
$Al(tfpybd)_3$	216.3	73.7	0.42
$Cr(tfpybd)_3$	216.3	6162.3	3.80
$Mn(tfpybd)_3$	216.3	11099.8	5.10
$Fe(tfpybd)_3$	216.3	5835.0	3.69
$Co(tfpybd)_3$	216.3	516.4	1.10

TABLE 26. Variable temperature magnetic measurement data (293 - 80K).

A. $Mn(tbd)_3$ DMC = -206.7×10^{-6} erg. gauss^{-2} mole^{-1}

T (K)	$\chi_{Mn} \times 10^{-6}$ (erg. gauss^{-2} mole^{-1})	$\chi_{Mn}^{-1} \times 10^{2}$ (mole gauss ^{2}erg^{-1})	$\mu_{eff.}$ (B.M.)
293	10626	0.94	4.99
261	11644	0.86	4.93
229	13217	0.76	4.92
197	14930	0.67	4.85
165	17899	0.56	4.86
133	22850	0.44	4.93
101	29724	0.34	4.90
93	31366	0.32	4.83
87	33113	0.30	4.80

B. $Fe(fbd)_3$ DMC = -185.7×10^{-6} erg. gauss^{-2} mole^{-1}

T (K)	$\chi_{Fe} \times 10^{-6}$ (erg. gauss^{-2} mole^{-1})	$\chi_{Fe}^{-1} \times 10^{2}$ (mole gauss ^{2}erg^{-1})	$\mu_{eff.}$ (M.B.)
293	14556	0.69	5.84
261	16339	0.61	5.84
229	18496	0.54	5.82
197	21499	0.47	5.82
165	25669	0.39	5.82
133	31735	0.32	5.81
101	41503	0.24	5.80
93	45073	0.22	5.80
87	48182	0.21	5.80

TABLE 26. Contd.

C. Fe(tfpybd)$_3$ DMC = -216.3×10^{-6} erg. gauss^{-2} mole^{-1}

T (K)	$\chi_{Fe} \times 10^{-6}$ (erg.gauss^{-2} mole^{-1})	$\chi^{-1}_{Fe} \times 10^{2}$ (mole gauss ^{2}erg.$^{-1}$)	$\mu_{eff.}$ (B.M.)
293	5674	1.76	3.69
261	5990	1.67	3.54
229	6544	1.53	3.46
197	7038	1.42	3.33
165	7789	1.28	3.21
133	8758	1.14	3.05
101	8541	1.17	2.63
93	7908	1.26	2.35
87	8204	1.21	2.47

D. Co(tbd)$_3$ DMC = -206.7×10^{-6} erg. gauss^{-2} mole^{-1}

T (K)	$\chi_{Co} \times 10^{-6}$ (erg.gauss^{-2} mole^{-1})	$\chi^{-1}_{Co} \times 10^{3}$ (mole. gauss ^{2}erg^{-1})	$\mu_{eff.}$ (B. M.)
293	444.99	2.25	1.02
261	432.36	2.31	0.95
229	472.25	2.12	0.93
197	514.15	1.94	0.90
165	641.41	1.56	0.92
133	729.93	1.37	0.88
101	869.57	1.15	0.84
87	908.26	1.10	0.80

TABLE 26. Contd.

E. $Co(tftbd)_3$ DMC = -237.0×10^{-6} erg. gauss^{-2} mole^{-1}

T (K)	$\chi_{Co} \times 10^{-6}$ (erg. gauss^{-2} mole^{-1})	$\chi_{Co}^{-1} \times 10^{4}$ (mole. gauss ^{2}erg^{-1})	$\mu_{eff.}$ (B .M.)
293	155.65	0.64	0.63
261	169.37	0.59	0.57
229	183.68	0.54	0.58
197	243.98	0.41	0.55
165	229.24	0.44	0.62
133	264.08	0.38	0.53
101	347.75	0.29	0.53
93	377.67	0.26	0.53
87	403.71	0.25	0.53

