METAL(II) TETRAFLUOROBORATE COMPLEXES OF SOME DICARBOXYLIC ACID HYDRAZIDES

By

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ABSTRACT

Eighty-eight divalent metal complexes derived from dihydrazides of oxalic, malonic, succinic, adipic, phthalic and terephthalic acids, with manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II) and magnesium tetrafluoroborates have been prepared. The effect of 1:1 and 1:2 metal to ligand reactant ratios have been examined. The complexes have been characterized on the basis of their analytical data, magnetic susceptibility, electronic and IR spectral studies as well as conductance measurements.

Reactions involving 1:1 and 1:2 metal to ligand ratios gave complexes with different metal to ligand stoichiometry in most cases. It is evident, from the analytical data, that complexes precipitated out mostly with 1:2 and 1:3 metal to ligand stoichiometry. However, complexes of oxalic dihydrazide with Cu(II) and Hg(II), succinic dihydrazide with Co(II), Ni(II), Zn(II) and Mg prepared using a 1:1 molar reactant ratio contained one and a half moles of ligands. Similarly, complexes of Mn(II), Ni(II) and Hg(II) prepared using a 1:2 molar ratio of metal salt to adipic dihydrazide contained one and a half moles of adipic dihydrazide. Nevertheless, reactions involving 1:1 and 1:2 molar reactant ratios gave the same set of compounds in phthalic dihydrazide with Co(II), Ni(II) and Zn(II)

tetrafluoroborates respectively. Likewise the complexes of adipic and malonic dihydrazides with $Zn(BF_4)_2 \cdot 6H_2O$ and $Cd(BF_4)_2 \cdot 7H_2O$ respectively.

The complexes have poor solubilities in methanol, ethanol, acetone, nitrobenzene, nitromethane, benzene, hexane, acetonitrile, dimethylformamide, dimethylsulfoxide and water. But the complexes of manganese(II), cobalt(II), zinc(II) and cadmium(II) with oxalic, malonic, succinic and adipic dihydrazides were found to be soluble in water. Similarly, nickel(II), copper(II) and magnesium complexes of malonic and succinic dihydrazides were soluble in water, so also is the complex of mercury(II) with adipic dihydrazide. In addition, the complexes of succinic dihydrazide, with manganese(II) and cadmium(II) tetrafluoroborates were soluble in dimethylsulfoxide.

The infrared spectra indicate that the bonding sites in these compounds are the carbonyl oxygen and the amino or amide nitrogens.

The electronic and magnetic data of the complexes of manganese(II), cobalt(II), nickel(II) and copper(II) at room temperature suggested that they assume octahedral geometry. Generally, for a given ligand, the 1:2 complex has a lower magnetic moment than the 1:3 complex. The variation of the moments with chain length does not appear to be systematic at

room temperature. However, the magnetic moments for the Zn(II), Cd(II), Hg(II) and Mg indicates that they are diamagnetic with some evidence of polarization paramagnetism.

The conductance data of the complexes that were soluble in water and dimethylsulfoxide revealed 1:2 type electrolytes.

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A special thanks to my loving mother whose care and concern saw me through my ambition.

And to GOD, for making everything possible.

CERTIFICATION BY SUPERVISOR

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DEDICATION

This work is dedicated
to the memory of
MY LATE FATHER
and to
GOD ALMIGHTY
whose Grace made this thesis a success.

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ABBREVIATIONS

ODH - oxalic dihydrazide
MDH - malonic dihydrazide
SDH - succinic dihydrazide
ADH - adipic dihydrazide
PDH - phthalic dihydrazide
TDH - terephthalic dihydrazide
EDTA - ethylenediaminetetraacetic acid disodium salt
DMF - dimethylformamide
DMSO - dimethylsulphoxide
IR - infrared
UV-VIS - ultraviolet visible
UV - ultraviolet
CT - charge transfer
Fig - figure
e.m.u. - electromagnetic unit
c.g.s. - centimetre-gram-second
B.M. - Bohr magneton
$\mu_{eff.}$ - effective magnetic moment
χ_A - the susceptibility per gram atom
χ_M - molar susceptibility
χ_L - ligand diamagnetic correction

χ_{M_c} - calculated molar susceptibility

χ_{M_e} - experimental molar susceptibility

β - beta

e - electronic charge

h - Planck's constant

m - electron mass

c - speed of light

k - Boltzmann's constant

M - metal(II) i.e. Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Mg

mpt - melting point

v - very

s - strong

sh - shoulder

m - medium

w - weak

br - broad

in - insoluble

S - soluble

SS - slightly soluble

SSH - slightly soluble in hot.

CHAPTER ONE

INTRODUCTION

1.1 General

Hydrazides are derivatives of monobasic and polybasic organic acids. They have the general formula, R-$(CONHNH_2)_n$, where n=1 and 2 for mono- and dihydrazides respectively. R can be alkyl, substituted alkyl, aryl, substituted aryl, heterocyclic or alicyclic group. The hydrazide is polyfunctional with the keto, amino and amide groups.

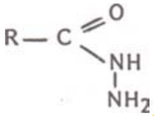


Fig. 1: Hydrazide showing the keto, amino and amide functional groups.

In aqueous solutions, most hydrazides tautomerise into the keto and enol forms[1,2,3]. The enol form could also be in equilibrium with its deprotonated form.

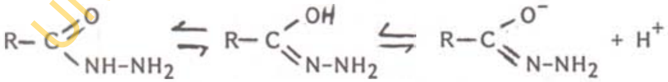
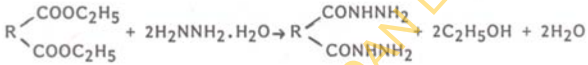


Fig. 2: Tautomeric forms of hydrazides.

The keto form is more in neutral or weakly acidic medium, while the enol form predominates at higher pH[2,4].

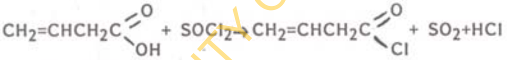
1.1.1 Synthesis of hydrazides

Hydrazides are prepared by refluxing the esters of the parent acids with an excess of 85% hydrazine hydrate with or without the use of solvent[5-8]. This may be represented by the following equation:



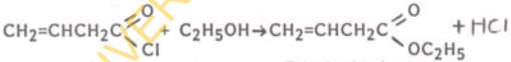
$$\mathrm{R}\begin{array}{l}\diagup \mathrm{COOC_2H_5}\\ \diagdown \mathrm{COOC_2H_5}\end{array} + \mathrm{2H_2NNH_2.H_2O} \rightarrow \mathrm{R}\begin{array}{l}\diagup \mathrm{CONHNH_2}\\ \diagdown \mathrm{CONHNH_2}\end{array} + \mathrm{2C_2H_5OH} + \mathrm{2H_2O}$$

In some cases[8,9], it may be necessary to first prepare the acid chloride from the parent acid, followed by esterification e.g.



$$\mathrm{CH_2{=}CHCH_2C}\begin{array}{l}\diagup\!\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{OH}\end{array} + \mathrm{SOCl_2} \rightarrow \mathrm{CH_2{=}CHCH_2C}\begin{array}{l}\diagup\!\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{Cl}\end{array} + \mathrm{SO_2 + HCl} \quad \ldots\ldots (1)$$

3-Butenoic acid



$$\mathrm{CH_2{=}CHCH_2C}\begin{array}{l}\diagup\!\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{Cl}\end{array} + \mathrm{C_2H_5OH} \rightarrow \mathrm{CH_2{=}CHCH_2C}\begin{array}{l}\diagup\!\!\!\diagup \mathrm{O}\\ \diagdown \mathrm{OC_2H_5}\end{array} + \mathrm{HCl} \quad \ldots . (2)$$

Ethyl vinyl acetate

The hydrazide is subsequently prepared as described above. This procedure is generally applied to the esterification of highly selective acids which might otherwise undergo isomerisation.

1.1.2 Infrared spectra of hydrazides

The infrared spectra of hydrazides and other N-substituted amides have been extensively studied[10-21]. The infrared spectra of hydrazides, irrespective of the nature of R are expected to comprise the following vibrational modes: the range 3000-3500 cm^{-1} contains broad complex bands assigned to the NH stretches of NH and NH_2 groups, and the region between 700-2000 cm^{-1} which usually contains a system of bands due to ν(C=O), ν(C-O), ν(C=N), ν(C-N), δ(NH), δ(NH_2), δ(NCO), δ(C-O), δ(C=N), δ(CCO) among others.

The amide I, II and III bands are found to be related to ν(C=O), (ν(CN)+δ(NH_2)) and (ν(CN)+δ(NH)) bands respectively. The amide I band occurs in the 1610-1690 cm^{-1} region whereas amide II absorbs around 1500-1570 cm^{-1} and amide III around 1200-1295 cm^{-1} respectively. Table 1 shows the IR frequencies of malonic and succinic dihydrazides.

1.1.3 Applications of hydrazides

Hydrazides are biologically active compounds. They are useful as antitubercular agents[5], as plant growth regulators[22], as antispasmodics[23], insecticides and fungicides[24,25]; they also have antitumor and anticancer activities[26-27]. A series of hydrazides also show chemiluminescent properties[7]. Hydrazides have also found use as mask-formers in colour photography[28], as antioxidants for glycerides[29] and an antiknock additives[30]. They

TABLE 1: IR FREQUENCIES (cm^{-1}) OF MALONIC AND SUCCINIC DIHYDRAZIDES [10 - 13]

Malonic dihydrazide	Succinic dihydrazide	Tentative assignments
3200sb	3300sb	ν(NH)
3150m	3180m	$\nu(NH_2)$
1670s	1620s	ν(C = O)
1600sb	1598sb	$\delta(NH_2)$, δ(NNH)
1563s	1550m	ν(CC), δ(CCO)
1540s	1540s 1520sh	ν(CN) + $\delta(NH)_2$
1408m 1310sh 1282sh	1450s 1375sh, 1340s 1320sh 1252w	ν(C – H), ν(CC) $\delta(CH_2)$, δ(HNC)
1247m	1232s	ν(CN) + δ(NH)
1203m 1163m 1142m 1053s	1172s 1120m	δ(HNC), δ(HNN)
1008m	1008s	δ(NN)
962m 908m 855w	942m 890w 850w	δ(C – H) δ(CC)
794m	797w 748m	δ(NCO)

Note: s = strong, m = medium, w = weak, sh = shoulder,
sb = strong and broad, ν= stretching frequency,
δ= bending frequency.

have also been used to enhance the bonding of free sulphur by rubbers during vulcanization[31], and in synthetic polymers[32].

1.2 Preparation of metal complexes of hydrazides

Various methods have been used in the synthesis of metal dihydrazide complexes.

(i) Equimolar amounts of the desired metal salt and ligand dissolved in water/methanol and stirred vigorously and left overnight. In most cases, the complex were formed within an hour of stirring[10,11]. The products were filtered off, washed with cold water and finally with hot methanol and dried in a desiccator over calcium chloride. The following complexes where L = malonic and succinic dihydrazides were synthesised among others using the method described above, or a slight modification of it: $NiL_{3/2}(ClO_4)_2$, $RhL_{3/2}Cl_3$, MnL_2Cl_2, $CdL_{3/2}SO_4$, $ZnL_{3/2}SO_4.2H_2O$, $AgLNO_3.H_2O$, $FeL_{3/2}SO_4.3H_2O$, $PbLCl_2$.

(ii) By refluxing a suspension of 1:3 molar ratio of metal salt to ligand for one hour, and keeping the mixture in ice for 30 minutes, $PrL_3(SCN)_3$, $LnL_3(ClO_4)_2$ (where L is malonic dihydrazide) were isolated[12]. Using the same molar ratio as stated above, $LnL_3(NO_3)_2$ and LnL_3Cl_3 precipitated out immediately[12].

(iii) Using warm aqueous solution and with a 1:1 molar ratio of $Mn(NCS)_2$ to malonic acid dihydrazide, $Mn(DM)_2(NCS)_2.H_2O$ was formed after two to three days[33]. Manganese thiocyanate complexes of succinic, glutaric, adipic, azelaic and sebacic acid dihydrazides have been similarly prepared[33].

1.3 Infrared spectra of hydrazide complexes

The interpretation of the infrared spectra of acid amides, acid hydrazides and similar compounds, have rested on the assignment and identification of amide I $(\nu(C=O))$, amide II $(\nu CN+\delta NH_2)$ and amide III $(\nu CN+\delta NH)$ as well as the NCO deformation vibration[10-12,33-59].

The complexity of the bands in the region 3000-3300 cm^{-1} probably due to the stretching vibrations of the NH bands of the amino and amide groups in which the absorption of H_2O may be superimposed in most cases have made assignments using this region unreliable[3,43-45].

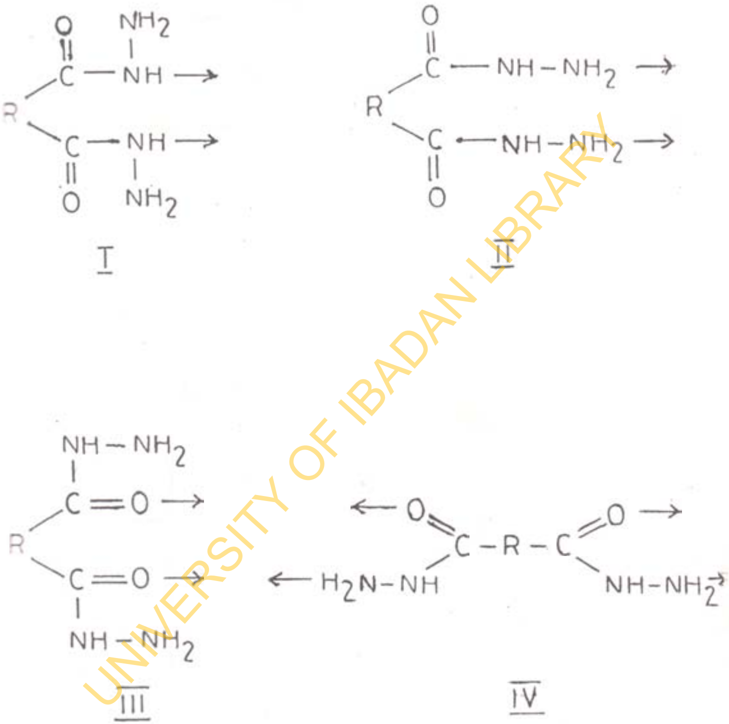
If frequencies are lowered in the spectra of the complexes compared to that of the free ligand, one can infer coordination because the vibrational energy is lowered on bond formation. However, if frequency is stationary, it suggests non-coordination. Likewise, if frequencies increase, it is an indication of non-coordination because vibrational energy increases due probably to some sort of back donation[60] of electrons by the metal ion to the ligands on coordination. The disappearance of the NCO deformation band in dihydrazide complexes may also be an indication of coordination through the amide III band[11].

From spectral data[10-12,33-54], several modes of coordination of dihydrazides were proposed. The potential donor sites are the carbonyl oxygen and the amide or amino nitrogens (Figure 3).

Kharitonov, Machkhosvili, Ahmed and others[10-12,33-54] have established from spectral data that the dihydrazides of carboxylic acids react preferentially as bidentate ligands, forming dimeric or polymeric complexes. The proposed structure[38] of $MnL(NCS)_2.nH_2O$, where L represents the dihydrazides of malonic, succinic, glutaric, adipic, azelaic and sebacic acids, and $n = 0,1,2$ or 3 is as shown in Figure 4.

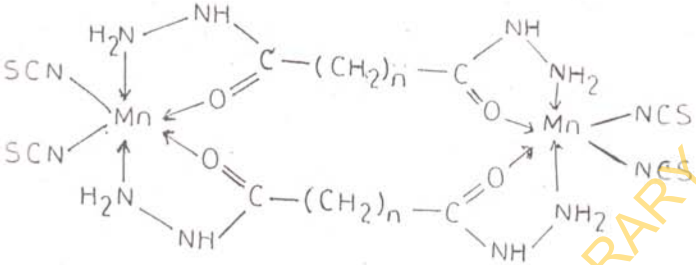
Ahmed and Chaudhuri[11] in their report on the complexes of malonic and succinic dihydrazides with some cobalt, nickel, copper and palladium salts discussed the possibility of a seven-membered ring for succinic dihydrazide. The preference for coordination via the amide nitrogen in their complexes was speculated to mean that the carbonyl group is relatively poorer in electron density than the amide nitrogen.

It should be noted that where the enol form of the hydrazide is involved in complex formation, the infrared spectrum should



R = $(CH_2)_n$, where n = 0, 1 2, 3, 4, ……… or C_6H_4

Fig. 3 Possible coordination modes of dihydrazides



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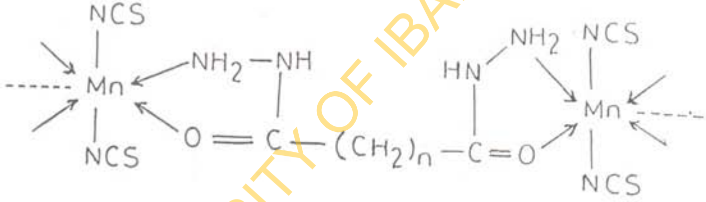


II

Fig. 4 Proposed structure of $MnL(NCS)_2 \cdot nH_2O$

contain an intense band around 1350 cm^{-1} associated with the stretching vibrations of a single C-O bond (ν(C-O)). This band should, of course, be absent from the infrared spectrum of the keto form where there are no C-O single bond[3,4]. The predominantly stretching vibrations of the C=N double bond (ν(C=N)) around 1580 cm^{-1} (inflection) and about 1636 cm^{-1} in the enol forms of hydrazides would also have served a useful diagonistic purpose. However, since this region also contains the bands due to $\delta(NH_2)$ deformation vibrations of the amino group, it is difficult to resolve unambiguously the ν(C=N) and $\delta(NH_2)$ bands without additional investigations.

1.4 Electronic spectra

The reflectance and mull spectral studies[11] on the nickel and cobalt complexes of malonic (MDH) and succinic (SDH) dihydrazides revealed an octahedral environment around nickel(II) and cobalt(II) ions, and signifies the perchlorate coordination[11] in the nickel perchlorate complex of MDH. (Table 2).

1.5 Magnetic properties

Magnetic data have not been generally utilized with dicarboxylic acid hydrazide complexes[10-11,47-48]. Table 3 gives a summary of the magnetic moments at room temperature of some

Table 2: Electronic Spectral Data (cm^{-1}) of Co(II) and Ni(II) complexes of malonic and succinic dihydrazide [11]

Cobalt complexes

Octahedral complexes, ground state $^4T_{1g}(F)$

	$^4T_{2g}(F)$	$^4T_{1g}(P)$
$Co(MDH)_2Cl_2$	9,389	20,000
$Co(MDH)_{3/2}Cl_2$*	10,000	21,053
$Co(SDH)_{3/2}Cl_2.3H_2O$	9,091	20,000

Nickel complexes

Octahedral environment, ground state $^3A_{2g}(F)$

	$^3T_{2g}(F)$	$^3T_{1g}(F)$
$Ni(MDH)_2Cl_2.2H_2O$	10,526	17,241
$Ni(MDH)_{3/2}(ClO_4)_2.H_2O$	10,000	16,393
$Ni(SDH)_{3/2}Cl_2.3H_2O$*	10,638	17,094

*In nujol mull; the rest taken as solids.

TABLE 3: ROOM TEMPERATURE MAGNETIC MOMENTS AND SUGGESTED STEREOCHEMISTRY FOR SOME DIHYDRAZIDE COMPLEXES

Compound	μ_{eff} (B.M.)	Proposed Stereochemistry	Reference
$Mn(C_3H_8N_4O_2)_2Cl_2.2H_2O$	5.64	Octahedral	[10]
$Mn(C_3H_8N_4O_2)_2SO_4.2H_2O$	6.13	Octahedral	[10]
$MnC_4H_{10}N_4O_2SO_4.H_2O$	6.00	Octahedral	[11]
$Mn(C_4H_{10}N_4O_2)_2Cl_2$	5.99	Octahedral	[11]
$FeC_3H_8N_4O_2SO_4.4H_2O$	4.73	Distorted Octahedron	[10]
$Fe(C_4H_{10}N_4O_2)_{3/2}SO_4.3H_2O$	5.65	Octahedral	[11]
$Co(C_3H_8N_4O_2)_2Cl_2$	4.74	Octahedral	[10]
$Co(C_3H_8N_4O_2)_{3/2}Cl_2$	4.49	Octahedral	[10]
$CoC_4H_{10}N_4O_2Cl_2.3H_2O$	4.76	Octahedral	[11]
$Ni(C_3H_8N_4O_2)_{3/2}SO_4.4H_2O$	3.04	Octahedral	[10]
$Ni(C_3H_8N_4O_2)_2Cl_2.2H_2O$	3.34	Octahedral	[11]
$Ni(C_3H_8N_4O_2)_{3/2}(ClO_4)_2.H_2O$	3.15	Octahedral	[11]
$Ni(C_4H_{10}N_4O_2)_{3/2}Cl_2.4H_2O$	3.18	Octahedral	[11]
$Ni(C_4H_{10}N_4O_2)_{3/2}SO_4.2H_2O$	3.01	Octahedral	[11]
$Cu(C_4H_{10}N_4O_2)_{3/2}Cl_2.3H_2O$	2.04	Octahedral	[11]

dihydrazide metal complexes. The values revealed that the complexes are magnetically dilute with absence of metal-metal interactions.

1.6 X-ray studies

X-ray diffraction studies of dihydrazide complexes, like for other coordination compounds, are of interest. The x-ray structure of the compound formed by zinc sulphate with malonic acid dihydrazide[34-35] showed that $ZnC_3H_8N_4O_2\ SO_4.3H_2O$ is made up of polymeric cations, $[ZnC_3H_8N_4O_2(OH_2)_2]^{2+}$ and tetrahedral anions, SO_4^{2-}. It showed[34] (Fig. 5) that malonic dihydrazide is bidentate, forming five-membered metal-containing rings through the oxygen atoms of the carbonyl group and the nitrogen atom of the amino group with different zinc atoms. Two of the water molecules were in the inner sphere to make up the cis-octahedral chain structure, while the sulphato group was outside apparently because of the relatively weak tendency of sulphato groups to enter the inner sphere of the complex.

1.7 Applications of metal complexes of hydrazides

Interest in the study of metal complexes of hydrazides has increased apparently because of their potential biological[34,36,59,61-64] and industrial[65-68] applications.

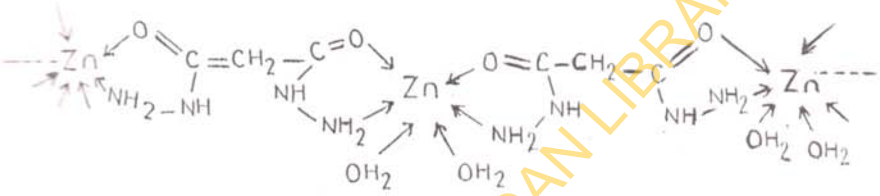


Fig. 5 Cis—octahedral chain structure of $ZnC_3H_8N_4O_2SO_4 \cdot 3H_2O$

(a) The cytostatic[36] and antibacterial[61] activities of hydrazides were further enhanced on complex formation. In vitro studies in animal cells on the behaviour of isonicotinoyl and its copper complex revealed a reduced activity on complexation[62]. This may be due to the fact that amino acids which are present in animal cells have better complexing tendency than the isonicotinic acid hydrazide used.in the study.

(b) Collizi and co-workers[63], in their work, reported the effectiveness of hydrazide complexes in the reduction of the toxic effects of heavy metals in animal cells.

(c) Metal complexes of hydrazides have also found use as synthetic high polymers[67].

(d) They are used in analytical chemistry in the spectrophotometric determination of gold, copper and cobalt[68].

Aim of the Work

Though the complexes of monocarboxylic acid hydrazides are well known[1,2,4], those of dicarboxylic acid hydrazides have received less attention[10-12,47,48]. Studies on the possible effect of varying metal to ligand reactant ratios have not been systematically carried out.

A survey of the literature showed that no work has yet been reported on metal(II) tetrafluoroborate complexes of dicarboxylic acid hydrazides.

Divalent tetrafluoroborates of manganese, cobalt, nickel, copper, zinc, cadmium, mercury and magnesium will be prepared and complexed with the hydrazides of oxalic, malonic, succinic, adipic, phthalic and terephthalic acids. This will be done using a 1:1 and 1:2 metal to ligand reactant ratios. The complexes will be characterized by elemental analysis, room temperature magnetic susceptibility, electronic and infrared spectral studies as well as conductance measurements.