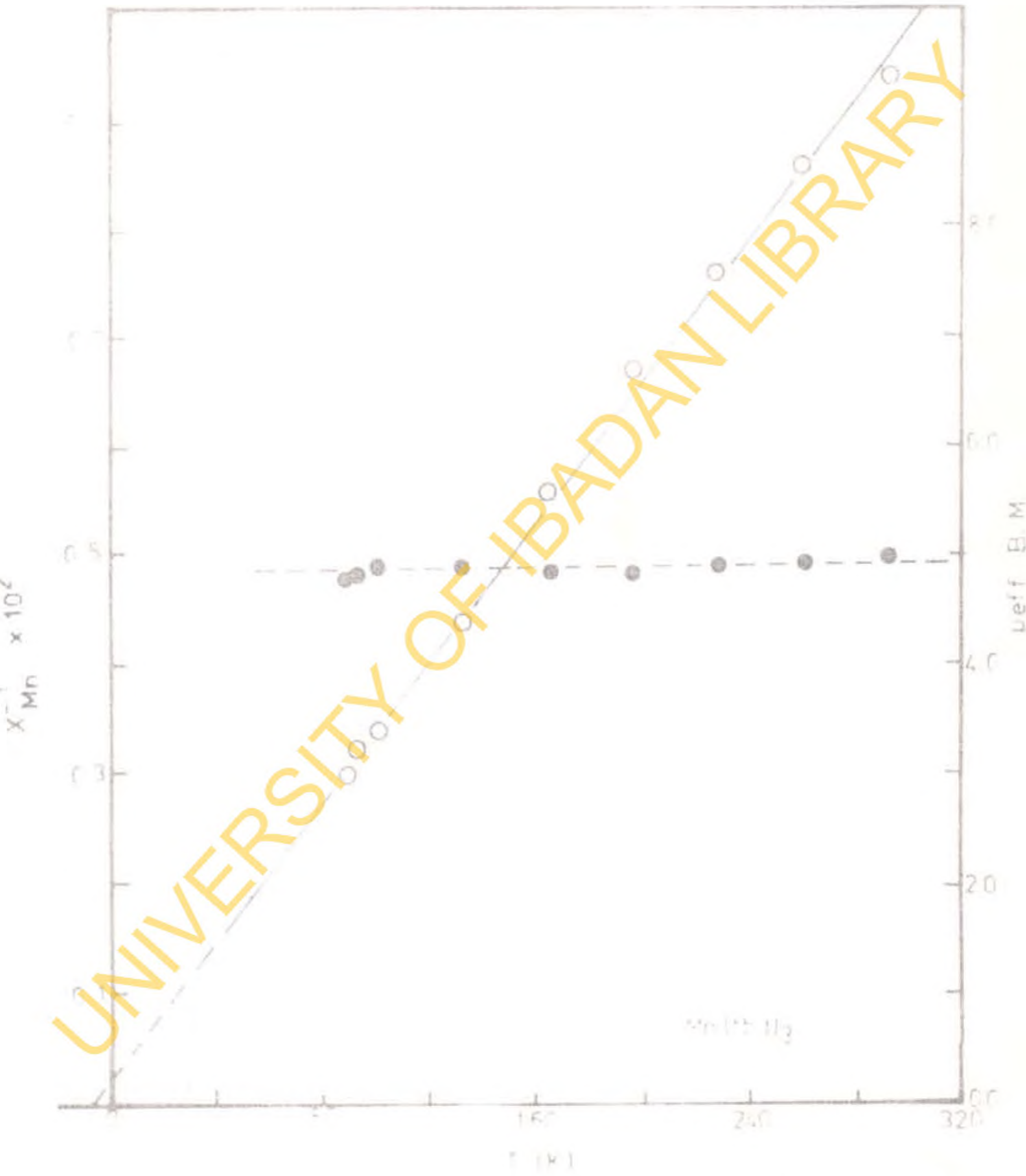
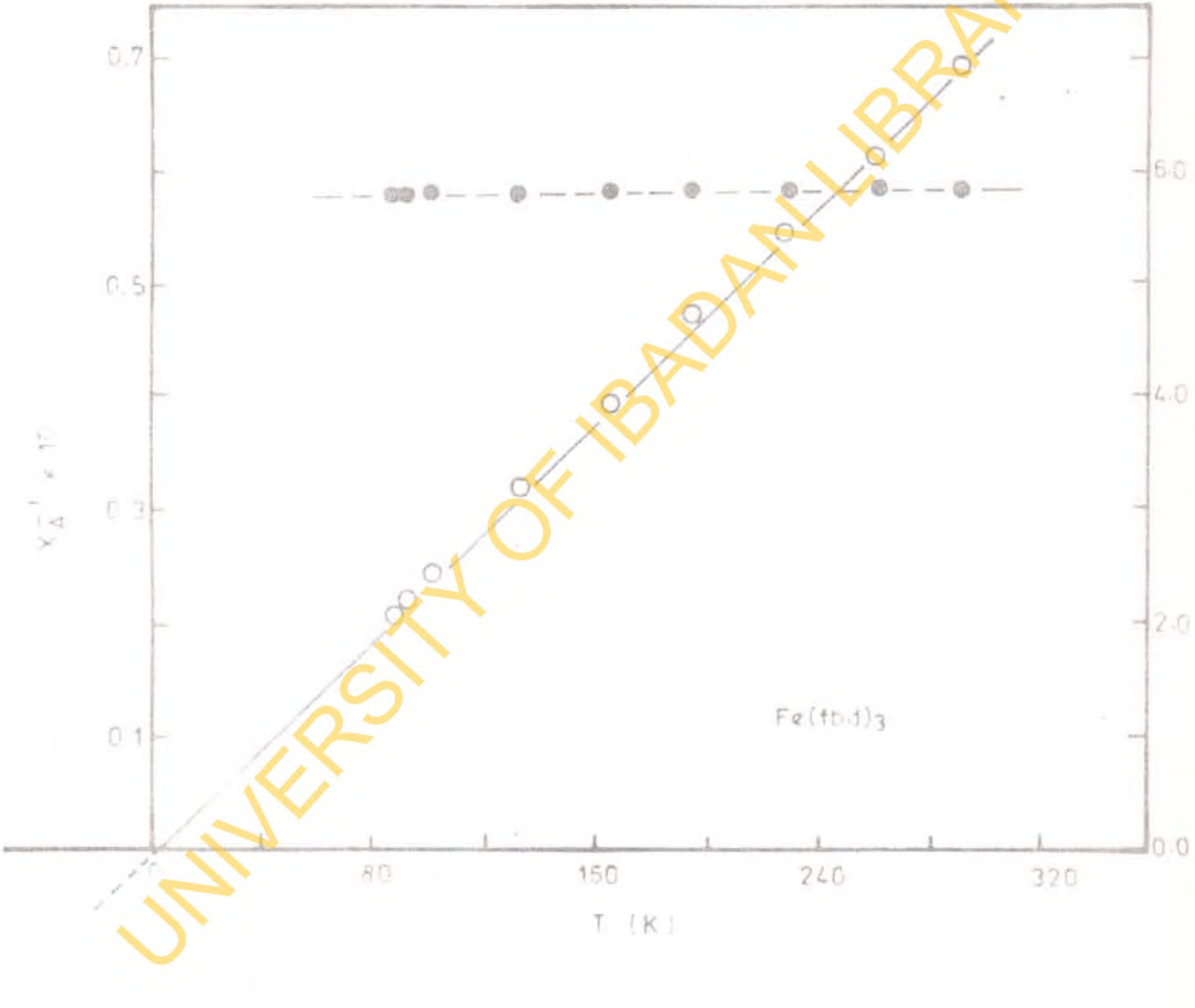


Fig. 43(b) Variable temperature μeff and χ_{A}^{-1} plots (293-80)K

(169)


0.7
0.5
0.3
0.1
$\chi_A^{-1} \times 10^{-2}$
6.0
4.0
2.0
0.0
μeff B.M.
0
80
160
240
320
T (K)
Fe(tbd)$_3$

(170)