The results are expected to provide information relating to their possible structures and also provide information that will be of use in future as to their possible biological and industrial applications.

CHAPTER TWO

THEORETICAL

2.1 Electronic spectra[60,69-75]

Each of the several electrons in a partly filled shell may be assigned its own set of four quantum numbers n, l, M_L, and s; where n is the principal quantum number, L azimuthal or orbital quantum number, M_L magnetic quantum number and s the spin quantum number.

In filling an orbital with two electrons for instance, the spin quantum number is employed so that the Pauli's exclusion principle is satisfied. There are usually strong interactions among these electrons. These are spin-spin coupling, orbit-orbit coupling and spin-orbit coupling.

Russel-Saunders or L-S coupling scheme

This scheme assumes that

$$\underset{s_1s_2}{\text{spin-spin coupling}} > \underset{l_1l_2}{\text{orbit-orbit coupling}} > \underset{s_1l_1}{\text{spin-orbit coupling}}$$

This situation is found to apply to the elements in the first transition series and the ground state of the heavier metals. For convenience, the terms which may arise by Russel-Saunders coupling from all d^n configurations are listed in Table 4.

TABLE 4: TERMS ARISING FROM THE d^n CONFIGURATION

Configuration	Terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F, ^4P, ^2G, ^2H, ^2F, $^2D_{(2)}$, ^2P
d^4, d^6	^5D, ^3H, ^3G, $^3F_{(2)}$, ^3D, $^3P_{(2)}$ ^1I, $^1G_{(2)}$, ^1F, $^1D_{(2)}$, $^1S_{(2)}$
d^5	^6S, ^4G, $^4F_{(2)}$, $^4P_{(2)}$, ^2I, $^2H_{(2)}$, $^2G_{(2)}$, $^2F_{(2)}$, $^2D_{(3)}$, $^2P_{(2)}$, ^2S.
d^0, d^{10}	$^1S_{(3)}$.

N.B.: Figures in parentheses refer to the number of times the term occurs.

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 (spin selection rule). Other transitions which involve redistribution of electrons in a single quantum shell (e.g. d→d, p→p, s→s, etc.) are orbitally forbidden (Laport rule). For an orbitally allowed transition, $\Delta L = \pm 1$. And for a transition to satisfy the electronic selection rule, the symmetry of the wave-function must change as excitation occurs, that is $\Delta \Psi = 0$, hence transitions of the type g→g and u u are described as being parity forbidden whereas g→u is parity allowed. g and u are spectroscopic terms describing the symmetry of the wave function (Ψ) where g = gerade and U = ungerade.

In an octahedral complex for example, 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 g→u and is therefore allowed.

"Intensity stealing": This phenomenon occurs when a ligand field transition occurs close to a charge-transfer band, causing the intensity of the ligand field to increase markedly. This is believed to be due to the mixing of the electronic wavefunctions of the forbidden excited term with the allowed level, resulting in electronic transitions to the excited term becoming allowed. This phenomenon decreases rapidly as the separation between the allowed and forbidden bands increases.

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

In a ligand field, the terms arising from free-ion d^n configurations in both octahedral and tetrahedral fields are listed in Table 5.

A high spin d^5 configuration is not expected to have strong d d transitions because there is no excited state of the same spin multiplicity as the ground term is $^6A_{1g}$ (Figure 6).

In high spin d^7 ion in an octahedral field, the ^4F ground state and ^4P lowest excited state of cobalt(II) ion splits according to the energy diagram shown in Figure 7.

In an octahedral field, the splitting pattern of d^8 nickel(II) ion is as shown in Figure 8.

TABLE 5: TERMS ARISING FROM d^n CONFIGURATIONS IN OCTAHEDRAL AND TETRAHEDRAL FIELDS

State of free ion	States in the crystal field
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$
H	$E + 2T_1 + T_2$

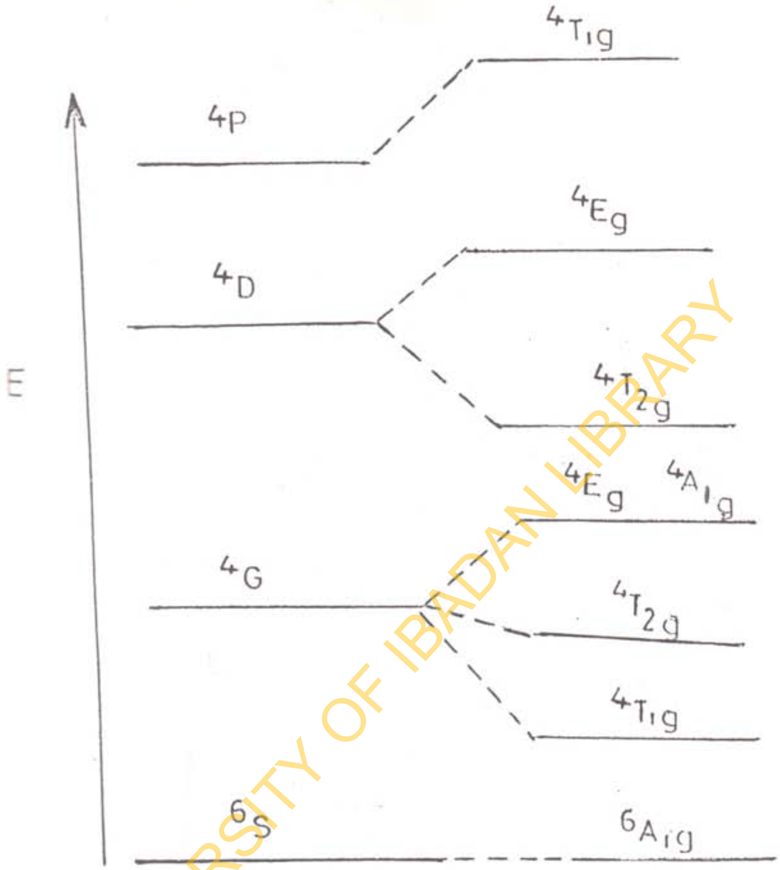


Fig. 6: Splitting of the d^5 ion in the presence of octahedral field (e.g Mn^{2+})

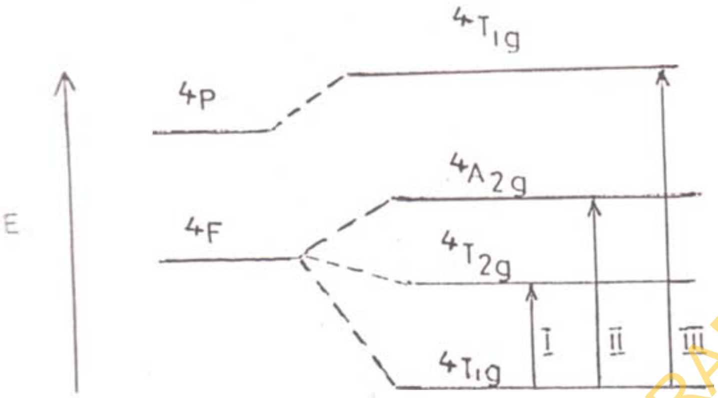


Fig. 7 Splitting of the d^7 ion in an octahedral field (e.g Co^{2+})

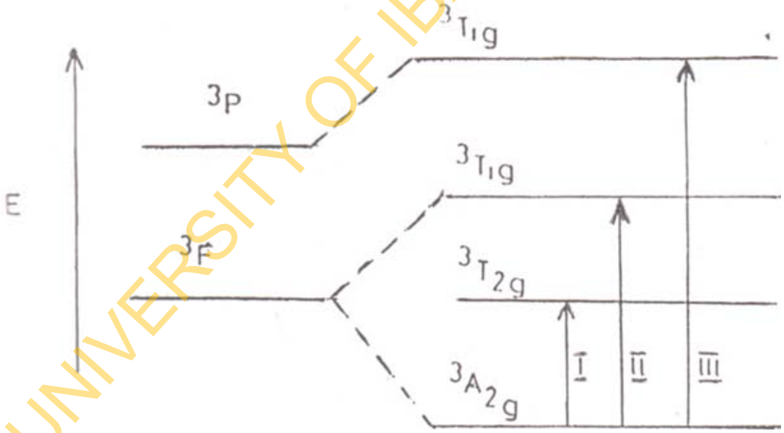


Fig. 8 Splitting of the d^8 ion in an octahedral field (e.g Ni^{2+})

The d^9 configuration gives rise to the ^2D ground term. In an octahedral field, the ground term is ^2Eg, hence there is only one transition in the octahedral field, ^2Eg $^2T_{2g}$ as shown in Figure 9. In a tetrahedral field, the transition is however $^2T_2$ ^2E. Though a single transition is predicted, there are actually several transitions in close proximity[60].

Magnetochemistry[60,69,72,77-79]

Magnetochemical measurements are associated with the presence of paramagnetism, which inturn may be related to the presence of unpaired electrons in the metal ion. When a substance is placed in a magnetic field of strength H, the magnetic flux B within the substance is given by:

$$B = H + 4\pi I \qquad \ldots \qquad (2.2.1)$$

where I is the intensity of magnetization or magnetic moment per unit volume. Alternatively, we can divide by H and write

$$P = 1 + 4\pi K \qquad \ldots \qquad (2.2.2)$$

where P is the permeability and K the susceptibility per unit volume.

If the field is introduced to a paramagnetic substance, there is a tendency for the magnetic dipoles of the paramagetic material to be aligned in the direction of the field. For a diagmagnetic substance there is polarization of the electron cloud.

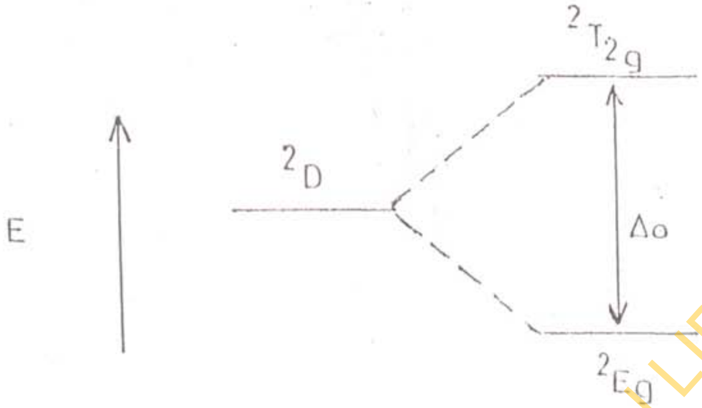


Fig. 9 Splitting of the d^9 ion in an octahedral field (e.g Cu^{2+})

In either case, equation (2.2.1) and (2.2.2) holds.

In practice, susceptibility is usually expressed per unit mass and given the symbol g

$$\chi_g = K/\rho \qquad \ldots \qquad (2.2.3)$$

where ρ is the density of the material. And the molar susceptibility χ_m is defined as

$$\chi_m = \chi_g . M \qquad \ldots \qquad (2.2.4)$$

where M is the molecular mass of the material.

On the basis of I, K and χ, therefore, substance may be divided into three categories: diamagnetic, paramagnetic and ferro- or antiferromagnetic.

Diagmagnetism: Substances with negative susceptibilities are said to be diamagnetic and have values of the order of -1 to -500×10^{-6} c.g.s. units are usually independent of field strength and temperature. The diamagnetic susceptibility of a molecule may be written as:

$$\chi_{mol} = \sum_i n_i\chi_i + \sum \varepsilon \qquad \ldots \qquad (2.2.5)$$

where the molecule contains n_i atoms of atomic susceptibility, χ_i (i.e. per gram atom), χ_i represents "constitutive" corrections which depend on the nature of the bonds involved. All substances have diamagnetic susceptibility hence it is necessary to attempt to correct for this in determining paramagnetic susceptibilities. Diamagnetism arises mostly from the interaction of paired electrons with the magnetic field.

Paramagnetism: Paramagnetic compounds have positive susceptibilities and these are of the order 0-100 x 10^{-6} c.g.s. units, and are independent of field strength, but dependent on temperature (inversely) because the ordering of the magnetic moments that give rise to them is resisted by thermal motion. The variation of paramagnetic susceptibility χ, with temperature T is given by Curie's law

$$\chi = C/T$$

where C is the Curie's constant. Normal paramagnetic substances substances obey the Curie law, and most substances obey the Curie-Weiss law.

$$\chi = C/T + \theta$$

θ is known as the Weiss constant.

The magnetic properties of paramagnetic substances are usually expressed in terms of the effective magnetic moment, μ_e shown by the equation

$$\chi_A = \frac{N\beta^2\mu_e^2}{3kT} + N\alpha$$

where β is the Bohr magneton = 0.9273×10^{20} erg/guass, K is the Boltzmann's constant = 1.3806×10^{-6} erg/deg, χ_A is the susceptibility per gram atom, $N\alpha$ is the temperatue independent paramagnetism, and N is the Avogadro's number.

$$\mu_e = 2.828\sqrt{(\chi_A - N\ )T} \quad \text{B.M.}$$

The temperature independent paramagnetism, N is often neglected and the effective magnetic moment μ_e becomes

$$\mu_e = 2.828\sqrt{\chi_A T} \quad \text{B.M.}$$

Usually, the effective magnetic moment, μ_e, of a paramagnetic material lies between $\mu_s = \sqrt{4s(s+1)}$ and $\mu_{s+L} = \sqrt{4s(s+1)+L(L+1)}$ that is μ_s (spin only magnetic moment) and μ_{s+L} (spin + orbital contribution) respectively. When μ_e exceeds μ_s, it is assumed to be finite value of L, i.e. of an "orbital contribution" to the magnetic moment. For an electron to have orbital angular moment about an axis, the orbital which it occupies must be transformable into an entirely equivalent and degenerate orbital by rotation about the axis in question. Both orbitals must contain electrons of the same spin. For a free ion, all the orbitals are degenerate and the dxy, dxz and dyz orbitals are transformable into each other by 90° rotations about the relevant axes. And 45° rotations of the dxy orbital about the z axis transform it into the dx^2-y^2 orbital.

For d^5 and d^{10}, L=O and no orbital contribution to the magnetic moment is expected. In these cases, every orbital contains electrons of the same spin, thus preventing the development of any orbital angular momentum.

In an octahedral or tetrahedral field, the d orbitals are split into triplet, t_{2g} (dxy, dyz, dxz) and a doublet eg (dz^2, dx^2-y^2), which are no longer degenerate. Thus, the dx^2-y^2 and dz^2 orbitals, being of different shapes, cannot be interchanged and hence have no orbital angular momentum associated with them. Also the interchange of dxy and dx^2-y^2 orbitals which hitherto was an important source of orbital contribution in the free ion has been quenched. In the octahedral field, therefore, the configurations t_{2g}^{3} and t_{2g}^{6} will now have a total angular momentum of zero, while among the high spin complexes only the configurations t_{2g}^{1}, t_{2g}^{2}, $t_{2g}^{4}eg^{2}$ and $t_{2g}^{5}eg^{2}$ have any orbital angular momentum. For tetrahedral species only, the configurations $e^2t_2^1$, $e^2t_2^2$, $e^4t_2^4$ and $e^4t_2^5$ is expected to have orbital angular momentum. However, in cases where orbital contributions are not expected of a particular configuration, the effective magnetic moment still differs from the spin only value. For instance, it is not expected that A and E terms should give any orbital contribution. But, if there is a T term of the same multiplicity at a higher energy level, it is possible for the spin-orbit coupling to "mix" some of this into the ground term, thus introducting certain amount of orbital angular momentum into the latter. A and E terms arising from F and D terms respectively are accompanied by a higher T term of the same multiplicity. For these, the "mixing-in" effect is expressed by the formula:

$$\mu_e = \mu_s \left(1 - \frac{\alpha h}{10Dq}\right)$$

where α is a constant which depends on the spectroscopic ground state and the number of d electrons, $\alpha = 4$ for A terms and 2 for E terms; λ is the spin-orbit coupling constant for the terms involved, and 10Dq is the separation between the ground level and the level being mixed in. The parameter λ is positive for less than half-filled shells and negative for more than half-filled shells, α and 10Dq are positive quantities. Hence, the observed moments may be greater or less than the spin only value.

The magnetic moments of the complexes with T ground terms generally vary with temperature and depart significantly from the spin-only value.

Ferromagnetism and Antiferromagnetism: These are special cases of paramagnetism where the magnetic dilution is inadequate, thus making the magnetic dipoles on adjascent paramagnetic centres interact. The two possibilities are either that adjascent 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. Ferro- and antiferromagnetism are known as "cooperative phenomena". In ferromagnetic materials, $P \gg 1$ and can be as high as 10^4, being both field and temperature dependent. In antiferromagnetic materials χ is usually less than for normal paramagnetic materials and it is temperature and sometimes field dependent.

Figure 10 compares the temperature dependence of the susceptibility for (1) a normal paramagnetism, (2) ferromagnetism, and (3) antiferromagnetism.

For ferromagnetism above T_c, the substance follows Curie or the Curie-Weiss law and susceptibility is independent of field strength. Below T_c, the susceptibility does not depend on temperature or field strength in a simple manner. For

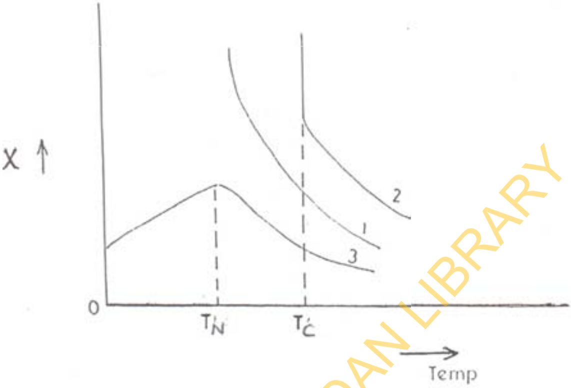


Fig. 10 The qualitative temperature dependence of magnetic susceptibility for (1) normal paramagnetism (2) Ferromagnetism and (3) Antiferromagnetism

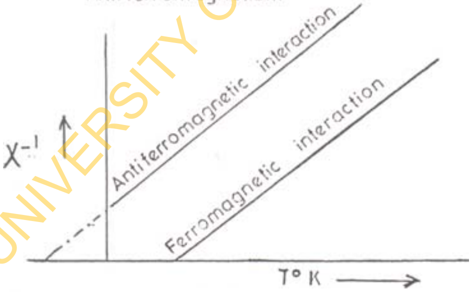


Fig. 11 Deviations from the Curie Law that may be fitted to the Curie – Weiss Law

antiferromagnetism there is again a characteristic temperature, T_N, called the Neel temperature. Above T_N the susceptibility drops with decreasing temperature.

In general, in magnetically concentrated systems a positive Weiss constant is characteristic of antiferromagnetism and a negative one of ferromagnetism (Figure 11).

Many methods have been employed in the measurements of the magnetic properties of materials in solid, liquid and gaseous states among which are the Gouy, Faraday, Quincke and NMR methods. The simplest and most commonly used method is the Gouy method.

2.3 Infrared spectra[69,80-83]

The energies required for molecular vibrations are comparable to those of quanta of infrared radiation. A simple diatomic covalent bond is considered as a spring with atomic masses at either side. The stiffness of the spring is described by a force constant, K. When in motion, the induced vibrations are adequately described by Hooke's law of simple harmonic

$$F = -kX \qquad \ldots \qquad (2.3.1)$$

where F is the force tending to restore it to equilibrium, k is the force constant and X is the displacement. The force constant (k) is a direct measure of the bond strength. The force constant (k) is a direct measure of the bond strength. The frequency of motion is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \ldots \qquad (2.3.2)$$

where μ is the reduced mass, i.e. the harmonic mean of the individual masses.

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \ldots \qquad (2.3.3)$$

or

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \ldots \qquad (2.3.4)$$

From quantum theory, only certain energy transitions are allowed, as determined by a quantum number, n

$$E_n = (n + \tfrac{1}{2})h\nu \qquad \ldots \qquad (2.3.5)$$

where n = 0,1,2,3, ... etc.

From the Bohr's principle, the frequency of a radiation exciting a molecule from the lowest energy level (n=0) of energy E_o to the first energy level (n=1) of energy E_1 is given by

$$h\nu = E_1 - E_o \qquad \ldots \qquad (2.3.6)$$

Equation (2.3.5) gives the value of $E_0 = \frac{1}{2}h\nu$ and $E_1 = 3/2h\nu$. By substituting therefore in Bohr's equation, give

$$\nu = \frac{(E_1+E_0)}{h} \qquad \ldots \qquad (2.3.7)$$

Selection rules

1. For a molecule to absorb infrared radiation, there must be a change in dipole moment during molecular vibrations.
2. The change in the vibrational quantum number must be equal to ±1.
3. For overtones and combinations, $n = \pm 2, \pm 3, \pm 4, \ldots$

The absorption bands in the infrared region of the spectrum, arising from excitation of molecular vibrations and rotations, are determined by the arrangement of atoms in space, their masses, bond lengths and angles and by the forces between them.

There are two types of fundamental vibrations: stretching, in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis, and bending (or deformation), in which the position of the atom changes relative to the original bond axis.

A non-linear molecule that contains n atoms has 3n-6 possible fundamental modes that can be responsible for the absorption of infrared radiation. For a linear molecule there are however, 3n-5 possible fundamental vibrational modes. However, if the absorption occurs outside the region ordinarily examined or if the resulting absorptions are so close that they cannot be resolved or of very weak intensity, the predicted number of peaks will not be observed.

Additional (non-fundamental) absorption bands may occur because of the presence of overtones (or harmonics), combination bands (the sum of two or more different vibrations) and difference bands (the difference of two or more different vibrations).

The spectrum of a coordinated ligand differs from that of the free ligand since an additional atom is introduced into the ligand vibrating system; the bond lengths, angles and interatomic forces are directly or indirectly affected. The differences between the spectra of free ligand and complex fall into three categories.

1. Band position: On coordination, bands associated with the stretching of bonds involving the coordinated atom(s) usually move to longer wavelength (lower energy). For example, the free carbonate anion absorption at 890 cm^{-1} shifts to 850 and 830 cm^{-1} on coordination as unidentate and bidentate ligand respectively.

2. Relative band intensities: While the band position remains unchanged, there is a change in the intensity.

3. Splitting of the bands: Single peaks in the free ligand may be split into several closely spaced bands in the complex.

In practice, the spectrum of the ligand is usually compared with that of a compound in which the ligand is coordinated.

CHAPTER THREE

EXPERIMENTAL

3.1 Reagents

Adipic acid, terephthalic acid, diethyl oxalate, diethyl malonate, diethyl succinate, diethyl phthalate, calcium carbonate, manganese carbonate, cobalt carbonate, nickel carbonate, copper carbonate (basic), zinc carbonate (basic), cadmium carbonate, mercury carbonate, magnesium carbonate, sodium sulphate, sodium hydrogen carbonate, hydrazine hydrate, fluoroboric acid, ethylenediamine tetraacetic acid (sodium salt), zinc sulphate heptahydrate, ammonium chloride, hexamine, solochrome black, xylenol orange, murexide, triethanolamine, hydroxylammonium chloride, potassium nitrate, sodium chloride (spectroscopic grade), perchloric acid, nitric acid, sulphuric acid, ammonium hydroxide.

Solvents. Methanol, ethanol, benzene, hexane, acetone, nitrobenzene, nitromethane, acetonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF). The solvents were further purified, using the appropriate methods outlined in the literature[8].

All the reagents were obtained from British Drug Houses (BDH) Chemical and the Fischer Scientific Company Ltd.

3.2 Preparation of the ligands[5,6,8,9,11,86]

3.2.1 Preparation of oxalic dihydrazide (ODH)

This was prepared by adding 20 g diethyl oxalate (0.137 mol) into 20 ml (0.382 mol) hydrazine hydrate in a 250 ml beaker while stirring with a Gallenkamp magnetic stirrer at room temperature. The white precipitates of ODH which separated were filtered, washed several times with ethanol and dried in a vacuum desiccator over silica gel.

3.2.2 Preparation of malonic dihydrazide (MDH)

A sample of 25 g diethyl malonate (0.156 mol) was slowly added into a 250 ml beaker containing 25 ml (0.479 mol) hydrazine hydrate and stirred as described above. The white precipitates which formed were filtered off, washed thoroughly with ethanol and dried in a desiccator over silica gel.

3.2.3 Preparation of succinic dihydrazide (SDH)

A quantity of 30 g diethyl succinate (0.172 mol} was slowly added to 30 ml (0.575 mol) hydrazine hydrate in a beaker with stirring. The white precipitates were filtered off, washed several times with ethanol and dried as before over silica gel.