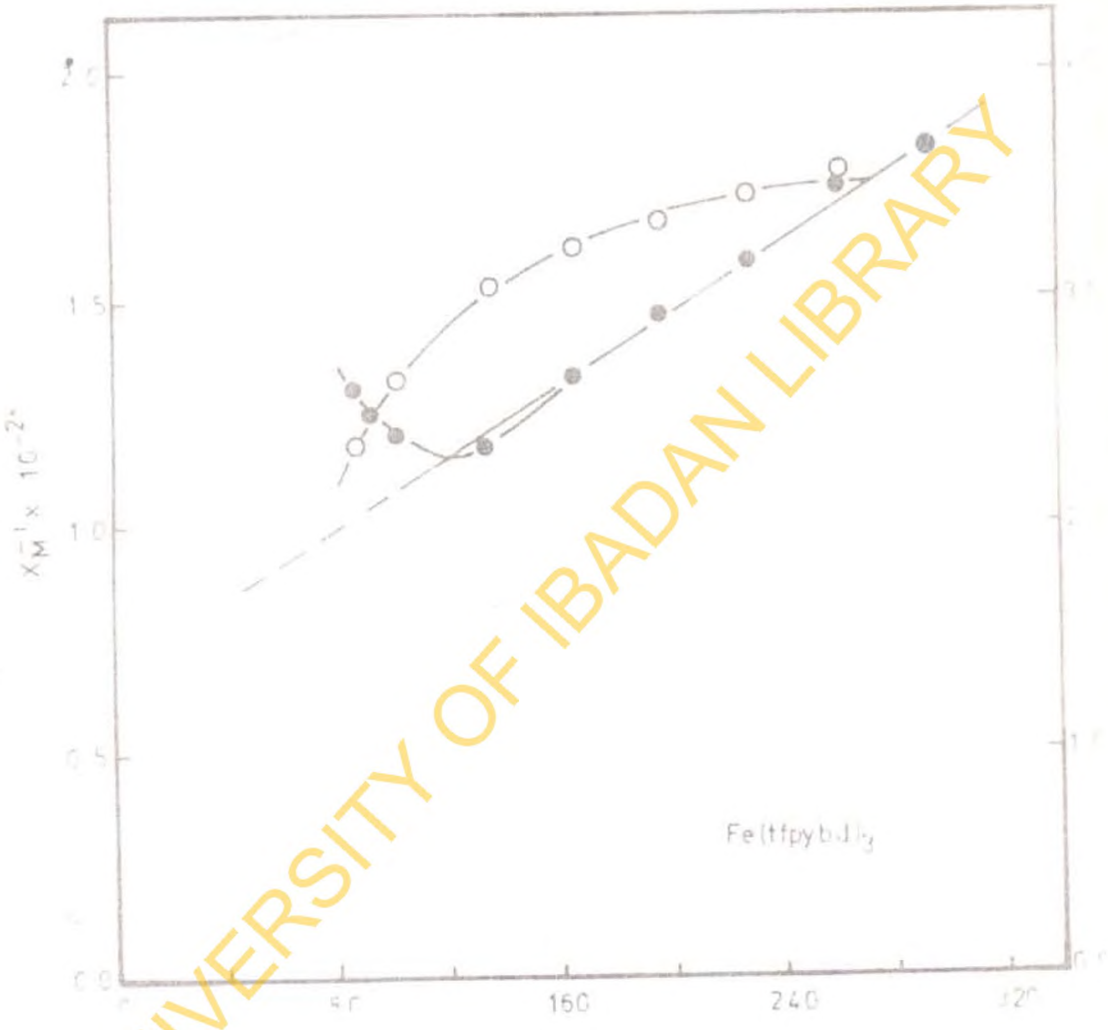

2.0
1.5
1.0
0.5
0.0
$\chi_M^{-1} \times 10^{-2}$
0
80
160
240
320
T (K)
3.0
1.0
0.0
μ_{eff} B.M.
Fe(tfpybd)$_3$

Fig. 43 d

(171)

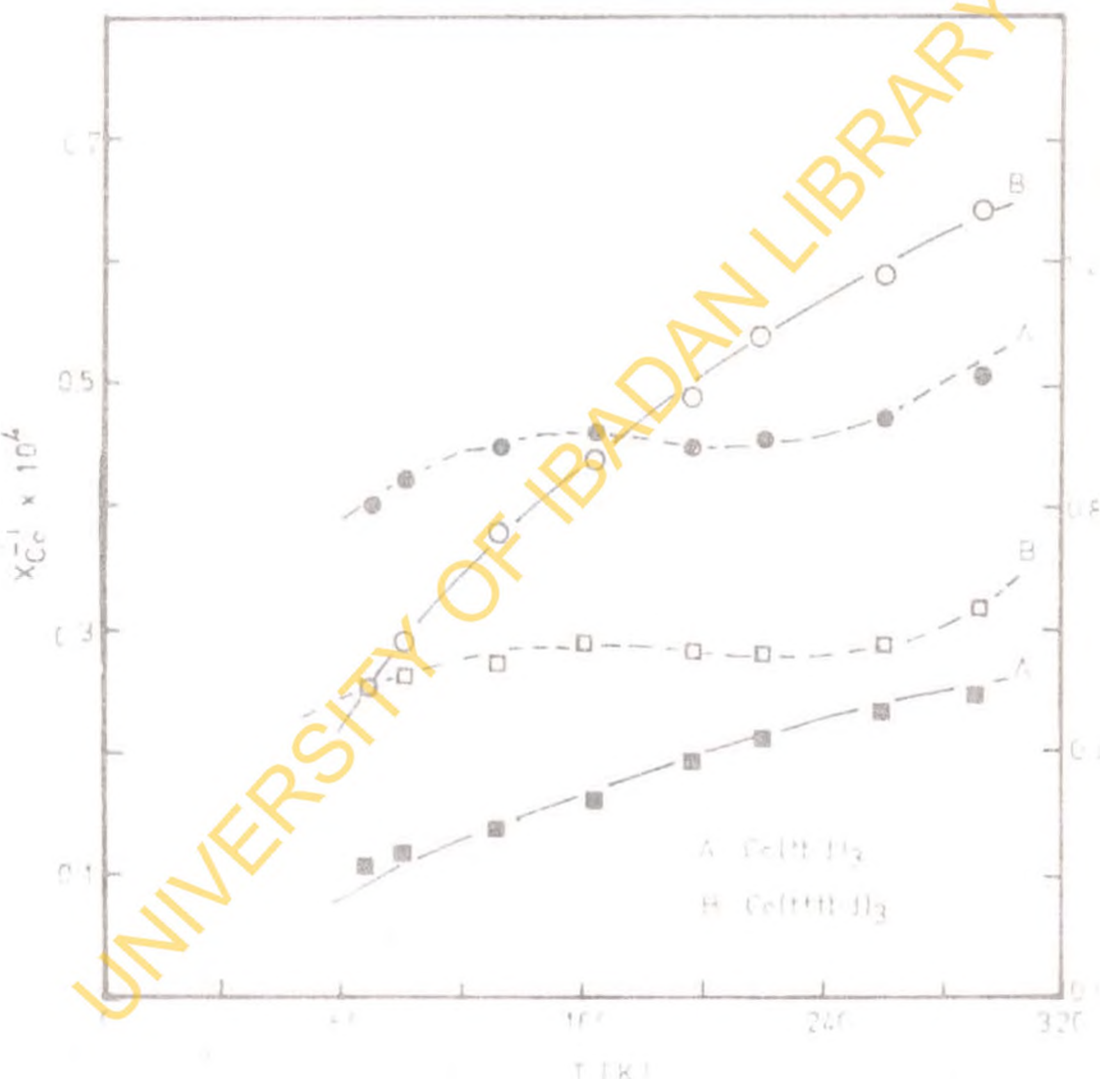

0.7
0.5
0.3
0.1
$\chi_{Co}^{-1} \times 10^4$
0
80
160
240
320
T (K)
1.2
0.8
0.4
0
μeff B.M.
A
B
A
B
A Co(
B Co(

Fig. 43 c.

CHAPTER 5

DISCUSSIONS

Among the series of metal β- diketonates studied, the following complexes: Al(fbd)$_3$, Mn(fbd)$_3$, Al(tftbd)$_3$, Co(tftbd)$_3$, Cr(tffbd)$_3$, Mn(tffbd)$_3$, Co(tffbd)$_3$, M(tbd)$_3$, M(tfpybd)$_3$ (where M = Al, Cr, Mn, Fe and Co), Fe(bzac)$_2$(tftbd), Fe(tftbd)$_2$(bzac), Fe(fbd)$_2$(tbd) and Fe(tbd)$_2$(fbd) have been investigated for the first time. The elemental analyses (Table 9) establish that all the metal(III) β-diketonates have an empirical formula of M(β-diketone)$_3$. All the complexes have varying degrees of solubilities in most of the organic solvents but are insoluble in water. Most of the compounds were found to be extremely soluble in chloroform, benzene, diethylether and petroleum ether. For each pair of series of compounds, the non-fluorinated metal β-diketonates have much higher melting points than the corresponding fluorinated ones. This observation confirms an earlier conclusion made by Berg and Truemper [26] regarding the volatility of fluorinated metal β-diketonates.

5.1. Infrared Spectra

The I.R. spectra of the β-diketones and their trivalent metal complexes studied are depicted in Figures 14-21. Tentative vibrational assignments for the bands (Tables 10 - 16) have been made with the aid of the extensive theoretical and empirical studies on the I.R. spectra of other metal β-ketoenolates [30-44]. Due to the electron delocalisation in the chelate rings leading to extensive coupling between various vibrational modes, very few bands can therefore be said to represent pure vibrations. Consequently, the concept of "group frequency" is not generally applicable in the assignment of the observed vibrational bands in the series of spectra obtained.

The formation of the metal β-diketonates most invariably involve the enolic tautomer of the β-diketone (Fig.1b) and the metal ion. The vibration best described as asymmetric C $\underline{\underline{---}}$ O stretching in the enol tautomer of the ligands absorbs broadly and strongly at 1640 - 1580 cm^{-1} [34, 118, 119]. As there are four nearly equivalent bonds in the enol nucleus (two CO and two CC bonds), four stretching frequencies are expected involving all the bonds. These usually occur near 1600, 1500, 1450 and 1260 cm^{-1} [34]. The regions for the vibrations of all the metal chelates under investigation, each involving all four " bond and a half" bonds are, 1600 - 1560; 1530 - 1500; ca. 1450, and ca. 1250 cm^{-1} (Tables 10 - 16). These bonds have been assigned to the $\nu_{as}\ C \underline{---} O$, $\nu_{as}\ C \underline{---} C \underline{---} C$, $\nu_{s}\ C \underline{---} O$ and $\nu_{s}\ C \underline{---} C \underline{---} C$ stretching modes respectively. Whereas for most of the β-diketones studied, the first intense vibrational band lies in the region 1640 - 1580 cm^{-1}, the infrared spectrum of Hfbd (Table 12), gives a sharp absorption at 1730 cm^{-1}. This band could be caused by a free carbonyl of the keto-form of the 1-(2-furyl)-1, 3-butanedione (Hfbd). On chelation however, this band is lowered by approximately 150 cm^{-1}. The trifluorofuroyl-acetone gives a similar band at 1680 cm^{-1} showing a comparatively greater acidic character than its non-fluorinated analog (see pKa values in Table 1). These assignments are supported by a more refined normal co-ordinate treatment of acetylacetonato platinum(II) complexes [42] and by ^{18}O-labelling of the carbonyl oxygen [120].

Difficulties are encountered in the identification of the bands around 1600 cm^{-1} in the phenyl-substituted β-diketones in which the carbonyl band is shifted into the same region of absorption. A third band appears near 1600 cm^{-1} in phenyl-substituted β-diketonates, which has been ascribed [48] to the first aromatic ring stretching vibration

(Tables 14 and 15). This particular band is metal insensitive and its frequency is close to that observed for monosubstituted benzenes. Pyridyl substituents behave similar in this region to monosubstituted pyridine compounds. For 2-furyl and 2-thienyl substituents, the ring stretching vibrations are at much lower frequencies (1523 $\pm$ 9cm^{-1}) [121]; and bands have been observed in this region in the spectra of Htbd, Htftbd, Hfbd, Htffbd as well as their metal chelates (Table 10-13). There are no complications from overlap of these bands with the νas C $\underline{---}$ O and νas C $\underline{---}$ C $\underline{---}$ C modes and unlike the phenyl - and pyridyl - substituted β-diketonates, the assignment is comparatively straightforward. Vibrational bands originating in the CF$_3$- group are assigned by comparison with the spectrum of CF$_4$[122] and normal coordinate studies of tri- and hexa- fluoroacetylacetonates [46].

In the 1300 - 600 cm^{-1} spectral region, the main absorption bands are due to the ligands. Based on theoretical analysis [39] and some supporting experimental data [40], this region could very well represent the overtone or combination zone for metal-oxygen fundamental modes which are thought to appear at frequencies below 600 cm^{-1} for all the spectra observed.

The most important bands in the spectral region 600 - 200 cm^{-1} are due to metal - oxygen vibrations. This is because organic substituents have very few strong absorptions in this region. In all the series of complexes studied, it is observed that the vibrational bands in this region appear to be metal sensitive and, at least, there is a correlation with one of the metal - oxygen stretching modes. These ν_{M-O} modes which show a variation with d-orbital population have therefore been assigned as the "most metal sensitive" modes. Figure 44 shows plots of ν_{M-O} (most sensitive) modes with d-orbital population. In all the series, it is observed that the ν_{M-O} frequencies follow the order:

Co > Al > Cr > Mn > Fe

The higher values of the aluminium(III) chelates suggest the covalent nature of the Al-O bonds since the usual $d\pi - p\pi$ bonding prevalent in transition metals is non-existent in the trivalent aluminium. The position of cobalt in the above order also indicates that cobalt III) with six 3d-electrons has a $t_{2g}^{6}e_{g}^{o}$ electronic configuration thus making available the vacant e_g orbitals to participate in covalent bonding in addition to the usual $d\pi - p\pi$ bonding. The other metals are in good agreement with the expected trend based on crystal field stabilization energy data [48]. Absorptions between 400 and 250 cm^{-1} although metal sensitive, are either insufficiently resolved to permit interpretation or followed no trend definite enough to warrant any general deductions.