3.2.4 Preparation of adipic dihydrazide (ADH)

Adipic acid (74.9 g,0.513 mol) was placed in a two-litre round-bottomed flask. Ethanol (95.3 ml) was added followed by benzene (187.5 ml) and concentrated sulphuric acid (16.5 ml), while gently swirling the contents of the flask. The mixture was then refluxed for six hours on a water bath. The contents of the flask were then poured into a large volume (500 ml) of distilled water. The benzene layer was separated from the aqueous layer using a separating funnel. The aqueous layer was further washed with ether and the ether extract added to the benzene layer. The mixture was then washed with a saturated solution of $NaHCO_3$ until effervescence ceased. It was further washed several times with water. Anhydrous Na_2SO_4 was then added to dry the mixture. The distillation of the diethyl ester was carried out under reduced pressure. The diethyl adipate collected was redistilled several times to ensure high purity[8].

The adipic dihydrazide (ADH) was obtained by adding 20 g (0.099 mol) of the diethyl adipate slowly into a beaker containing 20 ml (0.383 mol) of hydrazine hydrate with stirring for four hours. The white precipitates formed were filtered, washed with ethanol and dried in a vacuum desiccator over silica gel.

3.2.5 Preparation of phthalic dihydrazide (PDH)

Diethyl phthalate (27 g, 0.121 mol) was placed in a 250 ml round-bottomed flask containing hydrazine hydrate 27 ml

(0.517 mol). The mixture was refluxed for 3 hours on a water bath. The dirty white caky precipitate which formed was filtered, washed several times with ethanol and dried in vacuo over silica gel.

3.2.6 Preparation of terephthalic dihydrazide (TDH)

A mixture of terephthalic acid, 25 g (0.151 mol), ethanol (300 ml) and concentrated H_2SO_4 (12.5 ml) was refluxed for sixteen hours and distilled to half its volume and poured into aqueous Na_2CO_3 (250 ml). The brownish precipitate of diethyl terephthalate obtained was recrystallized from ethanol and dried in a vacuum desiccator over silica gel (M.pt. (°C) 42-44, literature value[84] 42-44). Terephthalic dihydrazide (TDH) was obtained by refluxing a mixture of diethyl terephthalate 14 g (0.063 mol), ethanol (150 ml) and 14 ml (0.268 mol) hydrazine hydrate in a round-bottomed flask for four hours on a water bath. The dirty white precipitates of TDH were washed thoroughly with ethanol and dried as described above.

3.3 Preparation of the complexes

3.3.1 Preparation of manganese(II) tetrafluoroborate ($Mn(BF_4)_2.6H_2O$)

Excess manganese(II) carbonate was added, pinchwise, to 30 ml of tetrafluoroboric acid in a 250 ml beaker with stirring until effervescence ceased. The mixture was then filtered and concentrated by heating on a hot plate and left in a desiccator over silica gel to crystallize. Manganese was determined by EDTA titration using Solochrome black as an indicator[85]. The analytical data are shown in Table 6.

3.3.1.1 Preparation of Mn(II) tetrafluoroborate complexes

3.3.1.2 Preparation of $Mn(ODH)_2(BF_4)_2$ and $Mn(ODH)_3(BF_4)_2$.

$Mn(ODH)_2(BF_4)_2$. A 1:1 molar ratio of oxalic dihydrazide (2.36 g, 0.02 mol), $Mn(BF_4)_2.6H_2O$ (6.74 g, 0.02 mol) in 90 ml methanol was stirred for 15 hours using a Gallenkamp magnetic stirrer at room temperature. The white compound which formed was filtered, washed thoroughly with methanol and dried over silica gel in a vacuum desiccator.

$Mn(ODH)_3(BF_4)_2$. A mixture of ODH (2.36 g, 0.02 mol) and $Mn(BF_4)_2.6H_2O$ (3.37 g, 0.01 mol) in 80 ml methanol was stirred for 16 hours. The product obtained was isolated as described for $Mn(ODH)_2(BF_4)_2$.

3.3.1.3 Preparation of $Mn(MDH)_2(BF_4)_2$ and $Mn(MDH)_3(BF_4)_2$.

$Mn(MDH)_2(BF_4)_2$. A quantity of 2.64 g (0.02 mol) malonic dihydrazide (MDH), and 6.74 g (0.02 mol) $Mn(BF_4)_2.6H_2O$, in

100 ml methanol was stirred for 19 hours using a magnetic stirrer. The white precipitates of $Mn(MDH)_2(BF_4)_2$ obtained were filtered, washed with methanol and dried in a vacuum desiccator over silica gel at room temperature.

$Mn(MDH)_3(BF_4)_2$. A mixture of MDH (2.64 g 0.02 mol) and (3.37 g 0.01 mol) $Mn(BF_4)_2.6H_2O$ in 95 ml methanol was stirred for 18 hours. The whitish compound which formed was filtered off, washed several times with methanol and dried in vacuo over silica gel.

3.3.1.4 Preparation of $Mn(SDH)_2(BF_4)_2$ and $Mn(SDH)_3(BF_4)_2$.

$Mn(SDH)_2(BF_4)_2$. This was prepared using the procedure outlined for $Mn(MDH)_3(BF_4)_2$ but with (2.92 g, 0.02 mol) succinic dihydrazide (SDH) and (6.74 g, 0.02 mol) $Mn(BF_4)_2.6H_2O$.

$Mn(SDH)_3(BF_4)_2$. Using a 2:1 molar ratio of SDH and $Mn(BF_4)_2.6H_2O$ and a similar procedure as outlined above, $Mn(SDH)_3(BF_4)_2$ was isolated.

3.3.1.5 Preparation of $Mn(ADH)_{3/2}(BF_4)_2$ and $Mn(ADH)_3(BF_4)_2$.

$Mn(ADH)_{3/2}(BF_4)_2$. With a 1:1 molar ratio of (1.74 g, 0.01 mol) adipic dihydrazide (ADH) and (3.37 g, 0.01 mol) $Mn(BF_4)_2.6H_2O$, stirred for 17 hours in 90 ml methanol, whitish

$Mn(ADH)_{3/2}(BF_4)_2$ was prepared.

$Mn(ADH)_3(BF_4)_2$. Using a similar procedure as outlined for $Mn(MDH)_3(BF_4)_2$ but with a 2:1 molar ratio of ADH to $Mn(BF_4)_2.6H_2O$, $Mn(ADH)_3(BF_4)_2$ was isolated.

3.3.1.6 Preparation of $Mn(PDH)_2(BF_4)_2$ and $Mn(PDH)_3(BF_4)_2$

$Mn(PDH)_2(BF_4)_2$. To a solution of $Mn(BF_4)_2.6H_2O$ (3.37 g, 0.01 mol) in 100 ml methanol was added (1.94 g, 0.01 mol) phthalic dihydrazide (PDH). The mixture was stirred for 18 hours at room temperature and the dirty white precipitates formed were isolated as before.

$Mn(PDH)_3(BF_4)_2$. With a similar procedure as described for $Mn(PDH)_2(BF_4)_2$ and a 2:1 molar ratio of PDH to $Mn(BF_4)_2.6H_2O$, $Mn(PDH)_3(BF_4)_2$ was isolated.

3.3.1.7 Preparation of $Mn(TDH)_3(BF_4)_2$

Using (1.94 g, 0.01 mol) terephthalic dihydrazide (TDH) and (3.37 g, 0.01 mol) of $Mn(BF_4)_2.6H_2O$, $Mn(TDH)_3(BF_4)_2$ was obtained in the manner $Mn(PDH)_2(BF_4)_2$ was isolated.

3.3.2 Preparation of cobalt(II) tetrafluoroborate ($CO(BF_4)_2.6\ H_2O$)

An excess of Co(II) carbonate was added, pinchwise, to 45 ml of tetrafluoroboric acid in a 250 ml beaker. $Co(BF_4)_2.6H_2O$

was then isolated as described for $Mn(BF_4)_2.6H_2O$ above. Cobalt was estimated by EDTA titrations using xylenol orange as an indicator[85]. The analytical result is presented in Table 6.

3.3.2.1 Preparation of Co(II) tetrafluoroborate complexes

3.3.2.2 Preparation of $Co(ODH)_2(BF_4)_2$ and $Co(ODH)_3(BF_4)_2$

$Co(ODH)_2(BF_4)_2$. A quantity of 2.36 g (0.02 mol) of ODH was mixed with 6.82 g (0.02 mol) of $Co(BF_4)_2.6H_2O$ in 90 ml of methanol and stirred using a Gallenkamp magnetic stirrer for 14 hours at room temperature. The pinkish product was filtered, washed several times with methanol and dried over silica gel in a vacuum desiccator.

$Co(ODH)_3(BF_4)_2$. A mixture of ODH (2.36 g, 0.02 mol) and $Co(BF_4)_2.6H_2O$ (3.41 g, 0.01 mol) in 80 ml of methanol was stirred. The pink coloured compound which precipitated was filtered off, washed thoroughly with methanol and dried as before.

3.3.2.3 Preparation of $Co(MDH)_{3/2}(BF_4)_2$ and $Co(MDH)_3(BF_4)_2$.

$Co(MDH)_{3/2}(BF_4)_2$. A mixture of malonic dihydrazide (2.64 g, 0.02 mol) and $Co(BF_4)_2.6H_2O$ (6.82 g, 0.02 mol) in 100 ml of methanol contained *in a quick-fit conical flask* was stirred for 16 hours. The pinkish powdery compound formed was isolated as described before.

$Co(MDH)_3(BF_4)_2$. A mixture of 2.64 g (0.02 mol) MDH and (3.41 g, 0.01 mol), $Co(BF_4)_2.6H_2O$ in 100 ml of methanol was stirred for 18 hours using a magnetic stirrer. The pinkish compound formed was separated by filtration, washed thoroughly with methanol and dried over silica gel.

3.3.2.4 Preparation of $Co(SDH)_2(BF_4)_2$ and $Co(SDH)_3(BF_4)_2$.

$Co(SDH)_2(BF_4)_2$. A quantity of SDH (2.92 g, 0.02 mol) and $Co(BF_4)_2.6H_2O$ (6.82 g, 0.02 mol) mixed together in 90 ml of methanol was stirred for 19 hours. The pink product was isolated as described before.

$Co(SDH)_3(BF_4)_2$. A 1:2 molar mixture of SDH (5.82 g, 0.04 mol) and $Co(BF_4)_2.6H_2O$ (6.82 g, 0.02 mol) in 100 ml of methanol was stirred for 20 hours in a conical flask at room temperature. The pinkish product was isolated by filtration and thorough washing with methanol and dried in vacuo over silica gel.

3.3.2.5 Preparation of $Co(ADH)_2(BF_4)_2$ and $Co(ADH)_3(BF_4)_2$

$Co(ADH)_2(BF_4)_2$. A 1:1 molar mixture of adipic dihydrazide (1.74 g, 0.01 mol) and $Co(BF_4)_2.6H_2O$ (3.41 g, 0.01 mol) in

80 ml of methanol was stirred for 16 hours. The pink precipitate was isolated and dried in the manner described above.

Co(ADH)$_3$(BF$_4$)$_2$. A mixture of ADH, 3.48 g (0.02 mol) and 3.41 g (0.01 mol) of Co(BF$_4$)$_2$.6H$_2$O in 90 ml methanol was stirred. The pink coloured compound formed was isolated as before.

3.3.2.6 Preparation of Co(PDH)$_3$(BF$_4$)$_2$

To a solution of Co(BF$_4$)$_2$.6H$_2$O (3.45 g, 0.01 mol) in 95 ml methanol was added 1.94 g (0.01 mol) of PDH. The mixture was stirred and the precipitates filtered off, washed thoroughly with methanol and dried in a vacuum desiccator over silica gel.

A 1:2 molar mixture of metal salt to PDH yielded the same product.

3.3.2.7 Preparation of Co(TDH)$_3$(BF$_4$)$_2$

A mixture of 1.94 g (0.01 mol) of terephthalic dihydrazide and 3.41 g (0.01 mol) of Co(BF$_4$)$_2$.6H$_2$O in 90 ml methanol was stirred for 20 hours at room temperature. The pink precipitate formed was isolated as described for Co(PDH)$_3$(BF$_4$)$_2$.

3.3.3 Preparation of Ni(II) tetrafluoroborate ($Ni(BF_4)_2.6H_2O$)

To 40 ml of HBF_4 was added, pinchwise, excess basic nickel(II) carbonate until effervescence ceased. The resulting mixture was filtered and concentrated by heating on a hot plate and left in a desiccator to crystallize. Nickel was determined by EDTA titration using murexide as an indicator[85]. The analytical data is shown in Table 6.

3.3.3.1 Preparation of Ni(II) tetrafluoroborate complexes

3.3.3.2 Preparation of $Ni(ODH)_2(BF_4)_2$ and $Ni(ODH)_3(BF_4)_2$

$Ni(ODH)_2(BF_4)_2$. A mixture of oxalic dihydrazide (2.95 g, 0.025 mol) and 8.50 g (0.025 mol) $Ni(BF_4)_2.6H_2O$ in methanol (98 ml) was stirred in a quick-fit conical flask for 16 hours using a magnetic stirrer at room temperature. The light blue compound which formed was filtered, washed thoroughly with methanol and dried over silica gel in a vacuum desiccator.

$Ni(ODH)_3(BF_4)_2$. A mixture of oxalic dihydrazide (5.90 g, 0.050 mol) and $Ni(BF_4)_2.6H_2O$ (8.50 g, 0.025 mol) in methanol (150 ml) was stirred as described above. A 2:1 molar ratio of ligand to metal was used. The light blue compound formed was filtered off, washed several times with methanol and dried in the manner described above.

3.3.3.3 Preparation of $Ni(MDH)_2(BF_4)_2$ and $Ni(MDH)_3(BF_4)_2$

$Ni(MDH)_2(BF_4)_2$. A quantity of 2.64 g (0.02 mol) malonic dihydrazide and 6.80 g (0.02 mol) $Ni(BF_4)_2.6H_2O$ in 100 ml methanol was stirred in a quick-fit conical flask for 18 hours using a magnetic stirrer. A small amount of a greenish precipitate was initially formed and the solution was left to stand for about 18 hours in an evaporating dish at room temperature. More of the precipitate was formed and was filtered, washed with methanol and dried at room temperature in a vacuum desiccator over silica gel.

$Ni(MDH)_3(BF_4)_2$. 5.28 g (0.04 mol) of MDH and 6.80 g (0.02 mol) $Ni(BF_4)_2.6H_2O$ in 120 ml methanol reacted on stirring in a quick-fit conical flask for 17 hours using a magnetic stirrer. The green compound which formed was filtered off, washed several times and dried as described for $Ni(MDH)_2(BF_4)_2$.

3.3.3.4 Preparation of $Ni(SDH)_{3/2}(BF_4)_2$ and $Ni(SDH)_2(BF_4)_2$

$Ni(SDH)_{3/2}(BF_4)_2$. A mixture of SDH (2.92 g, 0.02 mol) and $Ni(BF_4)_2.6H_2O$ (6.90 g, 0.02 mol) in methanol (100 ml) was stirred for 20 hours as described above. A small quantity of light blue precipitate was formed initially the solution was left to stand in an evaporating dish for 12 hours at room temperature. The product was isolated as described for $Ni(MDH)_2(BF_4)_2$.

$Ni(SDH)_2(BF_4)_2$. A mixture of SDH (5.84 g, 0.04 mol) and $Ni(BF_4)_2.6H_2O$ (6.80 g, 0.02 mol) in methanol (100 ml) was stirred for 15 hours. The light blue product was isolated by filtering, washing several times with methanol and drying over silica gel in vacuo.

3.3.3.5 Preparation of $Ni(ADH)_{3/2}(BF_4)_2$ and $Ni(ADH)_2(BF_4)_2$

$Ni(ADH)_{3/2}(BF_4)_2$. A 1:1 molar mixture of adipic dihydrazide (3.48g, 0.02 mol) and $Ni(BF_4)_2.6H_2O$ (6.80 g, 0.02 mol) in 100 ml (methanol) was stirred for 18 hours in a conical flask at room temperature. The light blue compound formed was filtered, washed thoroughly with methanol and dried over silica gel in a vacuum desiccator.

$Ni(ADH)_2(BF_4)_2$. A mixture of ADH (3.48 g, 0.02 mol) and 3.40 g (0.01 mol) $Ni(BF_4)_2.6H_2O$ in 80 ml methanol was stirred for 18 hours as described above. The bluish compound which precipitated was isolated as described for $Ni(ADH)_{3/2}(BF_4)_2$.

3.3.3.6 Preparation of $Ni(PDH)_3(BF_4)_2$

A 1:1 molar mixture of phthalic dihydrazide (3.88 g, 0.02 mol) and 6.80 g (0.02 mol) $Ni(BF_4)_2.6H_2O$ in 90 ml methanol was stirred for 20 hours and the light green precipitates formed were isolated as before.

When a 2:1 molar mixture of PDH and $Ni(BF_4)_2.6H_2O$ was reacted together as outlined above, the same product $Ni(PDH)_3(BF_4)_2$ was obtained.

3.3.3.7 Preparation of $Ni(TDH)_3(BF_4)_2$

1.94 g (0.01 mol) of terephthalic dihydrazide (TDH) and 3.40 g (0.01 mol) $Ni(BF_4)_2.6H_2O$ in 100 ml methanol was stirred for 22 hours at room temperature. The greenish compound which formed was isolated as before.

3.3.4 Preparation of Cu(II) tetrafluoroborate ($Cu(BF_4)_2.6H_2O$)

To 45 ml of tetrafluoroboric acid (HBF_4) in a 250 ml beaker was added excess basic Cu(II) carbonate portionwise, with stirring until effervescence ceased. The tetrafluoroborate salt was isolated as described for $Ni(BF_4)_2.6H_2O$. Copper was estimated by EDTA titration using murexide as an indicator[85] (Table 6).

3.3.4.1 Preparation of Cu(II) tetrafluoroborate complexes

3.3.4.2 Preparation of $Cu(ODH)_{3/2}(BF_4)_2$ and $Cu(ODH)_3(BF_4)_2$

$Cu(ODH)_{3/2}(BF_4)_2$. A mixture of oxalic dihydrazide (2.36 g, 0.02 mol) and $Cu(BF_4)_2.6H_2O$ (6.90 g, 0.02 mol) in methanol (95 ml) was stirred in a quick-fit conical flask for 14 hours using a magnetic stirrer at room temperature. The bluish compound which formed was filtered, washed thoroughly with methanol and dried in vacuo over silica gel.

$Cu(ODH)_3(BF_4)_2$. A mixture of ODH, 4.72 g (0.04 mol) and $Cu(BF_4)_2.6H_2O$ (6.90 g, 0.02 mol) in methanol (120 ml) was stirred as described above. A 2:1 molar ratio of ligand to metal was used. The bluish compound which formed was filtered off, washed several times with methanol and dried in the manner described above.

3.3.4.3 Preparation of $Cu(MDH)_2(BF_4)_2$ and $Cu(MDH)_3(BF_4)_2$

$Cu(MDH)_2(BF_4)_2$. A quantity of 2.64 g (0.02 mol) MDH, and 6.90 g (0.02 mol), $Cu(BF_4)_2.6H_2O$ in 90 ml (methanol) was stirred in a conical flask for 16 hours using a magnetic stirrer. A small amount of greenish precipitate was initially formed and the solution was left to stand for about 14 hours in an evaporating dish at room temperature. More of the precipitate was formed and was filtered, washed with methanol and dried at room temperature in a vacuum desiccator over silica gel.

$Cu(MDH)_3(BF_4)_2$. A mixture of 5.28 g (0.04 mol) of MDH and 6.90 g (0.02 mol), $Cu(BF_4)_2.6H_2O$ in 90 ml (methanol), reacted on stirring in a quick-fit conical flask for 18 hours using a magnetic stirrer. The bluish compound formed was filtered, washed several times with methanol and dried in vacuo over silica gel.

3.3.4.4 Preparation of $Cu(SDH)_2(BF_4)_2$ and $Cu(SDH)_3(BF_4)_2$

$Cu(SDH)_2(BF_4)_2$. A mixture of succinic dihydrazide (2.92 g, 0.02 mol) and $Cu(BF_4)_2.6H_2O$ (6.90 g, 0.02 mol) in methanol (80 ml) was stirred for 18 hours as described before. A small quantity of light green precipitates were formed initially. The solution was left to stand in an evaporating dish for about 10 hours at room temperature. The product was isolated as described for $Cu(MDH)_3(BF_4)_2$.

$Cu(SDH)_3(BF_4)_2$. A mixture of 5.84 g (0.04 mol) SDH and $Cu(BF_4)_2.6H_2O$ (6.90 g, 0.02 mol), in methanol (85 ml) was stirred for 14 hours. The greenish product was isolated by filtering, washing several times with methanol and drying over silica gel in vacuo.

3.3.4.5 Preparation of $Cu(ADH)_2(BF_4)_2$ and $Cu(ADH)_3(BF_4)_2$

$Cu(ADH)_2(BF_4)_2$. A 1:1 molar mixture of adipic dihydrazide (1.74g, 0.01 mol) and $Cu(BF_4)_2.6H_2O$, (3.45 g, 0.01 mol) was stirred for 15 hours in a conical flask at room temperature. The green product formed was filtered, washed thoroughly with methanol and dried over silica gel in a vacuum desiccator.

$Cu(ADH)_3(BF_4)_2$. A mixture of ADH, 3.48 g (0.02 mol), and 3.45 g (0.01 mol) $Cu(BF_4)_2.6H_2O$ in 85 ml methanol was stirred for 16 hours as described above. The precipitated greenish compound was isolated as described for $Cu(ADH)_2(BF_4)_2$.

3.3.4.6 Preparation of $Cu(PDH)_2(BF_4)_2$ and $Cu(PDH)_3(BF_4)_2$

$Cu(PDH)_2(BF_4)_2$. To a solution of $Cu(BF_4)_2.6H_2O$ (3.45 g, 0.01 mol) in 85 ml methanol was added 1.94 g (0.01 mol), phthalic dihydrazide. The mixture was stirred and the brownish precipitates formed were isolated as before.

$Cu(PDH)_3(BF_4)_2$. Using a similar procedure as outlined for $Cu(PDH)_2(BF_4)_2$ and 2:1 molar ratio of PDH to $Cu(BF_4)_2.6H_2O$, brownish $Cu(PDH)_3(BF_4)_2$ was obtained.

3.3.4.7 Preparation of $Cu(TDH)_2(BF_4)_2$

A suspension of 1.94 g (0.01 mol) of terephthalic dihydrazide (TDH) and 3.45 g (0.01 mol) $Cu(BF_4)_2.6H_2O$ in 80 ml methanol was stirred for 20 hours at room temperature. The light green precipitate formed was isolated as described for $Cu(PDH)_2(BF_4)_2$.

3.3.5 Preparation of Zn(II) tetrafluoroborate ($Zn(BF_4)_2.6H_2O$)

To 36 ml tetrafluoroboric acid in a 250 ml beaker was added, pinchwise, excess basic $ZnCO_3$ with stirring until effervescence ceased completely. The mixture was filtered several times, concentrated by heating on a hot plate and then left in a desiccator to crystallize. Zinc was determined by EDTA titration using solochrome black as an indicator[85]. The analytical data is presented in Table 6.

3.3.5.1 Preparation of Zn(II) tetrafluoroborate complexes

3.3.5.2 Preparation of $Zn(ODH)_2(BF_4)_2$ and $Zn(ODH)_3(BF_4)_2$

$Zn(ODH)_2(BF_4)_2$. A mixture of 3.47 g (0.01 mol) in methanol (80 ml) was stirred in a quick-fit conical flask for 11 hours using a magnetic stirrer at room temperature.

The whitish compound which formed was filtered, washed several times with methanol and dried in vacuo over silica gel.

$Zn(ODH)_3(BF_4)_2$. A mixture of oxalic dihydrazide (ODH), 2.36 g (0.02 mol) and $Zn(BF_4)_2.6H_2O$, 3.47 g (0.01 mol) in methanol (80 ml) was stirred as described above. A 2:1 molar ratio of ligand to metal was used. The whitish compound which separated was filtered, washed several times with methanol and dried at room temperature in the manner above.

3.3.5.3 Preparation of $ZnMDH(BF_4)_2$ and $Zn(MDH)_3(BF_4)_2$

$ZnMDH(BF_4)_2$. Malonic dihydrazide, 2.64 g (0.02 mol) and $Zn(BF_4)_2.6H_2O$, 6.94 g (0.02 mol) in 85 ml methanol reacted on stirring in a quick-fit conical flask for 14 hours using a magnetic stirrer. The faint yellow compound was filtered, washed with methanol and dried in a vacuum desiccator over silica gel at room temperature.

$Zn(MDH)_3(BF_4)_2$. A 2:1 molar mixture of MDH, 5.28 g (0.04 mol) and $Zn(BF_4)_2.6H_2O$, 6.94 g (0.02 mol) in methanol (90 ml) was stirred for 16 hours in a conical flask at room temperature. The whitish product was filtered, washed with methanol and dried in a vacuum desiccator with silica gel as a desiccant.

3.3.5.4 Preparation of $Zn(SDH)_{3/2}(BF_4)_2$ and $Zn(SDH)_2(BF_4)_2$

$Zn(SDH)_{3/2}(BF_4)_2$. Succinic dihydrazide, 2.92 g (0.02 mol) and $Zn(BF_4)_2.6H_2O$, 6.94 g (0.02 mol) in methanol (95 ml) reacted on stirring in a quick-fit conical flask for 12 hours to give a white-coloured compound. The complex was isolated by filtering, washing several times with methanol and drying in a vacuum desiccator with silica gel as a desiccant.

$Zn(SDH)_2(BF_4)_2$. A mixture of SDH, 5.84 g (0.04 mol) and $Zn(BF_4)_2.6H_2O$ 6.94 g (0.02 mol) in 100 ml methanol was stirred for 12 hours in a quick-fit conical flask at room temperature. The whitish compound was isolated as described for $Zn(SDH)_{3/2}(BF_4)_2$.

3.3.5.5 Preparation of $Zn(ADH)_3(BF_4)_2$

To a solution of $Zn(BF_4)_2.6H_2O$, 3.47 g (0.01 mol) in 90 ml methanol was added adipic dihydrazide, 1.74 g (0.01 mol). The mixture was stirred at room temperature in a conical flask for 14 hours using a Gallenkamp magnetic stirrer. The whitish precipitates were filtered, washed thoroughly with methanol and dried in vacuo over silica gel at room temperature.

When a 2:1 molar mixture of ADH to metal salt was reacted together the same product, $Zn(ADH)_3(BF_4)_2$ was obtained.

3.3.5.6 Preparation of $Zn(PDH)_3(BF_4)_2$

A mixture of PDH, (1.94 g, 0.01 mol) and $Zn(BF_4)_2.6H_2O$, 3.47 g (0.01 mol) in methanol (90 ml) was stirred for 20 hours by means of a magnetic stirrer. The whitish product was filtered, washed several times with methanol and dried in a vacuum desiccator over silica gel.

However, a 2:1 molar ratio of PDH to $Zn(BF_4)_2.6H_2O$ gave the same product, $Zn(PDH)_3(BF_4)_2$.

3.3.5.7 Preparation of $Zn(TDH)_3(BF_4)_2$

To a solution of 6.94 g (0.02 mol) $Zn(BF_4)_2.6H_2O$ in 90 ml methanol was added 3.88 g (0.02 mol) terephthalic dihydrazide (TDH). The mixture was stirred in a conical flask for 20 hours at room temperature. The whitish compound was isolated and dried as described above.

3.3.6 Preparation of Cd(II) tetrafluoroborate ($Cd(BF_4)_2.7H_2O$)

Excess of Cd(II) carbonate was added, pinchwise, to 55 ml of HBF_4 in a 250 ml beaker, until effervescence ceased. $Cd(BF_4)_2.7H_2O$ was obtained as described for $Zn(BF_4)_2.6H_2O$. Cadmium was estimated by EDTA titration[85], using xylenol orange as an indicator (Table 6).

3.3.6.1 Preparation of Cd(II) tetrafluoroborate complexes

3.3.6.2 Preparation of $Cd(ODH)_2(BF_4)_2$ and $Cd(ODH)_3(BF_4)_2$

$Cd(ODH)_2(BF_4)_2$. With a 1:1 molar ratio of 2.36 g (0.02 mol) ODH and 8.24 g, (0.02 mol) of $Cd(BF_4)_2.7H_2O$ stirred for 17 hours in 100 ml of methanol, white precipitates of $Cd(ODH)_2(BF_4)_2$ was formed, filtered, washed several times with methanol and dried at room temperature over silica gel in a vacuum desiccator.

$Cd(ODH)_3(BF_4)_2$. This was prepared as described above but with 2.36 g (0.02 mol) ODH and 4.12 g (0.01 mol) of $Cd(BF_4)_2.7H_2O$.

3.3.6.3 Preparation of $Cd(MDH)_2(BF_4)_2$

$Cd(MDH)_2(BF_4)_2$ was prepared using a quantity of 2.64 g (0.02 mol) MDH and 8.24 g (0.02 mol) of $Cd(BF_4)_2.7H_2O$ in the manner described above.

When a 2:1 molar ratio of malonic dihydrazide to $Cd(BF_4)_2.7H_2O$ was used the same compound was obtained.

3.3.6.4 Preparation of $Cd(SDH)_2(BF_4)_2$ and $Cd(SDH)_3(BF_4)_2$

$Cd(SDH)_2(BF_4)_2$. A mixture of SDH 2.92 g (0.02 mol) and 8.24 g (0.02 mol) of $Cd(BF_4)_2.7H_2O$ in methanol was used in the isolation of $Cd(SDH)_2(BF_4)_2$.

$Cd(SDH)_3(BF_4)_2$. When a 2:1 molar ratio of SDH to metal salt was used $Cd(SDH)_3(BF_4)_2$ was isolated.

3.3.6.5 Preparation of $Cd(ADH)_2(BF_4)_2$ and $Cd(ADH)_3(BF_4)_2$

$Cd(ADH)_2(BF_4)_2$. With 1.74 g (0.01 mol) adipic dihydrazide and (4.12 g, 0.01 mol) of $Cd(BF_4)_2.7H_2O$, the compound $Cd(ADH)_2(BF_4)_2$ was isolated.

$Cd(ADH)_3(BF_4)_2$. The use of (3.48 g, 0.02 mol) of ADH and (4.12 g, 0.01 mol) of $Cd(BF_4)_2.7H_2O$ resulted to the formation of $Cd(ADH)_3(BF_4)_2$.

3.3.6.6 Preparation of $Cd(PDH)_2(BF_4)_2$ and $Cd(PDH)_3(BF_4)_2$

$Cd(PDH)_2(BF_4)_2$. Using 1.94 g (0.01 mol) of PDH and 4.12 g (0.01 mol) of $Cd(BF_4)_2.7H_2O$ as described before, $Cd(PDH)_2(BF_4)_2$ was isolated.

$Cd(PDH)_3(BF_4)_2$. This was prepared with the use of 3.88 g (0.02 mol) phthalic dihydrazide and 4.12 g (0.01 mol) $Cd(BF_4)_2.7H_2O$, representing a 2:1 molar ratio of ligand to metal salt.

3.3.6.7 Preparation of $Cd(TDH)_3(BF_4)_2$

With a similar method described earlier, but using (3.88 g, 0.02 mol) of TDH and (8.24 g, 0.02 mol) of $Cd(BF_4)_2.7H_2O$, $Cd(TDH)_3(BF_4)_2$ was isolated.

3.3.7 Preparation of Hg(II) tetrafluoroborate ($Hg(BF_4)_2.6H_2O$)

$Hg(BF_4)_2.6H_2O$ was prepared using the method described for $Zn(BF_4)_2.6H_2O$, with 50 ml tetrafluoroboric acid and excess mercury(II) carbonate. Mercury was determined by EDTA titration[85] using xylenol orange as an indicator. The analytical result obtained is shown in Table 6.

3.3.7.1 Preparation of Hg(II) tetrafluoroborate complexes

3.3.7.2 Preparation of $Hg(ODH)_3(BF_4)_2$ and $Hg(ODH)_{3/2}(BF_4)_2$

$Hg(ODH)_3(BF_4)_2$. With a 1:1 molar ratio of (2.36 g, 0.02 mol) ODH and (9.64 g, 0.02 mol) $Hg(BF_4)_2.6H_2O$ stirred for 17 hours in 100 ml of methanol, brownish $Hg(ODH)_2(BF_4)_2$ was filtered, washed thoroughly with methanol and dried over silica gel in a vacuum desiccator

$Hg(ODH)_{3/2}(BF_4)_2$. Using a 2:1 molar ratio of oxalic dihydrazide to metal salt and with the procedure outlined above, brownish $Hg(ODH)_{3/2}(BF_4)_2$ was isolated.

3.3.7.3 Preparation of $Hg(MDH)_3(BF_4)_2$ and $Hg(MDH)_2(BF_4)_2$

$Hg(MDH)_3(BF_4)_2$. A quantity of (2.64 g, 0.02 mol) malonic dihydrazide and (9.64 g, 0.02 mol) $Hg(BF_4)_2.6H_2O$ in 100 ml methanol was stirred for 17 hours. The light brown precipitates obtained was filtered, washed several times with methanol and dried in vacuo with silica gel as a desiccant.

$Hg(MDH)_2(BF_4)_2$. With a 2:1 ligand to metal salt ratio, $Hg(MDH)_2(BF_4)_2$ was obtained as described for $Hg(MDH)_3(BF_4)_2$.

3.3.7.4 Preparation of $HgSDH(BF_4)_2$ and $Hg(SDH)_2(BF_4)_2$

$HgSDH(BF_4)_2$. A mixture of succinic dihydrazide (2.92 g, 0.02 mol) and (9.64 g, 0.02 mol). $Hg(BF_4)_2.6H_2O$ in 120 ml methanol was stirred for 19 hours. The product was isolated as described before.

$Hg(SDH)_2(BF_4)_2$. With a similar procedure as described for $HgSDH(BF_4)_2$ and a 2:1 molar ratio of succinic dihydrazide to $Hg(BF_4)_2.6H_2O$, brownish precipitates of $Hg(SDH)_2(BF_4)_2$ was obtained and isolated.

3.3.7.5 Preparation of $Hg(ADH)_2(BF_4)_2$ and $Hg(ADH)_{3/2}(BF_4)_2$

$Hg(ADH)_2(BF_4)_2$. Using (1.74 g, 0.01 mol) adipic dihydrazide and (4.82 g, 0.01 mol) $Hg(BF_4)_2.6H_2O$, $Hg(ADH)_2(BF_4)_2$ was obtained.

$Hg(ADH)_{3/2}(BF_4)_2$. With (3.48 g, 0.02 mol) of ADH (4.82g, 0.01 mol) $Hg(BF_4)_2.6H_2O$ and 100 ml methanol, the compound $Hg(ADH)_3(BF_4)_2$ was isolated.

3.3.7.6 Preparation of $Hg(PDH)_2(BF_4)_2$ and $Hg(PDH)_3(BF_4)_2$

$Hg(PDH)_2(BF_4)_2$. To a solution of $Hg(BF_4)_2.6H_2O$, (4.82 g, 0.01 mol) in 100 ml methanol was added (1.94 g, 0.01 mol) phthalic dihydrazide. The mixture was stirred for 18 hours and the light brown precipitates formed were isolated as before.

$Hg(PDH)_3(BF_4)_2$. Using a similar procedure as outlined for $Hg(PDH)_2(BF_4)_2$ and 2:1 molar ratio of PDH to $Hg(BF_4)_2.6H_2O$, brownish $Hg(PDH)_3(BF_4)_2$ was isolated.

3.3.7.7 Preparation of $HgTDH(BF_4)_2$

A quantity of (1.94 g, 0.01 mol) terephthalic dihydrazide and (4.82 g, 0.01 mol) $Hg(BF_4)_2.6H_2O$ in 100 ml methanol was stirred for 18 hours. The brown precipitates formed were filtered, washed several times with methanol and dried in the manner described before.

3.3.8 Preparation of Mg tetrafluoroborate ($Mg(BF_4)_2.6H_2O$)

To 50 ml HBF_4 in a 250 ml beaker was added, pinchwise, excess magnesium carbonate until effervescence ceased.The isolation of $Mg(BF_4)_2.6H_2O$ was done in the same manner as $Zn(BF_4)_2.6H_2O$. Magnesium was estimated[85] by EDTA titration using solochrome black as an indicator (Table 6).

3.3.8.1 Preparation of Mg tetrafluoroborate complexes

3.3.8.2 Preparation of $Mg(ODH)_2(BF_4)_2$ and $Mg(ODH)_3(BF_4)_2$

$Mg(ODH)_2(BF_4)_2$. To 3.06 g (0.01 mol) of $Mg(BF_4)_2.6H_2O$ in 80 ml methanol was added with stirring (1.18 g, 0.01 mol) of oxalic dihydrazide. The mixture was further stirred for 17 hours. The separated compound was filtered, washed with methanol and dried in a vacuum desiccator over silica gel at room temperature.

$Mg(ODH)_3(BF_4)_2$. With a 1:2 molar ratio of $Mg(BF_4)_2.6H_2O$ (3.06 g, 0.01 mol), and ODH (2.36 g, 0.02 mol), $Mg(ODH)_3(BF_4)_2$ was isolated as described before.

3.3.8.3 Preparation of $Mg(MDH)_{3/2}(BF_4)_2$ and $Mg(MDH)_2(BF_4)_2$

$Mg(MDH)_{3/2}(BF_4)_2$. A mixture of MDH (2.64 g, 0.02 mol) and $Mg(BF_4)_2.6H_2O$ (6.12 g, 0.02 mol) in 100 ml of methanol contained in a quick-fit conical flask was stirred for 16 hours with a magnetic stirrer. The light brown product was isolated as described for $Mg(ODH)_2(BF_4)_2$.

$Mg(MDH)_2(BF_4)_2$. A mixture of malonic dihydrazide (3.48 g, 0.02 mol), and (3.06 g, 0.01 mol) of $Mg(BF_4)_2.6H_2O$ in 110 ml methanol was stirred. The light brown compound formed was isolated as above.

3.3.8.4 Preparation of $MgSDH(BF_4)_2$ and $Mg(SDH)_3(BF_4)_2$

$MgSDH(BF_4)_2$. A quantity of SDH (2.92 g, 0.02 mol) and (6.12 g, 0.02 mol) of $Mg(BF_4)_2.6H_2O$ in 100 ml methanol was stirred for 17 hours. The product was isolated as described before.

$Mg(SDH)_3(BF_4)_2$. With a similar procedure as described for $MgSDH(BF_4)_2$ and a 2:1 molar ratio of SDH to $Mg(BF_4)_2.6H_2O$, white precipitates of $Mg(SDH)_3(BF_4)_2$ were obtained and isolated as before.

3.3.8.5 Preparation of $MgADH(BF_4)_2$ and $Mg(ADH)_3(BF_4)_2$

$MgADH(BF_4)_2$. A 1:1 molar mixture of adipic dihydrazide (3.48 g, 0.02 mol) and $Mg(BF_4)_2.6H_2O$ (6.12 g, 0.02 mol) in 110 ml of methanol was stirred for 17 hours. The light brown compound formed was isolated as above.

$Mg(ADH)_3(BF_4)_2$. Using 3.48 g (0.02 mol) of ADH and 3.06 g (0.01 mol) of $Mg(BF_4)_2.6H_2O$, $Mg(ADH)_3(BF_4)_2$ was obtained and isolated as before.

3.3.8.6 Preparation of $Mg(PDH)_2(BF_4)_2$ and $Mg(PDH)_3(BF_4)_2$

$Mg(PDH)_2(BF_4)_2$. With (1.94 g, 0.01 mol) of PDH and (3.06 g, 0.01 mol) $Mg(BF_4)_2.6H_2O$ in 90 ml of methanol, $Mg(PDH)_2(BF_4)_2$ was prepared as described before.

$Mg(PDH)_3(BF_4)_2$. A 2:1 molar ratio of phthalic dihydrazide to $Mg(BF_4)_2.6H_2O$ gave $Mg(PDH)_3(BF_4)_2$ as earlier outlined.

3.3.8.7 Preparation of $MgTDH(BF_4)_2$

A mixture of (1.94 g, 0.01 mol) of terephthalic dihydrazide and (3.06 g, 0.01 mol) of $Mg(BF_4)_2.6H_2O$ in 100 ml of methanol was stirred for 20 hours at room temperature. The precipitates formed were filtered off, washed thoroughly with methanol and dried in vacuo over silica gel.

3.4 Elemental Analysis

The metals, manganese, cobalt, nickel, copper, zinc, cadmium, mercury and magnesium were determined by EDTA titrations as outlined in the literature[85]. The disodium salt of ethylenediamine tetraacetic acid (EDTA) was first standardised against zinc sulphate solution[85].

3.4.1 Manganese(II) tetrafluoroborate complexes

The compounds were prepared for metal analysis by digesting mildly with 3 ml conc. H_2SO_4, about 0.2 g of each sample was mixed with 0.5 g hydroxylamine hydrochloride. The resulting solutions were made up to 100 ml in a standard flask with distilled water. 10 ml portions of solution was pipetted into a conical flask and 10 ml distilled water added. This was followed by the addition of 2 ml triethanolamine while gently swirling the contents of the flask. Ammonia/ammonium chloride buffer was then added until a pH of 10 was attained. A drop of Solochrome black indicator turned the solution into a wine-red colour. Standard (9.8×10^{-3} M) EDTA solution was then added dropwise until the wine-red colour changed to blue.

3.4.2 Cobalt(II) tetrafluoroborate complexes

About 0.2 g each of the cobalt(II) tetrafluoroborate complexes was digested with 3 ml conc. HNO_3. In all cases the volume was made up to the 100 ml mark in a 100 ml standard flask with distilled water. 10 ml portions of the solutions diluted further with 20 ml distilled water, were buffered using hexamine (pH 6). Xylenol orange indicator was added. With gentle swirling, the temperature of the solution in the flask was raised to 40°C on a hot-plate. The titration was done as this temperature with a colour change of red to yellow as the end point.

3.4.3 Nickel(II) tetrafluoroborate complexes

Nickel was estimated after about 0.2 g of each sample was digested with 3 ml conc. HNO_3. A pinch of murexide/potassium nitrate indicator was added to 10 ml portions of solution pipetted from 100 ml stock solution from a standard flask (100 ml) and diluted with 20 ml distilled water. NH_3/NH_4Cl buffer was added (about 3 ml) until the solution turned yellowish. The solution was then titrated with standard (9.8×10^{-3} M) EDTA solution until a violet colour was obtained.

3.4.4 Copper(II) tetrafluoroborate complexes

About 0.2 g of each complex was weighed into a platinum crucible with dropwise addition of few drops of 1:1 conc. HNO_3/60% $HClO_4$ mixture. The contents of the crucible was heated on a hot-plate to dryness. A little quantity of distilled water was added and the contents filtered into a standard flask. This was diluted to the 100 ml mark with distilled water. NH_3/NH_4Cl buffer was added dropwise to 10 ml portions of solution until it became light blue. A pinch of murexide/sodium chloride indicator was then added and titrated against EDTA solution until a violet colour was obtained.

3.4.5 Zinc(II) tetrafluoroborate complexes

In the determination of Zn in the Zn(II) complexes, conc. HNO_3 was used in the digestion as in the case of nickel complexes. 10 ml portions of solution was taken, diluted with 20 ml distilled water and buffered with NH_3/NH_4Cl buffer (pH 10). Solochrome black indicator was used, with the colour change from violet to blue.

3.4.6 Cadmium(II) tetrafloroborate complexes

Samples (about 0.2 g) of each complex was digested with 3 ml conc. HNO_3, made up to 100 ml with distilled water in a standard flask. Hexamine was used to bring 10 ml portions of solutions to pH 5, and titrated against standard (9.8×10^{-3} M) EDTA solution with xylenol orange as an indicator. Colour change was from red to yellow.

3.4.7 Mercury(II) tetrafluoroborate complexes

Following the procedure for estimating cadmium in cadmium(II) complexes but with a pH 6 using hexamine as buffer, 10 ml portions of Hg(II) solutions of the respective complexes were titrated against standard EDTA solution with xylenol orange as an indicator. The change in colour was from red to yellow.

3.4.8 Magnesium tetrafluoroborate complexes

About 0.2 g of complex was digested with 3 ml conc. HNO_3 and made up to the 100 ml mark in a standard flask with distilled water. The metal was then estimated by taking 10 ml portions with the pipette, buffered to pH 10 with NH_3/NH_4Cl solution and titrated against standard EDTA solution with Solochrome black as an indicator. The end point was noted when the colour of the solution changed from red to blue.

3.4.9 Microanalysis

Microanalysis for carbon, hydrogen and nitrogen was performed in the Microanalytical Laboratory of the University of Ibadan.

3.5 Melting point/Decomposition temperature

These were done for the ligands and complexes using a Gallenkamp melting point apparatus, with small quantities of the materials driven into melting point tubes. The values were corrected as dictated by the calibrant (benzoic acid).

3.6 Solubility

The test for the solubility of the complexes was carried out in some polar and non-polar solvents.

3.7 Conductance measurements

The molar conductances of the complexes soluble in DMSO and water (concentration $\sim 1\times10^{-3}$ M) were determined using an Electrolytic Conductivity Measuring Set, Model MC-1, Mark V, with a cell constant of 0.1.

3.8 Infrared spectra

The infrared spectra of the ligands and complexes as pressed KBr discs were recorded on a Unicam SP3-300 Infrared Spectrophotometer. In few cases, a Perkin-Elmer IR-457 Spectrophotometer was used. The instruments were calibrated with polystyrene film.

3.9 Electronic spectra

The electronic spectra of the ligands that were fairly soluble in water and methanol were obtained using Pye Unicam SP8-400 uv/vis Spectrophotometer.

The diffuse reflectance spectra of the complexes in the range 28,600-10,000 cm^{-1} were taken on a Unicam SP500 Spectrophotometer equipped with a reflectance attachment using $CaCO_3$ as a reference.

3.10 Magnetic susceptibility measurements

The magnetic susceptibilities of the complexes at room temperature were determined by the Gouy method as earlier described[86]. The diamagnetic corrections for the ligands were obtained from Pascal's constants[87]. The calibrant used was mercury tetrathiocyanato cobaltate, $Hg[Co(CNS)_4]$. The effective magnetic moments, μ_{eff} were calculated using the expression:

$$\mu_{eff} = 2.828\sqrt{\chi_A T}$$

where χ_A is the susceptibility per gram atom, and T is the temperature in Kelvin.

Procedure

(1) The volume of the tube was determined by weighing it empty and reweighing with the tube filled to the mark. This was done using the Gouy balance without the magnetic field. The volume of the tube was then calculated.

Weight of empty tube, field off = 1.2561 g

Weight of tube + water, field off = 1.5158 g

Mass of water = 0.2597 g

Temperature = 29°C (302 K)

Density of water (304 K) = 0.995976 g/cm^3

Volume of tube = $\frac{0.2597}{0.995976}$ = 0.2607 cm^3

(2) The tube was then dried and weighed with and without the magnetic field. The glass being diamagnetic lost weight on application of the magnetic field (x grams). The tube was packed to the mark with finely powdered $Hg[Co(CNS)_4]$ by tapping the tube on the table several times until the packing was uniform and the required mark attained, and ceases to pack with further tapping. The packed tube was then weighed with and without the magnetc field. The tube was found to increase in weight (y grams) apparently because of the paramagnetic nature of the calibrant, however, the effect of the glass was allowed for: $w = y+x$, w being the force exerted on the specimen. The weight of the sample (W) was obtained by difference, knowing the weight of the empty tube β was then calculated from the relationship

$$\chi = \frac{V_x + \beta_w}{W}$$

using $\chi = 16.44 \times 10^{-6}$ at 20°C (decreasing by approximately 0.04×10^{-6} per degree rise). This operation was repeated several times until an agreement of within 1% was obtained between consecutive β values.

(3) The tube was then unpacked and cleaned. The process outlined in (2) was followed using finely ground specimens of the respective complexes of interest. From the value of β obtained originally, the χ value was calculated. The value of χ obtained is the gram susceptibility of the complexes from which the molar susceptibility, χ_m were obtained by multiplying by the molecular masses of the respective complexes. The diamagnetic corrections for the ligands, χ_L were obtained from Pascal's constants[87]. χ_A (susceptibility of the metal ions) were then obtained from the relationship:

$$\chi_A = \chi_m - \chi_L$$

Finally, the effective magnetic moments were calculated from the equation:

$$\mu_{eff} = 2.828\sqrt{\chi_A T} \quad \text{B.M.}$$

Great care was taken during the packing of the sample as the experiment depends largely on the uniformity of the packing. For each complex, the packing was done thoroughly, three times.