5.2. Effects of substituents on major vibrational bands.

Table 27 shows the comparison of νas C $\underline{---}$ O, νas C $\underline{---}$ C $\underline{---}$ C and νM – O frequencies of the metal(III) β-diketonates. Phenyl substitution in $M(acac)_3$ is known to shift M-O and C $\underline{----}$ C stretches to higher frequencies and that of C $\underline{---}$ O to a lower frequency due to the mesomeric interaction of the phenyl group with the semi-aromatic metal chelate ring [46]. On the other hand, comparison of $M(acac)_3$ with the corresponding $M(tbd)_3$ and $M(fbd)_3$ (Table 27) reveals that M-O vibrations shifted to lower frequencies, while C $\underline{---}$ O stretching modes were irregular. However, a shift of C $\underline{---}$ O to a lower frequency for 2-thienyl and to a higher frequency for 2-furyl substitutions is observed. This could probably be **attributed** to a more electronegative oxygen atom in the furyl ring than sulphur in the thienyl ring which may affect the extent of the mesomeric interactions occurring between these five-membered heterocyclic aromatic rings and the corresponding semi-aromatic metal chelate rings.

TABLE 27. Comparison of νasC---O, νasC---C---C and νM–O frequencies*

of metal(III) complexes.

	Ligand	Al(III)	Cr(III)	Mn(III)	Fe(III)	Co(III)
νasC---O(Hacac)+	1577	1590	1575	1576	1572	1578
νasC---O (Htbd)	1620	1575	1570	1572	1570	1568
νasC---O (Htftbd)	1655	1600	1575	1595	1575	1580
νasC ---O (Hfbd)	1730	1605	1600	1595	1598	1600
νasC---O (Htffbd)	1680	1610	1600	1612	1600	1600
νasC---O (Hbzac)	1590	1600	1595	1595	1595	1592
νasC---O(Hbztfac)	1610	1610	1602	1600	1600	1598
νasC---O(Htfpybd)	1645	1620	1600	1630	1615	1618
νasC--- (Hacac)+	1529	1545	1524	1510	1526	1527
νasC---C(Htbd)	1535	1535	1535	1530	1535	1530
νasC---C---C(Htftbd)	1525	1550	1542	1540	1548	1540
νasC---C---C(Hfbd)	1620	1560	1550	1555	1550	1550
νasC---C ---(Htffbd)	1620	1585	1580	1582	1580	1575
νasC ---C---C(Hbzac)	1550	1570	1555	1560	1555	1560
νasC---C---C(Hbztfac)	1580	1580	1574	1570	1575	1570
νasC---C---C(Htfpybd)	1615	1580	1570	1580	1575	1580

Contd....

		Ligand	Al(III)	Cr(III)	Mn(III)	Fe(III)	Co(III)
νM-O	(Hacac)[+]	-	490	459	448	434	466
νM-O	(Htbd)	-	452	444	438	430	454
νM-O	(Htftbd)	-	428	410	392	283	435
νM-O	(Htbd)	-	468	450	440	432	470
νM-O	(Htffbd)	-	435	428	394	390	450
νM-O	(Hbzac)	-	475	466	465	450	488
νM-O	(Hbztfac)	-	560	558	550	545	570
νM-O	(Htfpybd)	-	350	342	340	330	350

•Frequencies expressed in cm^{-1}

[+] Values taken from Ref. [117].

In the case of $M(tfpybd)_3$ chelates, the assignments to the chelate ring vibrations are given in Table 16. Here, it is observed that while the $C\,\underline{---}\,O$ and $C\,\underline{---}\,C\,\underline{---}\,C$ vibrations are little perturbed, the M-O stretchings are fairly sensitive to metal substitution. The νM-O modes of $M(tfpybd)_3$ complexes also exhibit variation with d-orbital population (Fig.44).

The trifluoromethyl group substitution in place of a methyl one shows a more pronounced effect by shifting the $C\,\underline{---}\,O$ and $C\,\underline{---}\,C$ to higher frequencies and M-O to lower frequencies, a phenomenon commonly found with fluorosubstituted β-diketonates [123].

5.3. Ultraviolet Spectra

The diffuse reflectance spectral data for the complexes are summarised in Tables 17 - 20. In the UV region, four broad bands are located around 45,000; 37,000; 32,000 and 27,000 cm^{-1} for $M(tbd)_3$, $M(tftbd)_3$, $M(fbd)_3$ and $M(tffbd)_3$ complexes. The absorptions in the range 40,000 - 30,000 cm^{-1} are very broad and asymmetric, consequently, their band positions are only approximate. On the basis of previous assignments of related complexes [55, 56, 61], the bands have been assigned to $\pi_3 - \pi_5^*$; $\pi - \pi^*$ (Intraligand); $\pi_3 - \pi_4^*$ and $\pi - \pi^*$ (thienyl or furyl) transitions respectively. The assignments of the $\pi - \pi^*$ (thienyl or