CHAPTER FOUR

RESULTS

4.1 Physical and analytical data

The analytical data of the metal fluoroborates are shown in Table 6. A summary of the methods used in the synthesis of the complexes is given in Table 7. The analytical data, colours, percentage yields and melting/decomposition temperatures are summarised in Table 8.

4.2 Solubility data

The solubility of the ligands and complexes in the respective solvents are summarised in Table 9.

4.3 Molar conductivity

The conductance data of the complexes that were soluble in water and DMSO are given in Table 10.

4.4 Infrared spectra

The infrared spectra of the dihydrazides used and the metal complexes investigated are shown in Figures 16-39. The vibrational frequencies and their proposed assignments are listed in Table 11.

4.5 Electronic spectra

The electronic spectra of the ligands and some of the complexes at room temperature are shown in Figures 40-47. And the tentative assignments are given in Table 12.

TABLE 6: ANALYTICAL DATA OF THE METAL FLUOROBORATES[88]

Compound	Molecular Mass	Percentage (%) Metal
$Mn(BF_4)_2.6H_2O$	336.54	16.52(16.32)
$Co(BF_4)_2.6H_2O$	340.54	17.47(17.31)
$Ni(BF_4)_2.6H_2O$	340.31	17.07(17.25)
$Cu(BF_4)_2.6H_2O$	345.14	18.36(18.40)
$Zn(BF_4)_2.6H_2O$	346.97	18.90(18.84)
$Cd(BF_4)_2.7H_2O$	412.01	27.19(27.28)
$Hg(BF_4)_2.6H_2O$	482.19	41.52(41.60)
$Mg(BF_4)_2.6H_2O$	305.91	7.89(7.95)

The figures in parentheses are the calculated values.

TABLE 7: METHODS OF PREPARATION OF THE TETRAFLUOROBORATE COMPLEXES

No.	Compound	Reactant ratios	Methanol (ml)	Duration of stirring (hours)
1.	$Mn(ODH)_2(BF_4)_2$	1:1	90	15
2.	$Mn(ODH)_3(BF_4)_2$	1:2	90	16
3.	$Mn(MDH)_2(BF_4)_2$	1:1	92	19
4.	$Mn(MDH)_3(BF_4)_2$	1:2	95	18
5.	$Mn(SDH)_2(BF_4)_2$	1:1	100	18
6.	$Mn(SDH)_3(BF_4)_2$	1:2	110	19
7.	$Mn(ADH)_{3/2}(BF_4)_2$	1:1	90	17
8.	$Mn\ (ADH)_3(BF_4)_2$	1:2	100	18
9.	$Mn(PDH)_2(BF_4)_2$	1:1	95	17
10.	$Mn(PDH)_3(BF_4)_2$	1:2	100	19
11.	$Mn(TDH)_3(BF_4)_2$	1:1	95	18
12.	$Co(ODH)_2(BF_4)_2$	1:1	80	14
13.	$Co(ODH)_3(BF_4)_2$	1:2	100	16
14.	$Co(MDH)_{3/2}(BF_4)_2$	1:1	100	16
15.	$Co(MDH)_3(BF_4)_2$	1:2	100	18
16.	$Co(SDH)_2(BF_4)_2$	1:1	90	19
17.	$Co(SDH)_3(BF_4)_2$	1:2	100	20
18.	$Co(ADH)_2(BF_4)_2$	1:1	80	16
19.	$Co(ADH)_3(BF_4)_2$	1:2	90	18

TABLE 7 (Contd.)

No.	Compound	Reactant ratios	Methanol (ml)	Duration of stirring (hours)
20.	$Co(PDH)_3(BF_4)_2$	1:1	95	19
21.	$Co(PDH)_3(BF_4)_2$	1:2	100	19
22.	$Co(TDH)_3(BF_4)_2$	1:1	100	20
23.	$Ni(ODH)_2(BF_4)_2$	1:1	98	16
24.	$Ni(ODH)_3(BF_4)_2$	1:2	150	16
25.	$Ni(MDH)_2(BF_4)_2$	1:1	100	18
26.	$Ni(MDH)_3(BF_4)_2$	1:2	120	17
27.	$Ni(SDH)_{3/2}(BF_4)_2$	1:1	100	20
28.	$Ni(SDH)_2(BF_4)_2$	1:2	100	18
29.	$Ni(ADH)_{3/2}(BF_4)_2$	1:1	100	18
30.	$Ni(ADH)_2(BF_4)_2$	1:2	80	18
31.	$Ni(PDH)_3(BF_4)_2$	1:1	90	20
32.	$Ni(PDH)_3(BF_4)_2$	1:2	90	20
33.	$Ni(TDH)_3(BF_4)_2$	1:1	100	22
34.	$Cu(ODH)_{3/2}(BF_4)_2$	1:1	95	14
35.	$Cu(ODH)_3(BF_4)_2$	1:2	120	16
36.	$Cu(MDH)_2(BF_4)_2$	1:1	90	16
37.	$Cu(MDH)_3(BF_4)_2$	1:2	90	18
38.	$Cu(SDH)_2(BF_4)_2$	1:1	80	18
39.	$Cu(SDH)_3(BF_4)_2$	1:2	85	14

TABLE 7 (Contd.)

No.	Compound	Reactant ratios	Methanol (ml)	Duration of stirring (hours)
40.	$Cu(ADH)_2(BF_4)_2$	1:1	80	15
41.	$Cu(ADH)_3(BF_4)_2$	1:2	85	16
42.	$Cu(PDH)_2(BF_4)_2$	1:1	85	18
43.	$Cu(PDH)_3(BF_4)_2$	1:2	90	18
44.	$Cu(TDH)_3(BF_4)_2$	1:1	80	20
45.	$Zn(ODH)_2(BF_4)_2$	1:1	80	11
46.	$Zn(ODH)_3(BF_4)_2$	1:2	80	12
47.	$Zn\ MDH(BF_4)_2$	1:1	85	14
48.	$Zn(MDH)_3(BF_4)_2$	1:2	90	16
49.	$Zn(SDH)_{3/2}(BF_4)_2$	1:1	95	12
50.	$Zn(SDH)_2(BF_4)_2$	1:2	100	12
51.	$Zn(ADH)_3(BF_4)_2$	1:1	90	14
52.	$Zn(ADH)_3(BF_4)_2$	1:2	100	13
53.	$Zn(PDH)_3(BF_4)_2$	1:1	90	20
54.	$Zn(PDH)_3(BF_4)_2$	1:2	90	20
55.	$Zn(TDH)_3(BF_4)_2$	1:1	90	20
56.	$Cd(ODH)_2(BF_4)_2$	1:1	100	17
57.	$Cd(ODH)_3(BF_4)_2$	1:2	100	17
58.	$Cd(MDH)_2(BF_4)_2$	1:1	100	18
59.	$Cd(MDH)_2(BF_4)_2$	1:2	100	17

TABLE 7 (Contd.)

No.	Compound	Reactant ratios	Methanol (ml)	Duration of stirring (hours)
60.	$Cd(SDH)_2(BF_4)_2$	1:1	90	19
61.	$Cd(SDH)_3(BF_4)_2$	1:2	95	19
62.	$Cd(ADH)_2(BF_4)_2$	1:1	100	18
63.	$Cd(ADH)_3(BF_4)_2$	1:2	100	19
64.	$Cd(PDH)_2(BF_4)_2$	1:1	100	20
65.	$Cd(PDH)_3(BF_4)_2$	1:2	110	20
66.	$Cd(TDH)_3(BF_4)_2$	1:1	95	19
67.	$Hg(ODH)_3(BF_4)_2$	1:1	100	17
68.	$Hg(ODH)_{3/2}(BF_4)_2$	1:2	100	17
69.	$Hg(MDH)_3(BF_4)_2$	1:1	100	17
70.	$Hg(MDH)_2(BF_4)_2$	1:2	100	18
71.	$Hg\ SDH\ (BF_4)_2$	1:1	100	19
72.	$Hg(SDH)_2(BF_4)_2$	1:2	120	18
73.	$Hg(ADH)_2(BF_4)_2$	1:1	95	17
74.	$Hg(ADH)_{3/2}(BF_4)_2$	1:2	100	17
75.	$Hg(PDH)_2(BF_4)_2$	1:1	100	18
76.	$Hg(PDH)_3(BF_4)_2$	1:2	100	18
77.	$Hg\ TDH\ (BF_4)_2$	1:1	100	18
78.	$Mg(ODH)_2(BF_4)_2$	1:1	80	17
79.	$Mg(ODH)_3(BF_4)_2$	1:2	90	18

TABLE 7 (Contd.)

No.	Compound	Reactant ratios	Methanol (ml)	Duration of stirring (hours)
80.	$Mg(MDH)_{3/2}(BF_4)_2$	1:1	100	16
81.	$Mg(MDH)_2(BF_4)_2$	1:2	110	18
82.	$Mg\ SDH\ (BF_4)_2$	1:1	100	17
83.	$Mg(SDH)_3(BF_4)_2$	1:2	110	17
84.	$Mg\ ADH\ (BF_4)_2$	1:1	110	17
85.	$Mg(ADH)_3(BF_4)_2$	1:2	90	18
86.	$Mg(PDH)_2(BF_4)_2$	1:1	100	19
87.	$Mg(PDH)_3(BF_4)_2$	1:2	100	19
88.	$MgTDH(BF_4)_2$	1:1	100	20

TABLE 8: ANALYTICAL DATA OF THE LIGANDS AND THE TETRAFLUOROBORATE COMPLEXES

No.	Compound	Empirical Formula	Colour	M.P (^oC)	Yield (%)	Percentage Composition			
						M	C	H	N
1.	ODH	$C_2H_6N_4O_2$	White	241-243	90		20.30 (20.35)	5.11 (5.08)	47.52 (47.46)
2.	MDH	$C_3H_8N_4O_2$	White	152-154	83		27.45 (27.27)	6.04 (6.06)	42.28 (42.42)
3.	SDH	$C_4H_{10}N_4O_2$	White	167-168	87		32.91 (32.88)	6.79 (6.85)	38.34 (38.36)
4.	ADH	$C_6H_{14}N_4O_2$	White	171-172	89		41.53 (41.38)	8.02 (8.04)	32.57 (32.18)
5.	PDH	$C_8H_{10}N_4O_2$	Dirty white	> 300	91		50.01 (49.48)	5.17 (5.15)	28.57 (28.87)
6.	TDH	$C_8H_{10}N_4O_2$	Dirty white	>300	77		49.64 (49.48)	5.16 (5.15)	28.77 (28.87)
7.	$Mn(ODH)_2(BF_4)_2$	$MnC_4H_{12}N_8$-$O_4B_2F_8$	White	>300	78	11.94 (11.83)	10.29 (10.33)	2.60 (2.58)	24.09 (24.11)
8.	$Mn(ODH)_3(BF_4)_2$	$MnC_6H_{18}N_{12}$-$O_6B_2F_8$	White	>300	77	9.61 (9.43)	12.40 (12.36)	3.02 (3.09)	28.97 (28.84)
9.	$Mn(MDH)_2(BF_4)_2$	$MnC_6H_{16}N_8$-$O_4B_2F_8$	Dirty white	227-229	84	11.09 (11.15)	14.45 (14.62)	3.30 (3.25)	22.85 (22.74)
10.	$Mn(MDH)_3(BF_4)_2$	$MnC_9H_{24}N_{12}$-$O_6B_2F_8$	White	193-195	81	8.84 (8.80)	17.18 (17.29)	3.86 (3.84)	26.74 (26.90)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (^{o}C)	Yield (%)	Percentage Composition M	C	H	N
11.	$Mn(SDH)_2(BF_4)_2$	$MnC_8H_{20}N_8$ - $O_4B_2F_8$	White	195-197	68	10.60 (10.55)	18.38 (18.44)	3.90 (3.82)	20.99 (21.52)
12.	$Mn(SDH)_3(BF_4)_2$	$MnC_{12}H_{30}N_{12}$- $O_6B_2F_8$	White	135-137	69	8.38 (8.24)	21.81 (21.60)	4.55 (4.50)	25.08 (25.20)
13.	$Mn(ADH)_{3/2}(BF_4)_2$	$MnC_9H_{21}N_6$- $O_3B_2F_8$	White	271-273	72	11.21 (11.22)	22.14 (22.06)	4.33 (4.29)	17.22 (17.16)
14.	$Mn(ADH)_3(BF_4)_2$	$MnC_{18}N_{42}N_{12}$- $O_6B_2F_8$	White	153-155	76	7.19 (7.32)	29.03 (28.98)	5.60 (5.62)	22.51 (22.38)
15.	$Mn(PDH)_2(BF_4)_2$	$MnC_{16}H_{20}N_8$- $O_4B_2F_8$	Dirty white	>300	78	9.08 (8.97)	31.15 (31.14)	3.27 (3.24)	18.40 (18.17)
16.	$Mn(PDH)_3(BF_4)_2$	$MnC_{24}H_{30}N_{12}$- $O_6B_2F_8$	Dirty white	>300	80	6.96 (6.78)	35.41 (35.53)	3.69 (3.70)	20.91 (20.73)
17.	$Mn(TDH)_3(BF_4)_2$	$MnC_{24}H_{30}N_{12}$- $O_6B_2F_8$	White	>300	62	6.69 (6.78)	35.71 (35.53)	3.68 (3.70)	20.69 (20.73)
18.	$Co(ODH)_2(BF_4)_2$	$CoC_4H_{12}N_8$- $O_4B_2F_8$	Pink	215-217	85	12.61 (12.58)	10.38 (10.24)	2.60 (2.56)	24.01 (23.90)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (°C)	Yield (%)	Percentage Composition			
						M	C	H	N
19.	$Co(ODH)_3(BF_4)_2$	$CoC_6H_{18}N_{12}$- $O_6B_2F_8$	Pink	183-185	88	10.34 (10.05)	12.24 (12.28)	3.06 (3.07)	28.77 (28.64)
20.	$Co(MDH)_{3/2}(BF_4)_2$	$CoC_{4.5}H_{12}N_6$- $O_3B_2F_8$	Light pink	$>$300	69	13.61 (13.69)	12.39 (12.54)	2.90 (2.79)	19.46 (19.51)
21.	$Co(MDH)_3(BF_4)_2$	$CoC_9H_{24}N_{12}$- $O_6B_2F_8$	Pink	140-142	63	9.41 (9.38)	17.29 (17.18)	3.82 (3.82)	26.39 (26.73)
22.	$Co(SDH)_2(BF_4)_2$	$CoC_8H_{20}N_8$- $O_4B_2F_8$	Pink	245-247	70	11.17 (11.24)	18.36 (18.27)	3.77 (3.81)	20.99 (21.35)
23.	$Co(SDH)_3(BF_4)_2$	$CoC_{12}H_{30}N_{12}$- $O_6B_2F_8$	Pink	150-152	70	8.64 (8.79)	21.51 (21.48)	4.40 (4.47)	25.41 (25.05)
24.	$Co(ADH)_2(BF_4)_2$	$CoC_{12}H_{28}N_8$- $O_4B_2F_8$	Pink	200-202	84	9.81 (9.64)	24.68 (24.80)	4.82 (4.82)	20.02 (19.29)
25.	$Co(ADH)_3(BF_4)_2$	$CoC_{18}H_{42}N_{12}$- $O_6B_2F_8$	Pink	160-162	80	7.91 (7.80)	28.59 (28.63)	5.61 (5.57)	22.19 (22.27)
26.	$Co(PDH)_3(BF_4)_2$	$CoC_{24}H_{30}N_{12}$- $O_6B_2F_8$	Pink	$>$300	90	7.43 (7.24)	35.31 (35.36)	3.57 (3.68)	20.94 (20.63)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (°C)	Yield (%)	Percentage Composition			
						M	C	H	N
27.	$Co(TDH)_3(BF_4)_2$	$CoC_{24}H_{30}N_{12}O_6B_2F_8$	Pink	>300	71	7.28 (7.24)	35.40 (35.36)	3.70 (3.68)	20.79 (20.63)
28.	$Ni(ODH)_2(BF_4)_2$	$NiC_4H_{12}N_8O_4B_2F_8$	Light blue	>300	82	12.59 (12.53)	10.18 (10.24)	2.60 (2.56)	24.04 (23.90)
29.	$Ni(ODH)_3(BF_4)_2$	$NiC_6H_{18}N_{12}O_6B_2F_8$	Light blue	235-237	81	10.14 (10.01)	12.38 (12.27)	3.05 (3.07)	28.49 (28.63)
30.	$Ni(MDH)_2(BF_4)_2$	$NiC_6H_{16}N_8O_4B_2F_8$	Green	114-116	67	11.89 (11.82)	14.37 (14.50)	3.19 (3.22)	19.40 (19.33)
31.	$Ni(MDH)_3(BF_4)_2$	$NiC_9H_{24}N_{12}O_6B_2F_8$	Green	108-110	69	9.30 (9.34)	17.13 (17.18)	3.90 (3.82)	26.77 (26.72)
32.	$Ni(SDH)_{3/2}(BF_4)_2$	$NiC_6H_{15}N_6O_3B_2F_8$	Light blue	295-297	70	13.03 (13.00)	15.90 (15.94)	3.40 (3.32)	18.33 (18.60)
33.	$Ni(SDH)_2(BF_4)_2$	$NiC_8H_{20}N_8O_4B_2F_8$	Light blue	145-147	72	11.21 (11.19)	18.41 (18.30)	3.78 (3.81)	20.99 (21.35)
34.	$Ni(ADH)_{3/2}(BF_4)_2$	$NiC_9H_{21}N_6O_3B_2F_8$	Light blue	>300	88	11.98 (11.89)	21.74 (21.88)	4.30 (4.25)	17.19 (17.01)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (°C)	Yield (%)	Percentage Composition			
						M	C	H	N
35.	$Ni(ADH)_2(BF_4)_2$	$NiC_{12}H_{14}N_8$- $O_4B_2F_8$	Blue	>300	87	10.07 (10.11)	24.31 (24.80)	4.97 (4.82)	19.18 (19.29)
36.	$Ni(PDH)_3(BF_4)_2$	$NiC_{24}H_{30}N_{12}$- $O_6B_2F_8$	Light green	>300	85	7.17 (7.21)	35.47 (35.35)	3.70 (3.68)	20.41 (20.62)
37.	$Ni(TDH)_3(BF_4)_2$	$NiC_{24}H_{30}N_{12}$- $O_6B_2F_8$	Light green	>300	71	7.23 (7.21)	35.59 (35.35)	3.66 (3.68)	20.57 (20.62)
38.	$Cu(ODH)_{3/2}(BF_4)_2$	$CuC_3H_9N_6$- $O_3B_2F_8$	Blue	226-228	90	15.74 (15.33)	8.57 (8.69)	2.18 (2.19)	20.39 (20.28)
39.	$Cu(ODH)_3(BF_4)_2$	$CuC_6H_{18}N_{12}$- $O_6B_2F_8$	Blue	206-208	81	10.81 (10.74)	12.16 (12.18)	3.00 (3.04)	29.01 (28.42)
40.	$Cu(MDH)_2(BF_4)_2$	$CuC_6H_{16}N_8$- $O_4B_2F_8$	Green	248-250	63	12.75 (12.67)	14.51 (14.37)	3.22 (3.19)	22.26 (22.35)
41.	$Cu(MDH)_3(BF_4)_2$	$CuC_9H_{24}N_{12}$- $O_6B_2F_8$	Blue	106-108	71	9.88 (9.73)	16.59 (16.54)	3.64 (3.67)	26.71 (26.53)
42.	$Cu(SDH)_2(BF_4)_2$	$CuC_8H_{20}N_8$- $O_4B_2F_8$	Light green	>300	63	12.10 (12.00)	18.21 (18.14)	3.80 (3.78)	21.20 (21.17)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (°C)	Yield (%)	Percentage Composition M	C	H	N
43.	$Cu(SDH)_3(BF_4)_2$	$CuC_{12}H_{36}N_{12}$-$O_6B_2F_8$	Green	268-270	67	9.61 (9.41)	21.63 (21.33)	4.40 (4.44)	25.02 (24.88)
44.	$Cu(ADH)_2(BF_4)_2$	$CuC_{12}H_{28}N_8$-$O_4B_2F_8$	Green	210-212	74	10.54 (10.22)	23.11 (23.18)	4.73 (4.51)	19.09 (19.14)
45.	$Cu(ADH)_3(BF_4)_2$	$CuC_{18}H_{42}N_{12}$-$O_6B_2F_8$	Green	285-287	77	8.57 (8.36)	28.66 (28.45)	5.50 (5.53)	22.38 (22.13)
46.	$Cu(PDH)_2(BF_4)_2$	$CuC_{16}H_{20}N_8$-$O_4B_2F_8$	Greenish Brown	>300	82	9.98 (10.16)	30.70 (30.71)	3.22 (3.20)	18.01 (17.92)
47.	$Cu(PDH)_3(BF_4)_2$	$CuC_{24}H_{30}N_{12}$-$O_6B_2F_8$	Greenish Brown	>300	82	7.80 (7.75)	35.42 (35.16)	3.70 (3.66)	20.66 (20.51)
48.	$Cu(TDH)_3(BF_4)_2$	$CuC_{24}H_{30}N_{12}$-$O_6B_2F_8$	Light green	>300	75	7.92 (7.75)	35.13 (35.16)	3.58 (3.66)	20.49 (20.51)
49.	$Zn(ODH)_2(BF_4)_2$	$ZnC_4H_{12}N_8$-$O_4B_2F_8$	White	>300	82	13.88 (13.76)	10.24 (10.11)	2.50 (2.53)	23.67 (23.58)
50.	$Zn(ODH)_3(BF_4)_2$	$ZnC_6H_{18}N_{12}$-$O_6B_2F_8$	White	237-239	79	11.12 (11.02)	12.18 (12.14)	2.98 (3.04)	28.41 (28.33)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (^{o}C)	Yield (%)	Percentage Composition			
						M	C	H	N
51.	$ZnMDH(BF_4)_2$	$ZnC_3H_8N_4$- $O_2B_2F_8$	Light yellow	>300	69	17.58 (17.62)	9.63 (9.70)	2.14 (2.16)	15.02 (15.10)
52.	$Zn(MDH)_3(BF_4)_2$	$ZnC_9H_{24}N_{12}$- $O_6B_2F_8$	White	173-175	85	10.87 (10.29)	17.17 (17.01)	3.72 (3.78)	26.21 (26.46)
53.	$Zn(SDH)_{3/2}(BF_4)_2$	$ZnC_6H_{15}N_6$- $O_3B_2F_8$	White	255-257	75	14.16 (14.27)	15.78 (15.72)	3.26 (3.28)	18.44 (18.34)
54.	$Zn(SDH)_2(BF_4)_2$	$ZnC_8H_{20}N_8$- $O_4B_2F_8$	White	218-220	78	12.22 (12.31)	18.20 (18.08)	3.75 (3.77)	21.19 (21.09)
55.	$Zn(ADH)_3(BF_4)_2$	$ZnC_{18}H_{42}N_{12}$- $O_6B_2F_8$	White	268-270	69	8.71 (8.59)	28.26 (28.38)	5.57 (5.52)	22.20 (22.08)
56.	$Zn(PDH)_3(BF_4)_2$	$ZnC_{24}H_{30}N_{12}$- $O_6B_2F_8$	White	>300	57	8.06 (7.96)	35.04 (35.08)	3.69 (3.65)	20.51 (20.46)
57.	$Zn(TDH)_3(BF_4)_2$	$ZnC_{24}H_{30}N_{12}$- $O_6B_2F_8$	White	>300	55	7.90 (7.96)	34.84 (35.08)	3.70 (3.65)	20.51 (20.51)
58.	$Cd(ODH)_2(BF_4)_2$	$CdC_4H_{12}N_8$- $O_4B_2F_8$	Dirty white	>300	80	21.24 (21.53)	9.11 (9.20)	2.26 (2.30)	20.94 (21.46)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (^{o}C)	Yield (%)	Percentage Composition			
						M	C	H	N
59.	$Cd(ODH)_3(BF_4)_2$	$CdC_6H_{18}N_{12}$- $O_6B_2F_8$	Dirty white	>300	79	17.61 (17.56)	11.04 (11.25)	2.80 (2.81)	25.99 (26.25)
60.	$Cd(MDH)_2(BF_4)_2$	$CdC_6H_{16}N_8$- $O_4B_2F_8$	Dirty white	245-247	74	20.24 (20.44)	13.07 (13.09)	3.00 (2.91)	20.74 (20.36)
61.	$Cd(SDH)_2(BF_4)_2$	$CdC_8H_{20}N_8$- $O_4B_2F_8$	White	174-176	81	19.52 (19.45)	16.68 (16.61)	3.40 (3.46)	19.26 (19.38)
62.	$Cd(SDH)_3(BF_4)_2$	$CdC_{12}H_{30}N_{12}$- $O_6B_2F_8$	White	211-213	69	15.63 (15.52)	20.01 (19.89)	4.13 (4.14)	23.52 (23.20)
63.	$Cd(ADH)_2(BF_4)_2$	$CdC_{12}H_{28}N_8$- $O_4B_2F_8$	White	297-299	72	17.80 (17.73)	22.67 (22.71)	4.47 (4.42)	18.01 (17.67)
64.	$Cd(ADH)_3(BF_4)_2$	$CdC_{18}H_{42}N_{12}$- $O_6B_2F_8$	White	116-118	77	14.03 (13.91)	26.81 (26.73)	5.24 (5.20)	20.38 (20.79)
65.	$Cd(PDH)_2(BF_4)_2$	$CdC_{16}H_{20}N_8$- $O_4B_2F_8$	Dirty white	>300	70	16.80 (16.68)	28.46 (28.49)	3.01 (2.97)	17.01 (16.62)
66.	$Cd(PDH)_3(BF_4)_2$	$CdC_{24}H_{30}N_{12}$- $O_6B_2F_8$	Dirty white	283-285	80	13.04 (12.95)	33.16 (33.18)	3.39 (3.46)	19.24 (19.35)

TABLE 8 (Contd.)