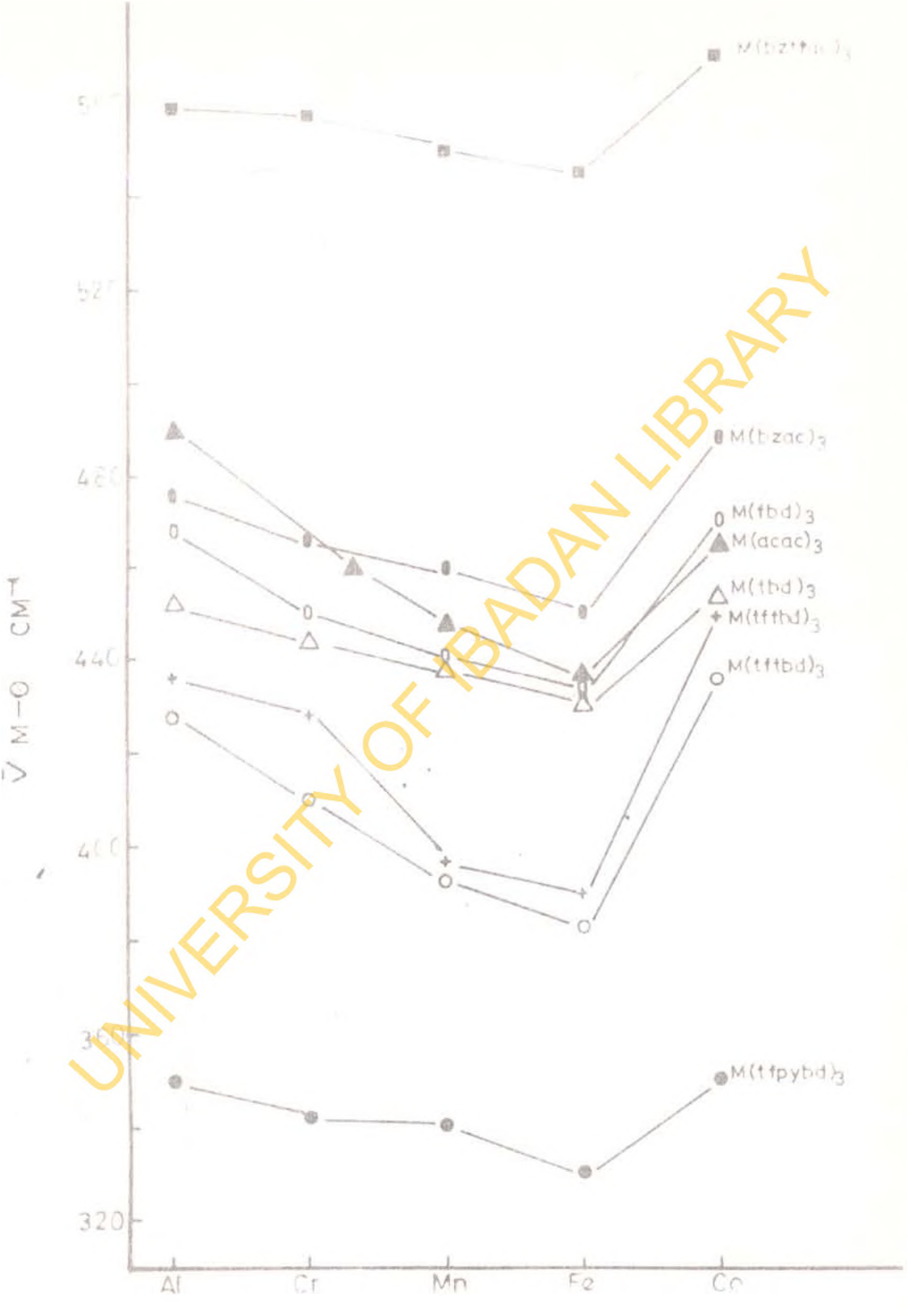


Fig. 44. Variation of M–O stretching frequency of the metal (III) β-diketonates

furyl) transitions are based on semi-empirical calculations on the π-electron system in furyl- and thienyl - sym - trinitrobenzenes [124]. These calculations placed the bands due to the five-membered aromatic rings at 28,409 and 27,470 cm^{-1} for the thienyl ring while those for the furyl ring at 26,390 and 25,840 cm^{-1} respectively.

The $M(bzac)_3$, $M(bztfac)_3$ and $M(tfpybd)_3$ complexes unlike their 2-thienyl - and 2-furyl- counterparts, show three main absorption bands around 45,000, 38,000 and 33,000 cm^{-1}. These are mainly due to the transitions within the ligand and other π-interactions in the metal chelate rings. While the bands around 45,000 cm^{-1} in all the complexes appear to be well defined and symmetrical but not significantly sensitive to the change in metal nucleus, those around 33,000 cm^{-1} mainly due to the lowest spin-allowed transitions, $\pi_3 - \pi_4^*$, are very broad and asymmetric. These latter transitions are very much metal sensitive due to their involvement in a considerable degree of metal-ligand π-interactions.

The solution spectra of these compounds in chloroform (Figs.29-36) show similar bands in the UV region as described above except that, owing to solvent perturbations, most of the bands are shifted to slightly higher energies. The effect of solvent on the spectra of the various complexes may probably result from different stabilities of the chelate rings in chloroform which would favour some rearrangements like dissociation and or polymer formation.

From the ultraviolet absorption data, it is evident that in the case of each series of metal β-diketonate studied, trifluoromethyl substitution in place of a methyl group resulted in the bathochromic shifts of $\pi_3 - \pi_4^*$ transition due to the inductive effect. Furthermore, the replacement of methyl groups by aromatic groups, more especially phenyl groups resulted in shifts of absorption bands towards lower energies in all transitions. This indicates the dominance of the resonance effect over the weak inductive effect of the phenyl ring.

5.4. Magnetic and Ligand-field Spectral Properties

The bands in the visible and near infrared regions are mostly due to ligand - field transitions and their assignments are summarised in Tables 17 - 24. The effect of each ligand on the metal ions investigated is the same. However, it appears that the only significant differences in bonding within the series arises because of different charge densities on the donor oxygen atoms.

Aluminium Chelates

As expected, all the aluminium(III) β-diketonates studied are diamagnetic and show no ligand field transitions.

Chromium(III) Chelates

The magnetic moments at 293K of the chromium(III) compounds are given in Table 25 and these values are in close agreement with the predicted value of slightly less than the spin-only moment of 3.88 B.M. [109].

The ligand-field transitions depend on the spectroscopic term of the metal ion as well as the magnitude of the ligand field strength of the coordinating ligand. With $^4A_{2g}$ ground state, three spin-allowed transitions are expected for chromium(III) compounds in an octahedral environment of donor atoms (Fig.7). These transitions have been found around 17,500; 23,400 and 30,000 cm^{-1} represented by BANDS I, II, III respectively. Usually BAND III may be obscured by a charge transfer band therefore making the assignment somehow doubtful. Their assignments $^4A_{2g} \rightarrow {}^4T_{2g}(F)$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ are straight-forward and are in good agreement with the values quoted in the literature on $Cr(tftbd)_3$ [76]. Tandon and Gupta [68] assigned the three bands observed in chromium(III) oxide as 16,500 cm^{-1} (BAND I); 21,740 cm^{-1} (BAND II) and 36,230 cm^{-1} as BAND III. Similarly for $Cr(acac)_3$, Barnum [52, 56] observed BAND I at 17,857 cm^{-1} and placed BAND II at 23,256 cm^{-1} on the assertion [69 - 71] that BAND II is expected at a frequency ca 7000 cm^{-1} higher than BAND I. Fatta and Lintvedt [72] also observed for $Cr(acac)_3$, BAND I at 17,860 cm^{-1} and BAND II at 23,260 cm^{-1}. They have also reported in an earlier paper [73] that the first spin-allowed transition (BAND I) whose energy is assumed to be equal to 10Dq, is nearly independent of the nature of the chelate ring substituent groups. Furthermore, they also suggested [72] that the second spin-allowed transition (BAND II) whose energy depends upon Dq and the Racah parameter B, has not been definitely assigned in the tris(β-diketonato)-chromium(III) spectra because of overlapping intense charge transfer bands. The assignment of this transition is somewhat uncertain. A band is observed in the range 26000 - 28000 cm^{-1} (log ϵ 4.00 - 4.60) for $Cr(tfpybd)_3$ which has been assigned to a charge transfer band, possibly $d_\epsilon \rightarrow \pi$ transitions.

Manganese(III) Chelates

The effective magnetic moments of $Mn(tbd)_3$, $Mn(tftbd)_3$, $Mn(fbd)_3$, Mn(tffbd)$_3$, Mn(bzac)$_3$, Mn(bztfac)$_3$ and Mn(tfpybd)$_3$ at 293K are 4.99, 5.08, 4.99, 4.98, 5.09, 5.00, and 5.10 B.M. respectively. For octahedral high-spin manganese(III) complexes in different environments, an appreciable effect of Jahn - Teller distortion is expected and magnetic moments with values ranging from 4.85 - 5.10 B.M. have been reported in the literature [88]. The value of 6.16 B.M. for Mn(tftbd)$_3$ quoted by Shephard and Thornton [91] seems to be rather high for a $t_{2g}^3 e_g^1$ configuration. An over-range temperature (293 - 80K) magnetic susceptibility measurements for Mn(tbd)$_3$ (Fig.43b) indicate that the values are independent of temperature. Variation of μeff. with T obeys the Curie-Weiss law with a θ value of -8°.

The electronic spectra of manganese(III) complexes have been interpreted [56, 60, 78, 80] in terms of an octahedral model and a band at ~ 20,000 cm^{-1} has been assigned to the spin-allowed crystal field transition $^5E_g \rightarrow {}^5T_{2g}$. In carbon tetrachloride solution spectra of tris (acetylacetonato)-manganese(III) complex, Dingle [80] reported three bands located around 8500; 17,600 and 22,000 cm^{-1}. The first two bands were assigned to charge transfer transitions and the last one as $^5E_g \rightarrow {}^5T_{2g}$. Similar bands with their corresponding assignments were also reported for tris (benzoylacetonato) manganese(III). In ethanolic solution, Barnum [52] observed a shoulder at 18,180 cm^{-1} and assigned it to the $^5E_g \rightarrow {}^5T_{2g}$ transition.

However, structural determinations on several six-coordinated manganese(III) complexes in a variety of molecular environments revealed that they are either distorted by flattening or elongation [23]. For $Mn(acac)_3$, distortion by flattening or compression has been reported [23] and this is supported by the two different average Mn - O bond distances. This would correspond to a $^5A'_{1g}$ ground state [125] (Fig. 9) instead of a $^5B'_{1g}$ ground state term on the basis of an elongated octahedral model (Fig. 8) [126]. The three d-d spin-allowed transitions in $Mn(acac)_3$ (21,300; 17,900 and 9500 cm^{-1}) were therefore assigned on the basis of the revised state [125] as $^5A_{1g} \rightarrow {}^5B_{2g}$, $^5A_{1g} \rightarrow {}^5E_g$ and $^5A_{1g} \rightarrow {}^5B_{1g}$ respectively. Since there are no X-ray structural data available on the manganese(III) complexes under investigation, a similar distortion (by compression) has been assumed and the ligand field bands have been assigned accordingly (Tables 17 - 24). From Tables 17 - 24, it is observed that, for all the manganese(III) β-ketoenolates, the three transitions are placed around 22,000; 16,500 and 9000 cm^{-1}.

Iron (III) Chelates

From Table 25, the magnetic moments of all the iron(III) β-diketonates apart from $Fe(tfpybd)_3$ are in the range 5.86 ± 0.04B.M. and these values are in reasonable agreement with those reported for $Fe(tftbd)_3$ (5.83B.M.) [84] and $Fe(acac)_3$ (5.97 B.M.) [92]. These values indicate that Fe(III) ions in these complexes adopt a high - spin d^5 electronic configuration. The variable temperature magnetic susceptibility of $Fe(fbd)_3$ (Fig. 43a) in the temperature region (293 - 80K) shows that the room temperature magnetic moment is 5.84 B.M., and Curie-Weiss law holds down to 80K with $\theta = 6^\circ$. A moment of 3.69 B.M. at 293K obtained for $Fe(tfpybd)_3$ appears to be rather unusual for a high - spin d^5 system. Variable temperature susceptibility measurements of $Fe(tfpybd)_3$ show dependence on temperature (Fig. 43d). However, this behaviour is similar to those reported for some ferric dithiocarbamates [127] for which a spin-crossover phenomena between two spin states $S = \frac{1}{2}$ and 5/2 were postulated.

Having $^6A_{1g}$ as a ground state in octahedral high-spin iron(III) complexes, moments around 5.90 B.M. were expected. The absence of higher T terms of sextuplet multiplicity and the occurrence of quartet and doublet terms in the excited states make the transitions spin-forbidden.

The reflectance spectra of the Fe(III) β-diketonates show four bands in the visible region, located near 27,000; 23,400; 20,000; and 12,300 cm^{-1}; and have been tentatively assigned to $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$; $^6A_{1g}(S) \rightarrow {}^4E_g\ {}^4A_{1g}(G)$; $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transitions respectively. Similar bands have been reported for Fe(tftbd)$_3$ [84] but no assignment was proposed for the band at 27,000 cm^{-1}. Low frequency bands around 9500 cm^{-1} similar to that reported for Fe(acac)$_3$ which were assigned by Barnum [52] as $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transitions, were also observed in the spectra of Fe(tbd)$_3$, Fe(tftbd)$_3$, Fe(fbd)$_3$, Fe(bzac)$_3$, while the corresponding bands were found to be absent in the spectra of Fe(tffbd)$_3$, Fe(bztfac)$_3$ and Fe(tfpybd)$_3$.

Cobalt(III) Chelates

The majority of the octahedral cobalt(III) complexes are diamagnetic with the exception of $[CoF_6]^{3-}$ and $[Co(H_2O)_3F_3]$ which are paramagnetic. The magnetic moments at 293K obtained for most of the cobalt(III) β-diketonates studied, are 0.75± 0.09 B.M., except for Co(tftbd)$_3$ and Co(tfpybd)$_3$ which gave moments of 1.02 and 1.10 B.M. respectively. These latter two moment values are certainly high for low-spin cobalt(III) complexes. The former values within reasonable limits of experimental errors could be indicative of diamagnetic behaviour. The values for Co(tftbd)$_3$ (1.02 B.M.) and Co(tfpybd)$_3$ (1.10 B.M.) neither suggest the presence of high-spin cobalt(III) - nor cobalt(II) - species as impurities. The extent of paramagnetism exhibited by these two compounds therefore, may possibly be due to the contribution of the T.I. P term, which arises as a result of second order Zeeman effect with higher ligand field terms. Their ligand field bands are similar to those reported for Co(acac)$_3$ by Barnum [52], indicating that the central metal ion is predominantly of the low-spin cobalt(III) type. The ground state term of low-spin cobalt(III) ion in an octahedral environment is $^1A_{1g}$ and the transitions reported (Tables 17-24), like many other workers [52, 56, 75], consist of those from the $^1A_{1g}$ ground state to higher singlet upper states and to some triplet excited states.