No:	Compound	Empirical Formula	Colour	M.P (^{o}C)	Yield (%)	Percentage Composition M	C	H	N
67.	$Cd(TDH)_3(BF_4)_2$	$CdC_{24}H_{30}N_{12}$-$O_6B_2F_8$	White	>300	62	13.00 (12.95)	33.30 (33.18)	3.39 (3.46)	19.41 (19.35)
68.	$Hg(ODH)_3(BF_4)_2$	$HgC_6H_{18}N_{12}$-$O_6B_2F_8$	Light brown	267-269	78	27.64 (27.55)	9.84 (9.89)	2.51 (2.47)	23.19 (23.07)
69.	$Hg(ODH)_{3/2}(BF_4)_2$	$HgC_3H_9N_6$-$O_3B_2F_8$	Light brown	>300	72	36.41 (36.39)	6.66 (6.53)	1.65 (1.63)	15.43 (15.24)
70.	$Hg(MDH)_3(BF_4)_2$	$HgC_9H_{24}N_{12}$-$O_6B_2F_8$	Light brown	>300	62	26.10 (26.04)	14.21 (14.02)	3.10 (3.12)	22.02 (21.81)
71.	$Hg(MDH)_2(BF_4)_2$	$HgC_6H_{16}N_8$-$O_4B_2F_8$	Brown	258-260	62	31.39 (31.43)	11.22 (11.28)	2.52 (2.51)	17.47 (17.55)
72.	$HgSDH(BF_4)_2$	$HgC_4H_{10}N_4$-$O_2B_2F_8$	Dirty white	198-200	66	38.71 (38.56)	9.28 (9.23)	2.01 (1.92)	10.98 (10.77)
73.	$Hg(SDH)_2(BF_4)_2$	$HgC_8H_{20}N_8$-$O_4B_2F_8$	Brown	222-224	66	30.07 (30.11)	14.62 (14.41)	3.04 (3.00)	16.56 (16.81)
74.	$Hg(ADH)_2(BF_4)_2$	$HgC_{12}H_{28}N_8$-$O_4B_2F_8$	Dirty white	117-119	74	27.41 (27.77)	19.87 (19.84)	3.91 (3.88)	15.38 (15.51)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (°C)	Yield (%)	Percentage Composition			
						M	C	H	N
75.	$Hg(ADH)_{3/2}(BF_4)_2$	$HgC_9H_{21}N_6$ - $O_3B_2F_8$	Light brown	>300	79	31.50 (31.58)	17.08 (17.00)	3.39 (3.31)	13.46 (13.22)
76.	$Hg(PDH)_2(BF_4)_2$	$HgC_{16}H_{20}N_8$ - $O_4B_2F_8$	Light brown	>300	82	26.41 (26.32)	25.08 (25.19)	2.64 (2.62)	14.50 (14.68)
77.	$Hg(PDH)_3(BF_4)_2$	$HgC_{24}H_{30}N_{12}$ - $O_6B_2F_8$	Light brown	>300	82	20.91 (20.98)	30.20 (30.12)	3.09 (3.14)	17.62 (17.57)
78.	$HgTDH(BF_4)_2$	$HgC_8H_{10}N_4$ - $O_2B_2F_8$	Brown	>300	78	35.24 (35.30)	16.82 (16.90)	1.82 (1.76)	10.03 (9.86)
79.	$Mg(ODH)_2(BF_4)_2$	$MgC_4H_{12}N_8$ - $O_4B_2F_8$	White	>300	85	5.64 (5.60)	11.05 (11.06)	2.56 (2.77)	26.04 (25.81)
80.	$Mg(ODH)_3(BF_4)_2$	$MgC_6H_{18}N_{12}$ - $O_6B_2F_8$	White	>300	81	4.32 (4.41)	13.12 (13.05)	3.21 (3.26)	30.17 (30.44)
81.	$Mg(MDH)_{3/2}(BF_4)_2$	$MgC_{4.5}H_{12}$- $N_6O_3B_2F_8$	Light brown	>300	76	6.09 (6.14)	13.46 (13.64)	2.98 (3.03)	21.24 (21.22)
82.	$Mg(MDH)_2(BF_4)_2$	$MgC_6H_{16}N_8$ - $O_4B_2F_8$	Light brown	>300	80	5.19 (5.26)	15.30 (15.59)	3.46 (3.46)	24.44 (24.25)

TABLE 8 (Contd.)

No.	Compound	Empirical Formula	Colour	M.P (^oC)	Yield (%)	Percentage Composition			
						M	C	H	N
83.	$MgSDH(BF_4)_2$	$MgC_4H_{10}N_4-O_2B_2F_8$	White	>300	71	7.05 (7.07)	14.04 (13.96)	3.02 (2.91)	16.71 (16.28)
84.	$Mg(SDH)_3(BF_4)_2$	$MgC_{12}H_{30}N_{12}-O_6B_2F_8$	White	>300	70	3.91 (3.82)	22.53 (22.64)	4.69 (4.72)	26.27 (26.42)
85.	$MgADH(BF_4)_2$	$MgC_6H_{14}N_4-O_2B_2F_8$	Light brown	>300	81	6.47 (6.54)	9.45 (9.36)	3.72 (3.76)	14.99 (15.06)
86.	$Mg(ADH)_3(BF_4)_2$	$MgC_{18}H_{42}N_{12}-O_6B_2F_8$	White	>300	88	3.34 (3.38)	30.16 (30.00)	5.79 (5.83)	23.45 (23.34)
87.	$Mg(PDH)_2(BF_4)_2$	$MgC_{16}H_{20}N_8-O_4B_2F_8$	White	>300	81	4.21 (4.15)	32.89 (32.77)	3.36 (3.41)	19.28 (19.12)
88.	$Mg(PDH)_3(BF_4)_2$	$MgC_{24}H_{30}N_{12}-O_6B_2F_8$	Dirty white	>300	82	3.20 (3.12)	37.02 (36.93)	3.79 (3.85)	21.41 (21.54)
89.	$MgTDH(BF_4)_2$	$MgC_8H_{10}N_4-O_2B_2F_8$	Light brown	>300	70	6.16 (6.20)	24.58 (24.50)	2.60 (2.55)	14.16 (14.29)

Figures in parentheses are the calculated values.

TABLE 9: SOLUBILITY DATA OF THE LIGANDS AND TETRAFLUOROBORATE COMPLEXES

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
1.	ODH	SS	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
2.	MDH	SH	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
3.	SDH	SS	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
4.	ADH	SS	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
5.	PDH	SS	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
6.	TDH	SS	SS	SSH	SSH	In	In	In	SSH	SSH	In	In
7.	$Mn(ODH)_2(BF_4)_2$	S	SSH	SSH	In	SSH	SSH	SSH	In	SSH	In	In
8.	$Mn(ODH)_3(BF_4)_2$	S	SSH	SSH	SSH	In	In	SSH	In	SSH	In	SSH
9.	$Mn(MDH)_2(BF_4)_2$	S	SSH	SSH	In	In	In	SSH	In	SSH	SSH	SSH
10.	$Mn(MDH)_3(BF_4)_2$	S	In	SSH	SSH	In	In	SSH	SSH	In	In	SSH
11.	$Mn(SDH)_2(BF_4)_2$	S	SSH	In	SSH	SSH	In	SSH	SSH	SSH	SSH	SSH
12.	$Mn(SDH)_3(BF_4)_2$	S	In	In	In	In	In	SSH	In	SSH	In	In
13.	$Mn(ADH)_{3/2}(BF_4)_2$	S	SSH	In	In	In	In	In	SSH	SSH	In	In

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
14.	$Mn(ADH)_3(BF_4)_2$	S	In	In	In	In	In	In	SSH	In	In	In
15.	$Mn(PDH)_2(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In
16.	$Mn(PDH)_3(BF_4)_2$	In	In	In	In	In	In	In	SSH	SSH	In	SSH
17.	$Mn(TDH)_3(BF_4)_2$	In	In	In	In	In	In	SSH	In	In	In	In
18.	$Co(ODH)_2(BF_4)_2$	S	SSH	SSH	SSH	In	In	In	SSH	In	In	SSH
19.	$Co(ODH)_3(BF_4)_2$	S	SSH	SSH	SSH	In	In	SSH	SSH	In	In	In
20.	$Co(MDH)_{3/2}(BF_4)_2$	S	In	SSH	In	In	In	SSH	In	In	In	In
21.	$Co(MDH)_3(BF_4)_2$	S	In	In	In	In	In	In	In	In	In	In
22.	$Co(SDH)_2(BF_4)_2$	S	In	In	In	In	In	In	In	In	In	In
23.	$Co(SDH)_3(BF_4)_2$	S	SSH	In	In	In	In	In	In	In	In	In
24.	$Co(ADH)_2(BF_4)_2$	S	SSH	SSH	SSH	In	In	In	SSH	In	In	In
25.	$Co(ADH)_3(BF_4)_2$	S	SSH	SSH	SSH	In	In	In	SSH	In	In	In
26.	$Co(PDH)_3(BF_4)_2$	SSH	SSH	SSH	SSH	In	In	SSH	In	In	In	SSH

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
27.	$Co(TDH)_3(BF_4)_2$	In	In	In	In	In	In	In	In	In	In	SSH
28.	$Ni(ODH)_2(BF_4)_2$	SSH	SSH	SSH	In	In	In	SSH	In	In	SSH	In
29.	$Ni(ODH)_3(BF_4)_2$	SSH	SSH	In	In	In	In	SSH	In	In	In	In
30.	$Ni(MDH)_2(BF_4)_2$	S	SSH	In	In	In	In	In	In	In	In	In
31.	$Ni(MDH)_3(BF_4)_2$	S	SSH	In	In	In	In	In	In	In	In	In
32.	$Ni(SDH)_{3/2}(BF_4)_2$	S	In	In	In	In	In	In	In	In	In	In
33.	$Ni(SDH)_2(BF_4)_2$	S	In	In	In	In	In	In	In	In	In	In
34.	$Ni(ADH)_{3/2}(BF_4)_2$	SSH	SSH	In	In	In	In	In	In	In	In	In
35.	$Ni(ADH)_2(BF_4)_2$	SSH	SSH	SSH	In	In	In	In	SSH	In	SSH	In
36.	$Ni(PDH)_3(BF_4)_2$	In	SSH	SSH	SSH	In	In	SSH	In	In	In	In
37.	$Ni(TDH)_3(BF_4)_2$	In	In	In	In	In	In	SSH	In	SSH	In	In
38.	$Cu(ODH)_{3/2}(BF_4)_2$	SSH	SSH	In	In	In	In	SSH	SSH	SSH	In	In
39.	$Cu(ODH)_3(BF_4)_2$	SSH	SSH	SSH	In	SSH	In	SSH	In	SSH	In	In

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
40.	$Cu(MDH)_2(BF_4)_2$	S	SSH	SSH	In	In	In	SSH	In	In	In	In
41.	$Cu(MDH)_3(BF_4)_2$	S	SSH	SSH	In	In	In	SSH	In	SSH	In	In
42.	$Cu(SDH)_2(BF_4)_2$	S	In	SSH	In	In	In	SSH	SSH	SSH	SSH	In
43.	$Cu(SDH)_3(BF_4)_2$	S	In	SSH	In	In	In	SSH	SSH	SSH	In	In
44.	$Cu(ADH)_2(BF_4)_2$	SSH	SSH	In	In	In	In	In	SSH	SSH	In	In
45.	$Cu(ADH)_3(BF_4)_2$	SSH	SSH	In	In	In	In	In	In	SSH	SSH	SSH
46.	$Cu(PDH)_2(BF_4)_2$	SSH	SSH	In	In	In	In	SSH	SSH	SSH	SSH	In
47.	$Cu(PDH)_3(BF_4)_2$	SSH	SSH	SSH	In	In	SSH	In	SSH	SSH	In	In
48.	$Cu(TDH)_2(BF_4)_2$	In	In	In	In	In	In	SSH	SSH	SSH	In	In
49.	$Zn(ODH)_2(BF_4)_2$	S	SSH	In	In	In	In	In	In	SSH	In	SSH
50.	$Zn(ODH)_3(BF_4)_2$	S	In	In	In	In	In	In	In	SSH	In	In
51.	$Zn\ MDH\ (BF_4)_2$	S	SSH	SSH	In	In	In	In	SSH	SSH	In	In
52.	$Zn(MDH)_3(BF_4)_2$	S	SSH	In	In	In	In	In	SSH	SSH	In	In
53.	$Zn(SDH)_{3/2}(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
54.	$Zn(SDH)_2(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
55.	$Zn(ADH)_3(BF_4)_2$	S	SSH	In	In	In	In	In	In	In	In	In
56.	$Zn(PDH)_3(BF_4)_2$	In	SSH	In	In	In	In	In	In	SSH	SSH	SSH
57.	$Zn(TDH)_3(BF_4)_2$	In	In	In	In	In	In	In	In	In	SSH	In
58.	$Cd(ODH)_2(BF_4)_2$	S	SSH	In	In	In	In	In	SSH	SSH	In	In
59.	$Cd(ODH)_3(BF_4)_2$	S	SSH	In	In	In	In	In	SSH	SSH	In	In
60.	$Cd(MDH)_2(BF_4)_2$	S	SSH	SSH	In	In	In	In	SSH	In	In	In
61.	$Cd(SDH)_2(BF_4)_2$	S	In	In	In	In	In	In	SSH	In	In	In
62.	$Cd(SDH)_3(BF_4)_2$	S	In	In	In	In	In	In	SSH	In	SSH	In
63.	$Cd(ADH)_2(BF_4)_2$	S	In	In	In	In	In	In	SS	In	SSH	In
64.	$Cd(ADH)_3(BF_4)_2$	S	In	SSH	In	In	In	In	SSH	In	In	In
65.	$Cd(PDH)_2(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In
66.	$Cd(PDH)_3(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In
67.	$Cd(TDH)_3(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
68.	$Hg(ODH)_3(BF_4)_2$	SSH	SSH	SSH	In	In	In	In	SSH	SSH	In	In
69.	$Hg(ODH)_{3/2}(BF_4)_2$	SSH	SSH	In	In	In	In	In	SSH	SSH	In	In
70.	$Hg(MDH)_3(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In
71.	$Hg(MDH)_2(BF_4)_2$	In	In	In	In	In	In	In	SSH	In	In	In
72.	$Hg(SDH)(BF_4)_2$	SSH	In	In	In	In	In	In	In	SSH	In	In
73.	$Hg(SDH)_2(BF_4)_2$	SSH	In	SSH	In	In	In	In	In	In	In	SSH
74.	$Hg(ADH)_2(BF_4)_2$	S	In	In	In	In	In	In	SSH	SSH	In	SSH
75.	$Hg(ADH)_{3/2}(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
76.	$Hg(PDH)_2(BF_4)_2$	In	In	In	In	In	In	In	In	In	In	In
77.	$Hg(PDH)_3(BF_4)_2$	SSH	In	In	In	In	In	In	In	In	In	In
78.	$HgTDH(BF_4)_2$	In	In	In	In	In	In	In	In	In	In	In
79.	$Mg(ODH)_2(BF_4)_2$	SSH	SSH	In	In	In	In	In	In	In	In	In
80.	$Mg(ODH)_3(BF_4)_2$	In	SSH	In	In	In	In	In	SSH	In	In	In
81.	$Mg(MDH)_{3/2}(BF_4)_2$	S	SSH	In	In	In	In	In	SSH	SSH	In	In

TABLE 9 (Contd.)

No.	Compound	Water	Methanol	Ethanol	Acetone	Hexane	Benzene	Acetonitrile	DMSO	DMF	Nitrobenzene	Nitromethane
82.	$Mg(MDH)_2(BF_4)_2$	SSH	In	SSH	In	In	In	In	SSH	SSH	In	In
83.	$MgSDH(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
84.	$Mg(SDH)_3(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
85.	$MgADH(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
86.	$Mg(ADH)_3(BF_4)_2$	SSH	In	In	In	In	In	In	SSH	In	In	In
87.	$Mg(PDH)_2(BF_4)_2$	In	In	In	In	In	In	SSH	SSH	SSH	In	In
88.	$Mg(PDH)_3(BF_4)_2$	SSH	In	In	In	In	In	SSH	SSH	In	In	In
89.	$MgTDH(BF_4)_2$	In	In	In	In	In	In	SSH	SSH	In	In	In

Notes: S = Soluble

SS = Slightly soluble

SSH = Slightly soluble in hot

In = Insoluble.

TABLE 10: CONDUCTANCE DATA OF THE TETRAFLUOROBORATE COMPLEXES IN WATER AND DMSO ($\sim 10^{-3}$ M)

No.	Compound	Λ_m ($ohm^{-1}\ cm^2\ mol^{-1}$)
1.	$Mn(ODH)_2(BF_4)_2$	194
2.	$Mn(ODH)_3(BF_4)_2$	207
3.	$Mn(MDH)_2(BF_4)_2$	193
4.	$Mn(MDH)_3(BF_4)_2$	218
5.	$Mn(SDH)_2(BF_4)_2$	187
6.	$Mn(SDH)_3(BF_4)_2$	193
7.	$Mn(ADH)_{3/2}(BF_4)_2$	204
8.	$Mn(ADH)_3(BF_4)_2$	195
9.	$Co(ODH)_2(BF_4)_2$	198
10.	$Co(ODH)_3(BF_4)_2$	206
11.	$Co(MDH)_{3/2}(BF_4)_2$	189
12.	$Co(MDH)_3(BF_4)_2$	197
13.	$Co(SDH)_2(BF_4)_2$	186
14.	$Co(SDH)_3(BF_4)_2$	201
15.	$Co(ADH)_2(BF_4)_2$	159
16.	$Co(ADH)_3(BF_4)_2$	180
17.	$Ni(MDH)_2(BF_4)_2$	211
18.	$Ni(MDH)_3(BF_4)_2$	197
19.	$Ni(SDH)_{3/2}(BF_4)_2$	184

TABLE 10 (Contd.9)

No.	Compound	Λ_m (ohm^{-1} cm^2 mol^{-1})
20.	$Ni(SDH)_2(BF_4)_2$	175
21.	$Cu(MDH)_2(BF_4)_2$	187
22.	$Cu(MDH)_3(BF_4)_2$	205
23.	$Cu(SDH)_2(BF_4)_2$	157
24.	$Cu(SDH)_3(BF_4)_2$	183
25.	$Zn(ODH)_2(BF_4)_2$	204
26.	$Zn(ODH)_3(BF_4)_2$	198
27.	$Zn\ MDH(BF_4)_2$	180
28.	$Zn(MDH)_3(BF_4)_2$	169
29.	$Zn(ADH)_3(BF_4)_2$	197
30.	$Cd(ODH)_2(BF_4)_2$	170
31.	$Cd(ODH)_3(BF_4)_2$	184
32.	$Cd(MDH)_2(BF_4)_2$	181
33.	$Cd(SDH)_2(BF_4)_2$	151
34.	$Cd(SDH)_3(BF_4)_2$	166
35.	$Cd(ADH)_2(BF_4)_2$	161
36.	$Cd(ADH)_3(BF_4)_2$	156
37.	$Hg\ SDH(BF_4)_2$	219
38.	$Hg(ADH)_2(BF_4)_2$	192
39.	$Mg(MDH)_{3/2}(BF_4)_2$	175
*40.	$Mn(SDH)_2(BF_4)_2$	86
*41.	$Mn(SDH)_3(BF_4)_2$	89
*42.	$Cd(MDH)_2(BF_4)_2$	82

N.B. *Conductance in DMSO, the rest in water.