5.5. Nephelauxetic and Spectrochemical Series

In octahedral complexes, the partly filled d shell having the symmetry types γ_3 (e_g) and γ_5 (t_{2g}) is distorted by the formation of delocalised molecular orbitals and no longer necessarily corresponds to the angular function characterising the d-orbitals. Thus, γ_3 is the antibonding molecular orbital with a certain σ component in the ligands, while the corresponding bonding molecular orbital is completely filled in the ground state of the complex. In the same way, γ_5 of the partly filled shell becomes antibonding with respect to the occupied π-orbitals of the ligands. If empty, high-energy π-orbitals of the ligands should turn out to be important, the partly filled γ_5 should be bonding with respect to these components. In other words, the energy difference Δo (also called $(E_{\gamma_3} - E_{\gamma_5})$ or 10 Dq) between the subshells γ_3 and γ_5 consists in octahedral complexes of the following contributions, among others:

(a) the difference in electrostatic perturbation of the ligands on the two subshells;

(b) the effect of σ-bonding (L → M) on γ_3;

(c) the negative effect of π-bonding with filled orbitals (L → M) on γ_5; and

(d) the positive effect of π-bonding with empty ligand orbitals (M → L) on γ_5.

Contribution (b) is considerably more important than the other three effects in most complexes, while contributions (a) and (c) possibly change Δo some 10 to 30%. These contributions are appreciated more if the magnitude of the ligand field parameters B_{35}, Dq and β_{35}, where B_{35} is the interaction between γ_3 and γ_5 subshells, Dq being the crystal field splitting energy parameter and β_{35}, the extent of covalency, are known.

The crystal field splitting energy parameter 10 Dq was calculated from the relationship [128].

$$10\ Dq = f(\text{ligand}).\ g(\text{metal ion}) \times 10^{3}\text{cm}^{-1}.$$

The f(ligand) values for the series were derived from the spectra of the chromium(III) chelates since the $^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transition (BAND I) in chromium(III) compounds is a direct measure of 10 Dq. The values of the Racah parameters B_{35} and C were calculated from standard equations which include configurational interactions.

$$E\left\{^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)\right\} = 7.5B_{35} + 15Dq - \tfrac{1}{2}\left\{225B_{35}^{2} + 100\ Dq^{2} - 180\ DqB_{35}\right\}^{\frac{1}{2}}$$

BAND II

$$C = 4\ B_{35}$$

$$\beta_{35} = \frac{B_{35}}{B_{o}}$$

(where B_o is the B term for the free ion. A value of 920 cm^{-1} for B_o is used in the calculation).

Table 28 is a summary of the calculated 10Dq, f(ligand), B_{35}, β_{35} and C parameters for the chromium(III) complexes. The spin-allowed transitions from which B_{35} values were calculated take

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TABLE 28. Calculated 10Dq, f(ligand), B_{35}, β_{35} and C parameters for Chromium(III) β-diketones.

Compound	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$ E(BANDII)$\times10^3$ cm^{-1}	$^4A_{2g} \rightarrow {}^4T_{2g}(F)$ $10D_q$ $\times10^3$ cm^{-1}	g(metal) $\times10^3$ cm^{-1}	f(ligand)	B_{35} cm^{-1}	β_{35}	C cm^{-1}
Cr(tbd)$_3$	23.82	17.79	17.0	1.04(6)	575	0.63	2300
Cr(tftbd)$_3$	22.99	17.86	17.0	1.05(0)	475	0.52	1900
Cr(fbd)$_3$	23.40	17.60	17.0	1.03(5)	551	0.60	2204
Cr(tffbd)$_3$	24.69	17.68	17.0	1.04(0)	699	0.76	2796
Cr(bzac)$_3$	21.74	17.86	17.0	1.05(1)	347	0.38	1388
Cr(bztfac)$_3$	22.73	17.50	17.0	1.02(9)	488	0.53	1952
Cr(tfpybd)$_3$	20.83	17.40	17.0	1.02(4)	305	0.33	1220
Cr(acac)$_3$	23.26	17.86	17.0	1.05(1)	505	0.55	2020

TABLE 29. Calculated $\Delta o \times 10^3 cm^{-1}$ value

Compound	$\Delta o \times 10^3 cm^{-1}$
$Cr(tbd)_3$	17.78
$Cr(tftbd)_3$	17.87
$Cr(fbd)_3$	17.60
$Cr(tffbd)_3$	17.68
$Cr(bzac)_3$	17.86
$Cr(bztfac)_3$	17.50
$Cr(tfpybd)_3$	17.41
$Mn(tbd)_3$	21.97
$Mn(tdbd)_3$	22.07
$Mn(fbd)_3$	21.74
$Mn(tffbd)_3$	21.84
$Mn(bzac)_3$	22.05
$Mn(bztfac)_3$	21.61
$Mn(tfpybd)_3$	21.50
$Fe(tbd)_3$	14.64
$Fe(tftbd)_3$	14.71
$Fe(fbd)_3$	14.49
$Fe(tffbd)_3$	14.56
$Fe(bzac)_3$	14.70
$Fe(bztfac)_3$	14.41
$Fe(tfpybd)_3$	14.34
$Co(tbd)_3$	19.87
$Co(tftbd)_3$	19.97
$Co(fbd)_3$	19.67
$Co(tffbd)_3$	19.76
$Co(bzac)_3$	19.95
$Co(bztfac)_3$	19.55
$Co(tfpybd)_3$	19.46

place between, the strong-field configurations t_{2g}^{3} and $t_{2g}^{2}e_{g}^{1}$. Hence repulsions within both the π - and σ - bonding subsets are believed to determine the value of B_{35}. B_{35} is therefore reduced more by complexation. The fact that β_{35} changes markedly with changes in the substituent groups R_1 and R_2, leads one to conclude that induction has its main effects through σ - bonding system. The order of decreasing β_{35} is equivalent to increasing covalency. This order is independent of the metal ion and is known as the nephelauxetic series of the β-diketones. From the calculated values of β_{35}, the nephelauxetic series of the β-diketones studied is:

Htffbd > Htbd > Hfbd > Hacac > Hbztfac >
Htftbd > Hbzac > Htfpybd.

From Δo (10Dq) values of the complexes (Table 29), one can say that, for each particular β-diketone, the metal ions fall in a decreasing order of Δo, which is in agreement with the spectrochemical series of the metal ions:

Mn(III) > Co(III) > Cr(III) > Fe(III)

Also from the f(ligand) values of the β-diketones the spectrochemical series is,

tfpybd$^-$ < bztfac$^-$ < fbd$^-$ < tffbd$^-$ < tbd$^-$ <
acac $\simeq$ bzac$^-$ <tftbd$^-$.

Although no X-ray crystallographic studies have been done on these compounds except for $Mn(acac)_3$ [23] and $Fe(acac)_3$ [20], it could be safely assumed from the spectral and magnetic properties that, the Al(III), Cr(III), Mn(III), Fe(III) and Co(III) metal ions are all in octahedral environments. Hence, their chelates could likely have octahedral geometries except in the manganese(III) complexes where there is evidence of distortions due to Jahn-Teller effects.

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