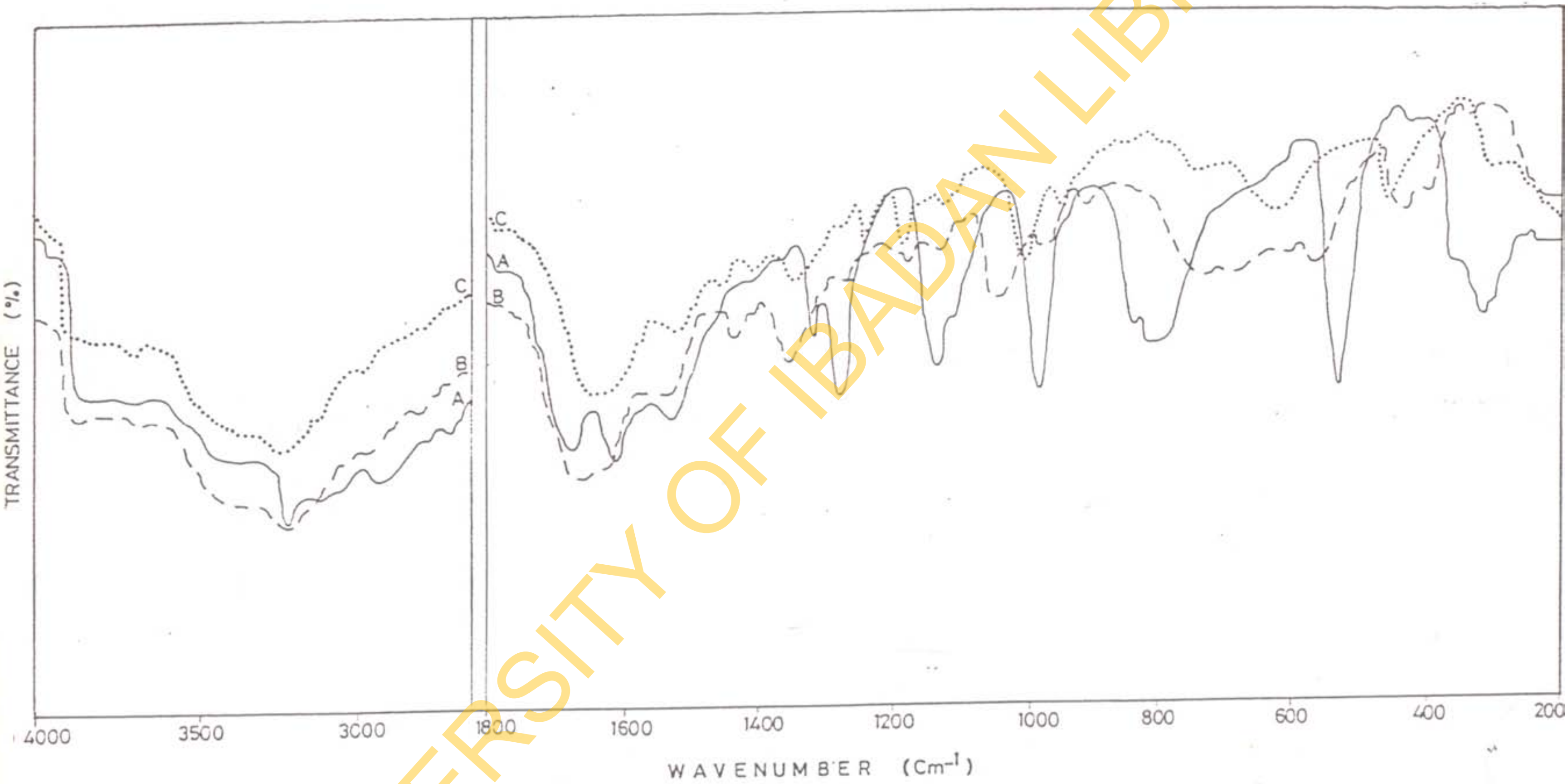


Fig. 12 I.R. Spectra of the Ligands

Fig. 12 A - Oxalic dihydrazide

B - Malonic dihydrazide

C - Succinic dihydrazide

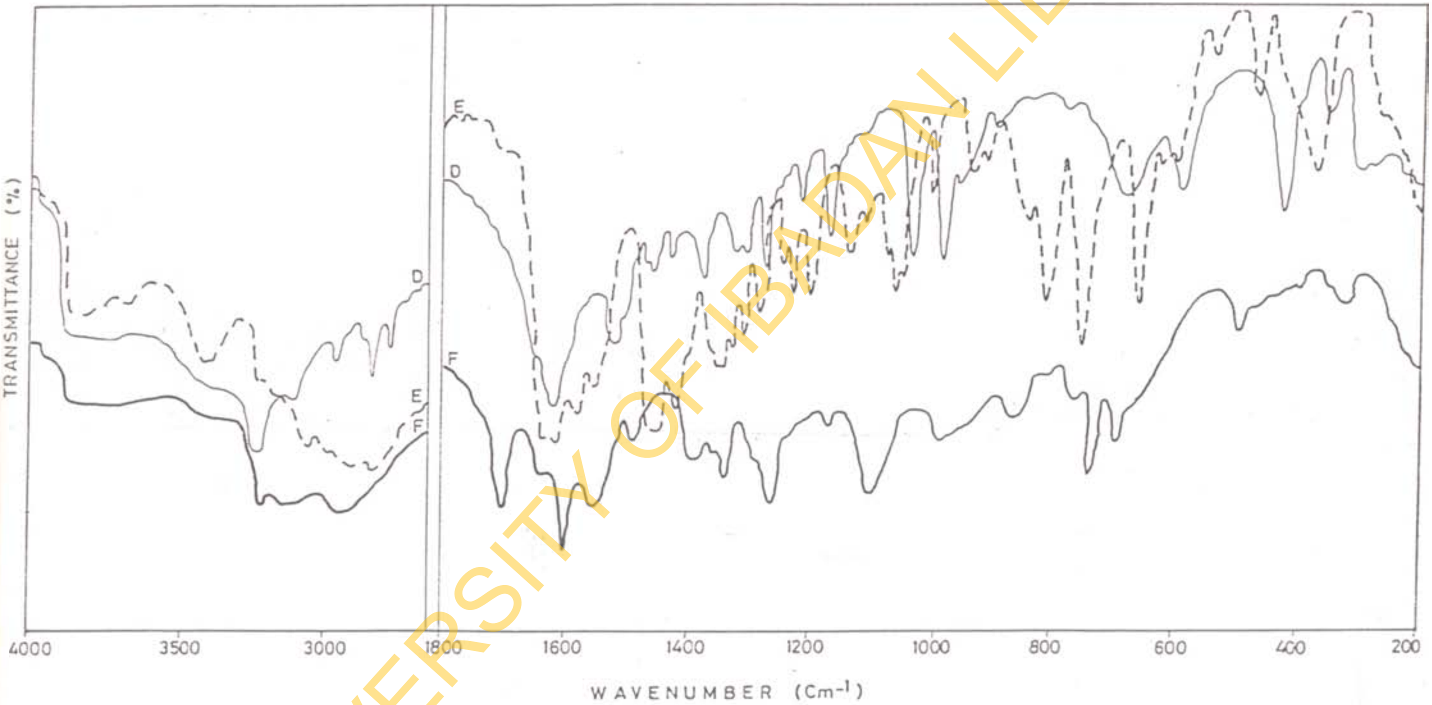


Fig.13 IR Spectra of the Ligands (continued)

Fig. 13 D - Adipic dihydrazide

E - Phthalic dihydrazide

F - Terephthalic dihydrazide

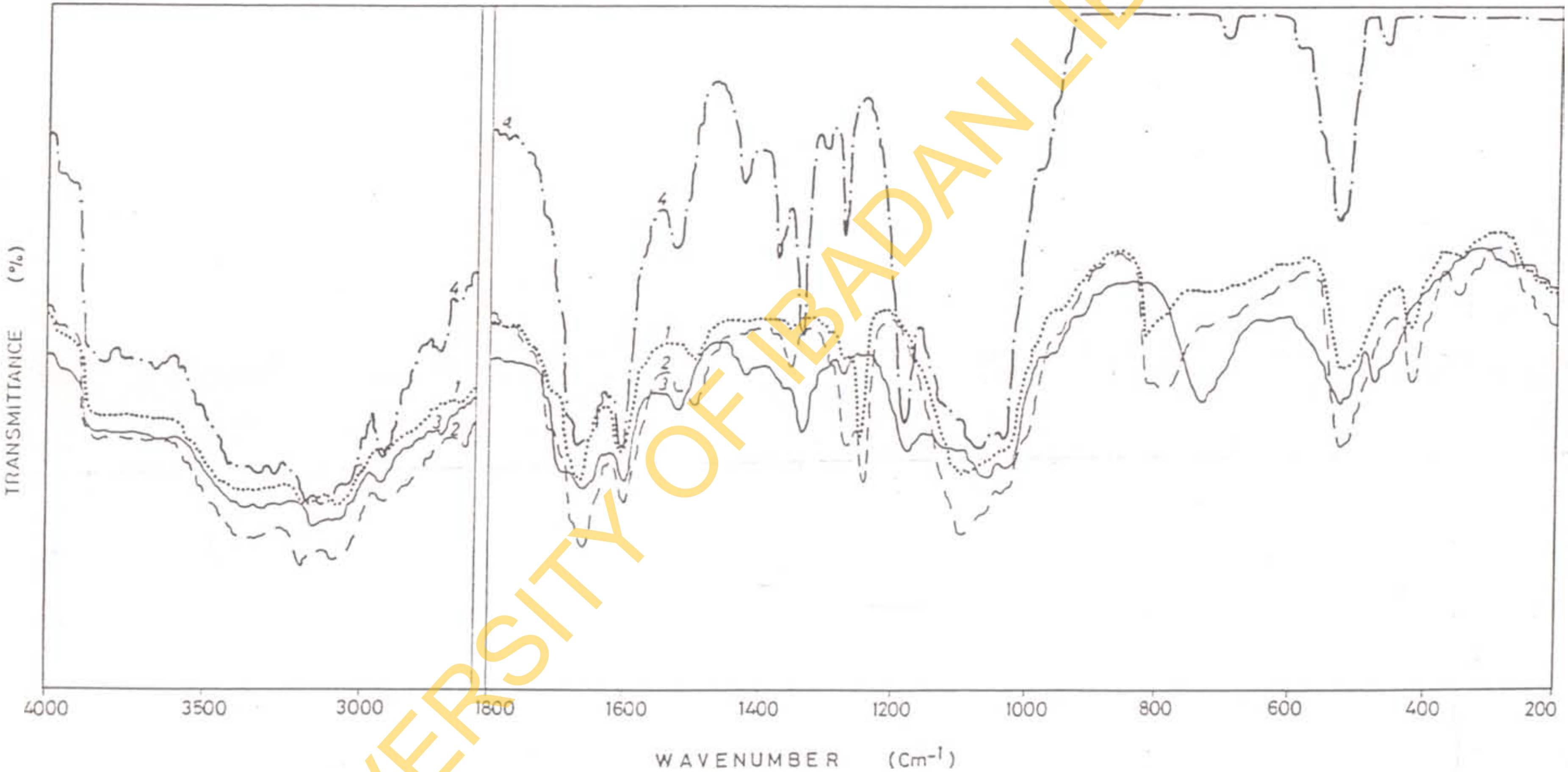


Fig. 14 IR. Spectra of manganese(II) tetrafluoroborate Complexes

Fig. 14
1. $Mn(ODH)_2(BF_4)_2$
2. $Mn(ODH)_3(BF_4)_2$
3. $Mn(MDH)_2(BF_4)_2$
4. $Mn(MDH)_3(BF_4)_2$

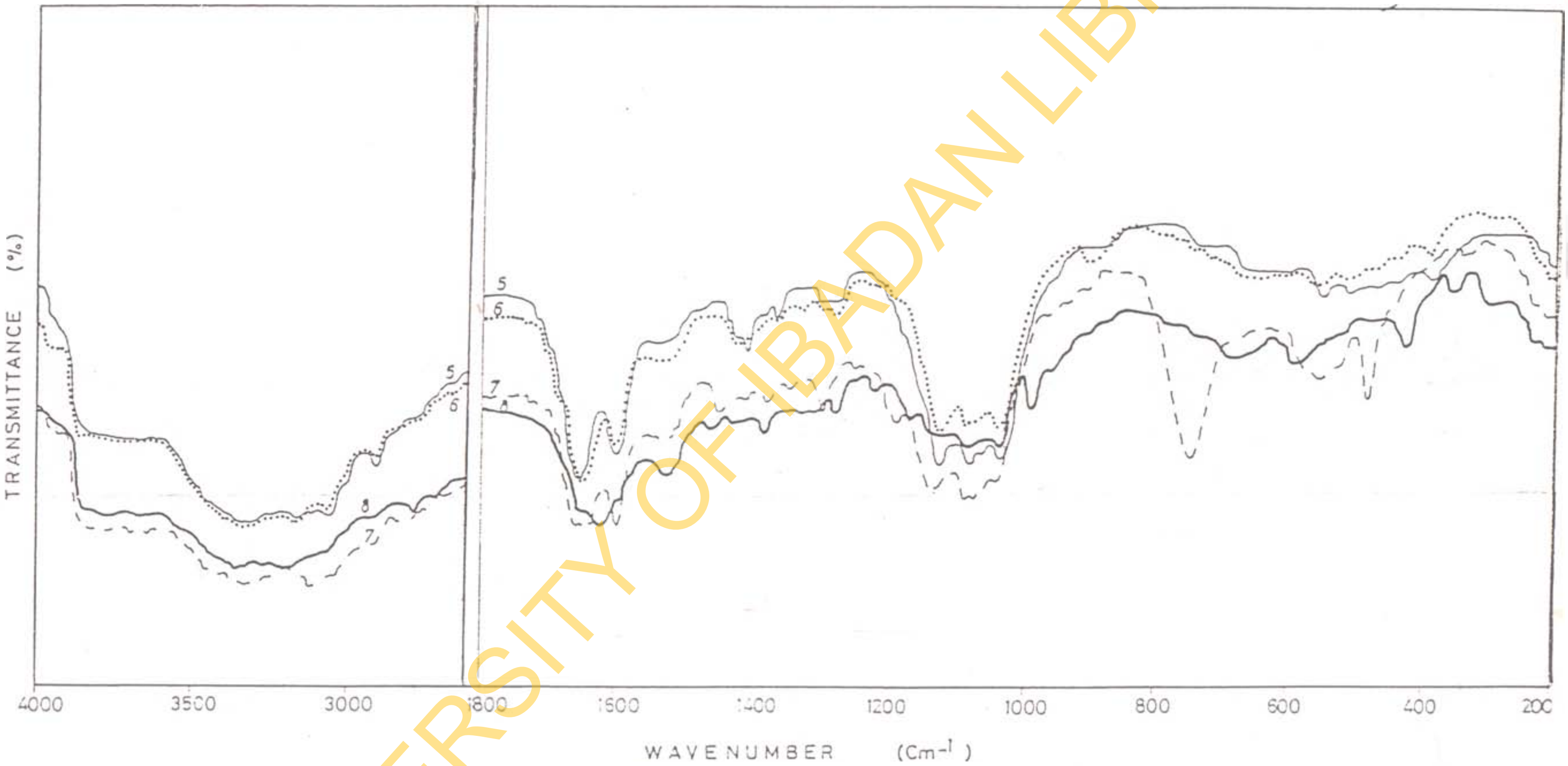


Fig.15: IR spectra of manganese (II) tetrafluoroborate Complexes. (continued)

Fig. 15·

5. $Mn(SDH)_2(BF_4)_2$

6. $Mn(SDH)_3(BF_4)_2$

7. $Mn(ADH)_{3/2}(BF_4)_2$

8. $Mn(ADH)_3(BF_4)_2$

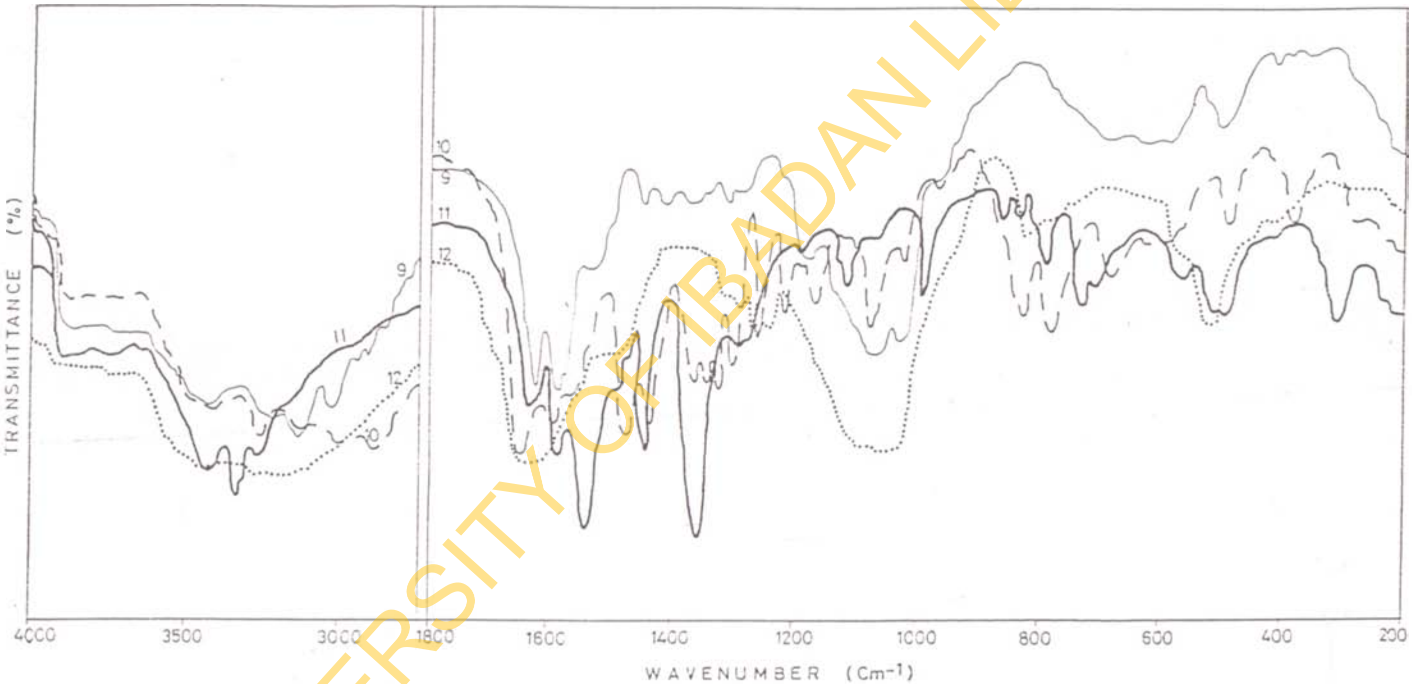


Fig. 16 I.R Spectra of manganese(II) and cobalt(II) tetrafluoroborate Complexes

Fig. 16: 9. $Mn(PDH)_2(BF_4)_2$

10. $Mn(PDH)_3(BF_4)_2$

11. $Mn(TDH)_3(BF_4)_2$

12. $Co(ODH)_2(BF_4)_2$

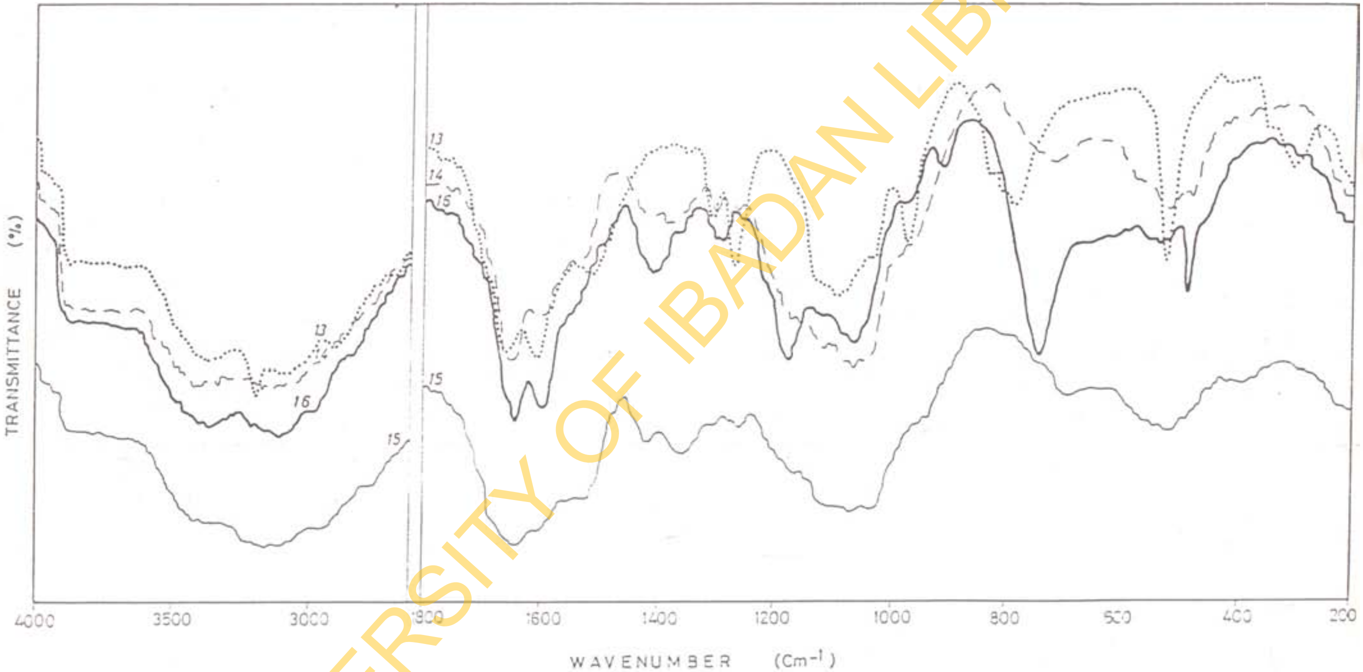


Fig.17 : IR Spectra of cobalt (II) tetrafluoroborate Complexes. (continued)

Fig. 17: 13. $Co(ODH)_2(BF_4)_2$

14. $Co(MDH)_{3/2}(BF_4)_2$

15. $Co(MDH)_3(BF_4)_2$

16. $Co(SDH)_2(BF_4)_2$

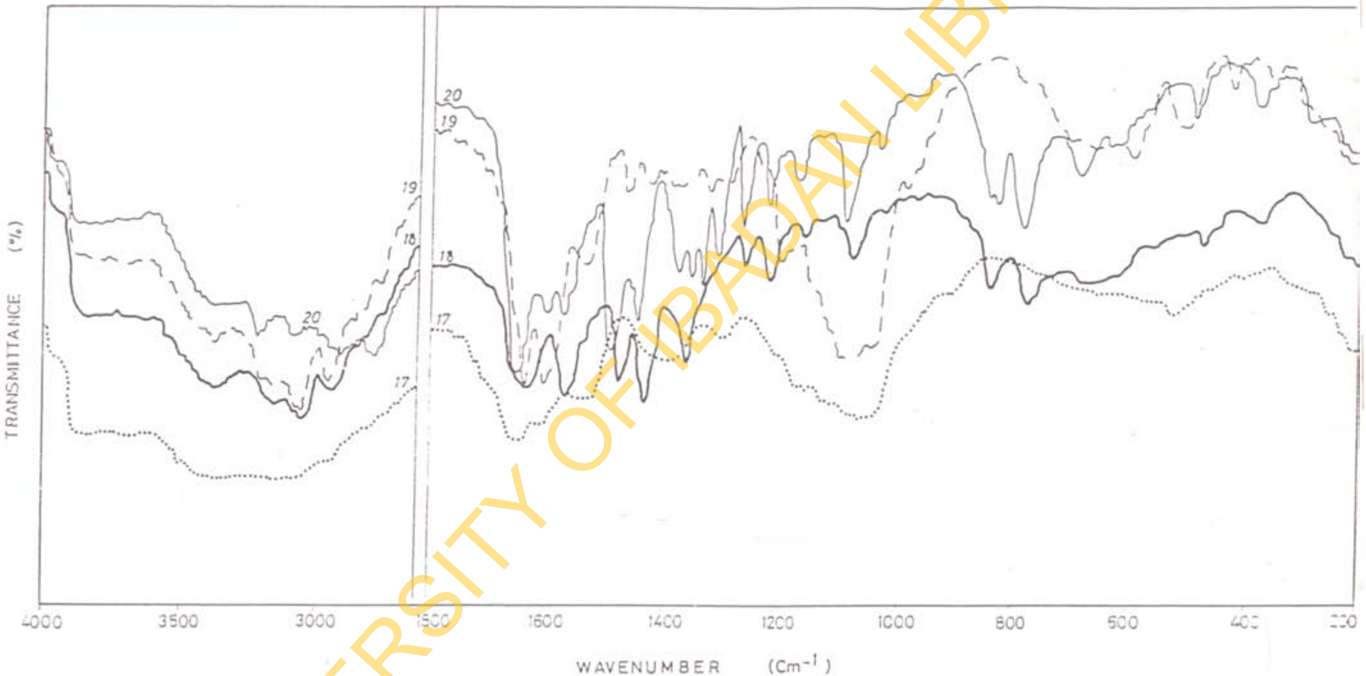


Fig. 18 : IR Spectra of cobalt (II) tetrafluoroborate Complexes. (continued)

Fig. 18. 17. $Co(SDH)_2(BF_4)_2$

18. $Co(ADH)_2(BF_4)_2$

19. $Co(ADH)_3(BF_4)_2$

20. $Co(PDH)_3(BF_4)_2$

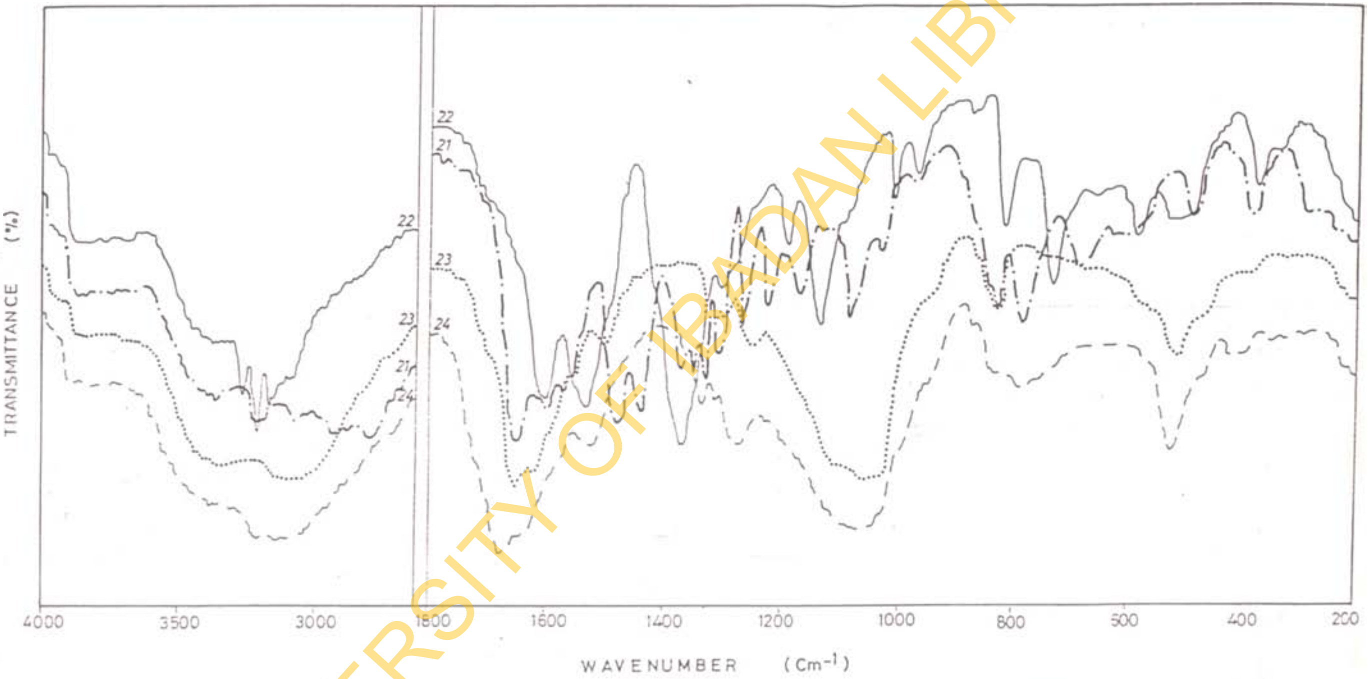


Fig. 19: IR Spectra of cobalt(II) and nickel(II) tetrafluoroborate Complexes (continued)

Fig. 19: 21. $Co(PDH)_3(BF_4)_2$

22. $Co(TDH)_3(BF_4)_2$

23. $Ni(ODH)_2(BF_4)_2$

24. $Ni(ODH)_3(BF_4)_2$

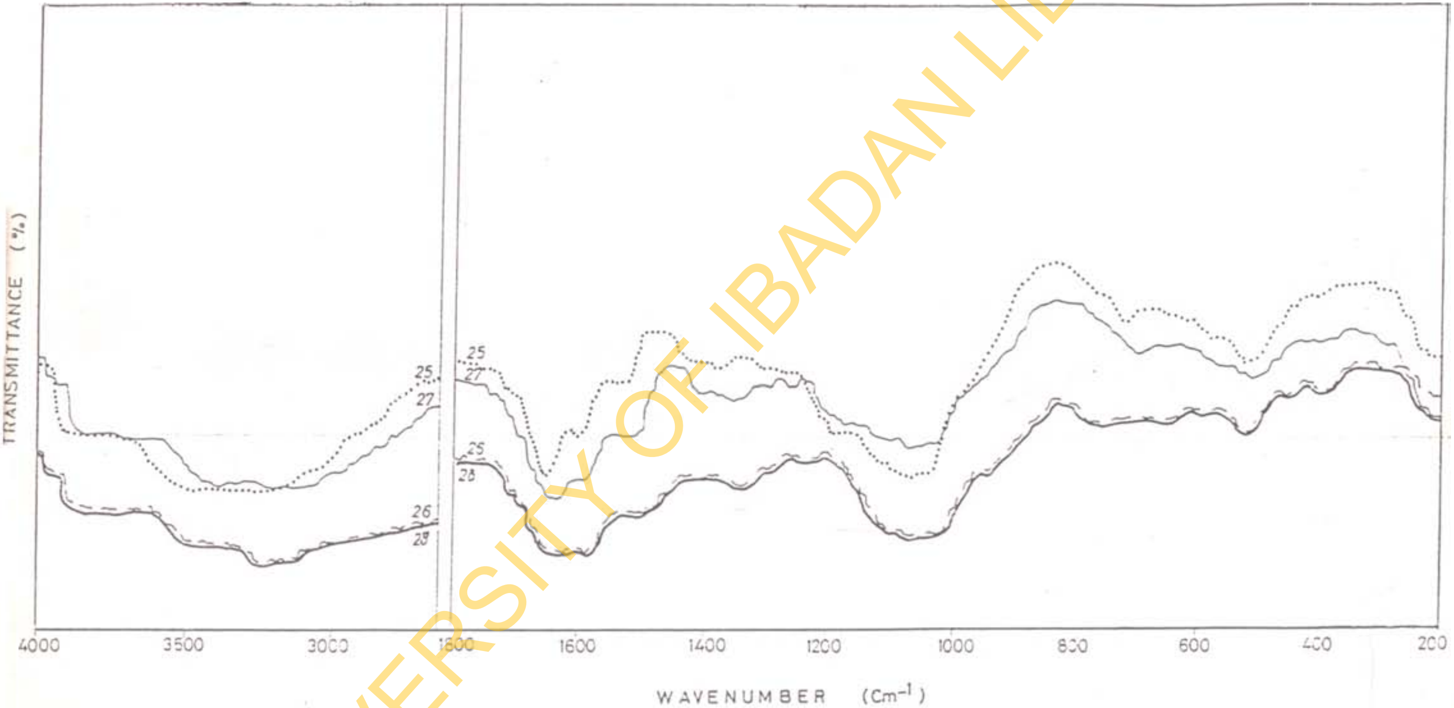


Fig.20: IR Spectra of nickel(II) tetrafluoroborate Complexes. (continued)

Fig. 20 25. $Ni(MDH)_2(BF_4)_2$

26. $Ni(MDH)_3(BF_4)_2$

27. $Ni(SDH)_{3/2}(BF_4)_2$

28. $Ni(SDH)_2(BF_4)_2$

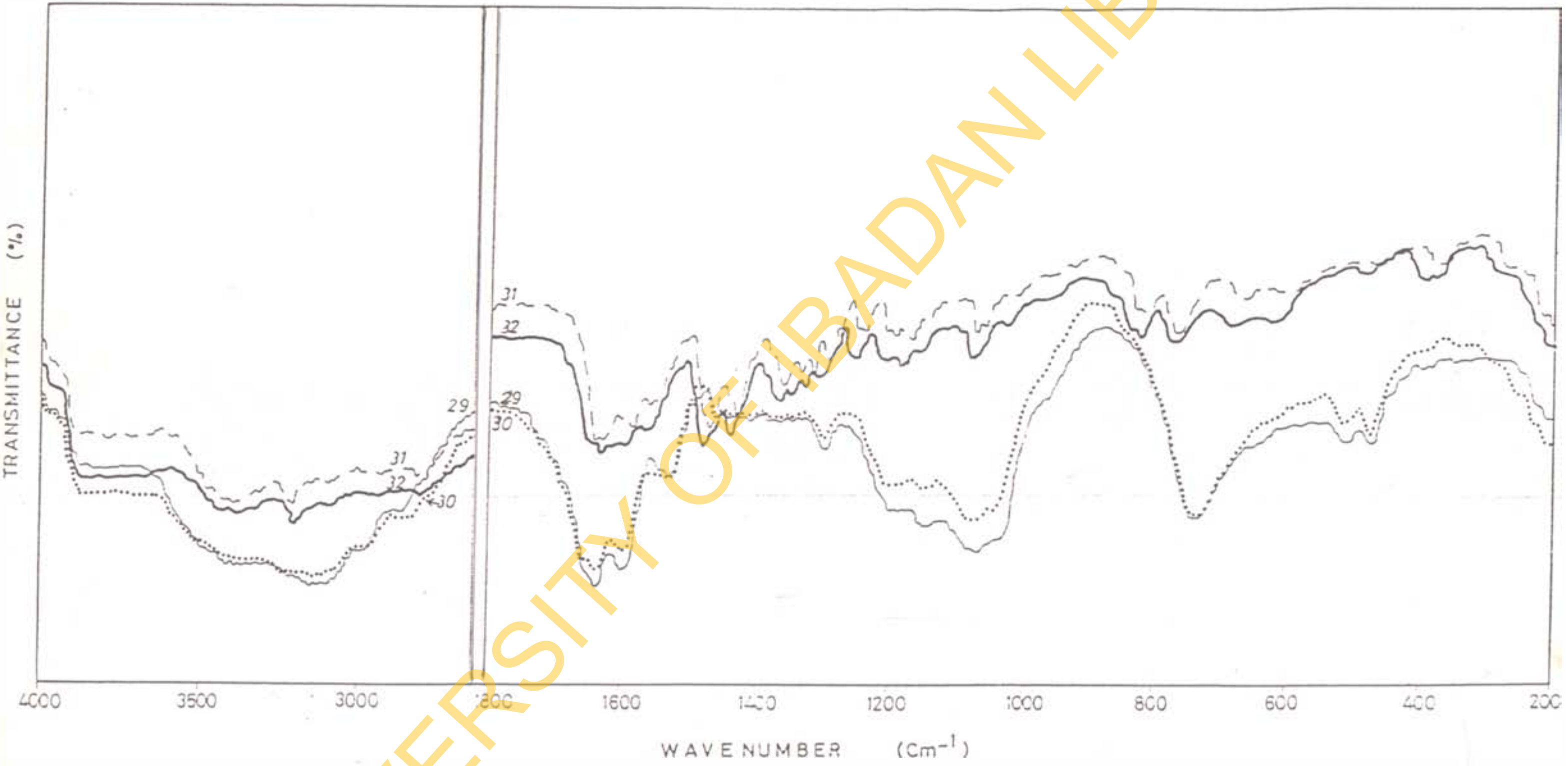
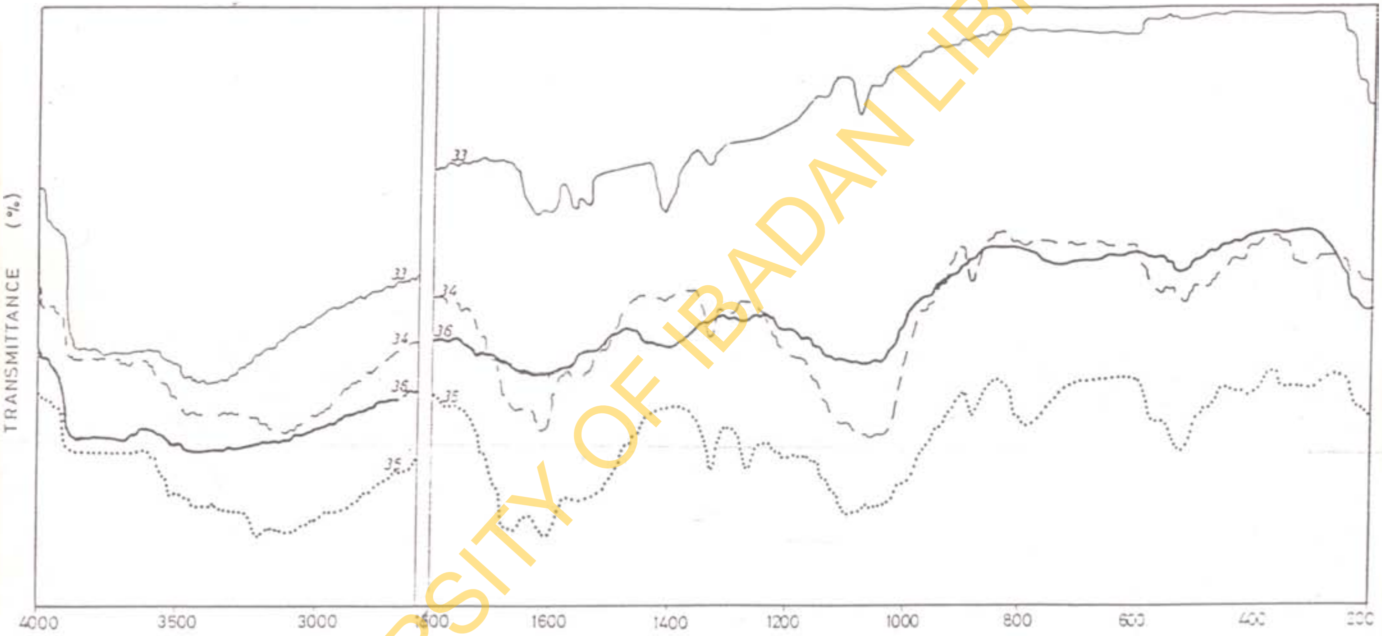


Fig. 21 IR Spectra of nickel(II) tetrafluoroborate Complexes. (continued)

Fig. 21: 29. $Ni(ADH)_{3/2}(BF_4)_2$

30. $Ni(ADH)_2(BF_4)_2$

31. $Ni(PDH)_3(BF_4)_2$



WAVENUMBER (Cm^{-1})

Fig.22. IR Spectra of nickel (II) and Copper (II) tetrafluoroborate Complexes.

Fig. 22 33. $Ni(TDH)_3(BF_4)_2$

34. $Cu(ODH)_{3/2}(BF_4)_2$

35. $Cu(ODH)_3(BF_4)_2$

36. $Cu(MDH)_3(BF_4)_2$

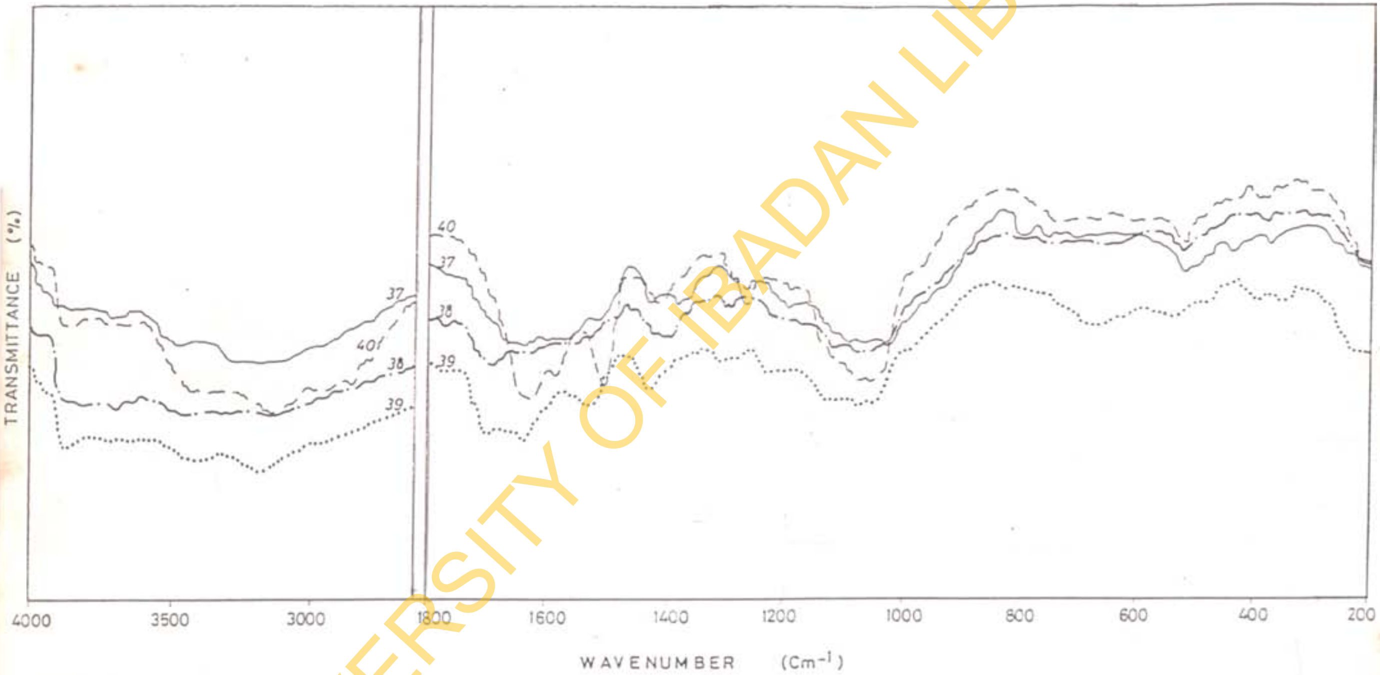


Fig. 23: IR Spectra of copper (II) tetrafluoroborate Complexes. (continued)

Fig. 23 37. $Cu(MDH)_3(BF_4)_2$

38. $Cu(SDH)_2(BF_4)_2$

39. $Cu(SDH)_3(BF_4)_2$

40. $Cu(ADH)_2(BF_4)_2$

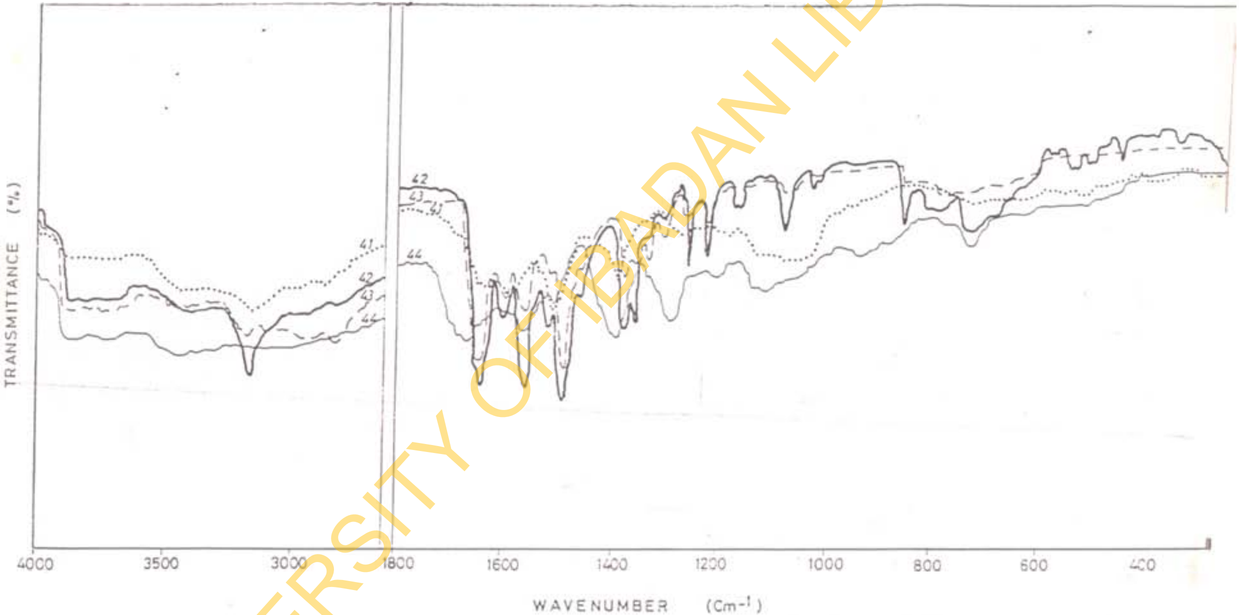


Fig. 24. IR Spectra of copper(II) tetrafluoroborate Complexes. (continued)

Fig. 24

41. $Cu(ADH)_3(BF_4)_2$

42. $Cu(PDH)_2(BF_4)_2$

43. $Cu(PDH)_3(BF_4)_2$

44. $Cu(TDH)_3(BF_4)_2$

TABLE 11: INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF OXALIC DIHYDRAZIDE COMPLEXES

ODH	$Mn(ODH)_2-(BF_4)_2$	$Mn(ODH)_2-(BF_4)_2$	$Co(ODH)_3-(BF_4)_2$	$Co(ODH)_3-(BF_4)_2$	$Ni(ODH)_2-(BF_4)_2$	$Ni(ODH)_3-(BF_4)_2$	Tentative assignments
32645	3240m,br	3243m,br	3260m,br	3260s,br	3280m,br	3260s,br	$\nu as(NH_2)$
3160w	3140m	3145m	3152w	3150m,br	3180m,br	3190w	$\nu(NH)$, $\nu s(NH_2)$
2995m	3010w	3000w	2990w	2998w	2850w	2910w	) Overtone
2780w	2760w	2760w	2772vw	2778w	2610w	2030w	) and) Combination
1768w							
1710 sh	1710 sh	1708 sh					
1660s	1628s	1623s	1630vs,br	1632s	1645vs	1650s	$\nu C = O$
1610s	1596m	1590s			1615vs		
1510s	1490w	1490w	1515w	1520w	1500m,br	1506m,br	$\nu CN + \delta NH_2$
1340w	1340w	1343m	1310w	1350w	1390w	1333w	
1303s			1290w	1305m	1310m		$\nu C - C$
1265vs	1265m	1265m	1260m,br	1259s	1290w	1270m	$\nu CN + \delta NH$
1125vs					1108w		)
1096 sh	1060s,br	1050s,br	1080vs,v.br	1090s,br	1060s,v,br	1070s,v.br	)) $\nu BF_4 - \nu CH_2$) δHNC) δHNN
968vs	940w	940w	975vw	970s	864w	870w	$\delta C - H$
829w	809s	809 sh	828m	830w	830m	838w	$\delta C - C$
795vs,br	792m,br	790s,br	790w	790s	798m	798m,br	δNCO
523vs	516s,br	518vs	520vs	529vs	510m	528s	)
	415m	412s	450w	425w	465w	480w	) M – L +
			415w	390w	380w	420m,br	) ligand vibra-
350 sh	340w	340m	320w	356m			) tional modes
310s		320w	290w	309m		350w	)

TABLE 11 (Contd.)

ODH	Cu(ODH)$_{3/2}$(BF$_4$)$_2$	Cu(ODH)$_3$(BF$_4$)$_2$	Zn(ODH)$_2$(BF$_4$)$_2$	Zn(ODH)$_3$(BF$_4$)$_2$	Cd(ODH)$_2$(BF$_4$)$_2$	Cd(ODH)$_3$(BF$_4$)$_2$	Tentative assignments
3264s	3400m,br	3400m,br 3270m,br	3255m	3265s	3258s	3250s	$\nu_{as}(NH_2)$
3160w	3190m,br		3005vw	3155w	3135w	3130w	$\nu(NH)$, $\delta_s(NH_2)$
2995m	2910w	3000w		2985m,br	2900m	3000w	)
2780w	2785w	2780w	2705w	2775w	2750w	2780w	) Overtone and
1768w	1768w	1775w		1773w,br			) combination
1710sh	1710sh	1715sh					)
1660s	1650s	1655s	1660s	1670s	1664s	1650s	$\nu C = O$
1610s	1610s	1605s	1615s	1605s	1640s		
1510s	1550m	1530m,br	1500m	1505s	1510m,br	1515m	$\nu CN + \delta NH_2$
1340w	1406w			1353m	1410m,br	1410w	$\nu C - H$
1303s	1303m	1330m		1305w	1312w	1310w	$\nu C - C$
1265vs	1295w	1265m	1265s	1270s	1255s	1265vs	$\nu CN + \delta NH$
1125vs		1200w					
1096sh	1070vs,v.br	1060vs,br	1070vs,br	1078vs,br	1064vs,v.br	1060vs,v,br)	νBF_4^-, νCH_2
968vs			990w	990sh	950m	995w	) δHNC, δHNN
	880s	880m		975s		950w	) $\delta C - H$
829w			830w	835w			) $\delta C - C$
795vs,br	790w,br	790m,br	790s	790vs	715s	795vs	δNCO
523vs	555m	570w					
	515m	525m	480s	485vs	515vs	520vs	) M - L +
350sh	415w	415m,br	397w	420m	420m	415m	) Ligand
310s	320m,br	330m,br	353w	320w	362w	340m,br	) Vibrational
					320w	300w	) modes

TABLE 11 (Contd)

INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF OXALIC DIHYDRAZIDE COMPLEXES (Contd.)

ODH	$Hg(ODH)_3(BF_4)_2$	$Hg(ODH)_{3/2}(BF_4)_2$	$Mg(ODH)_2(BF_4)_2$	$Mg(ODH)_2(BF_4)_2$	Tentative assignments
3264s	3310s	3310w			
	3260vs	3260s	3260vs	3260vs	$\nu as(NH_2)$
3160w			3180vs	3250m,br	$\nu(NH)$, $\nu s(NH_2)$
2995m	3010vw	3009vw	3015m	2980m,br	
2780w	2789w				Overtone and
1768w		2782w	2780m	2780w	combination
1710sh	1774w	1768w	1770w	1775w	
1660s	1645vs	1640s	1660vs	1660vs	$\nu C = O$
1610s	1570vs	1570s	1598m	1600m	
1510s	1512s	1515m	1535m	1504s,br	$\nu CN + \delta NH_2$
			1490s		
1340w	1405m,br	1410m	1350m	1350s	$\nu C - H$
1303s	1302m	1315w			
	1292m	1288m			$\nu C - C$
1265vs	1255s	1255s	1260s	1265vs	$\nu CN + \delta NH$
1125vs	1132m	1115s	1205m		
1096sh	1070vs,v,br	1080s,v,br	1090s,br	1090s,br	νBF_4^-, νCH_2, δHNC, δHNN
968vs	955s	955s	1000w	990s	$\delta C - H$
829w	825m	825m	860vs,br		$\delta C - C$
795vs,br	720s	720s		796vs	δNCO
523vs	525vs	510vs	528vs	528s	
			485vs	415m	M - L + Ligand
350vs	340m,br	365m		350m	Vibrational modes
310s		330m	310s	350m	
			245w	317m	

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF MALONIC DIHYDRAZIDE COMPLEXES

MDH	$Mn(MDH)_2-(BF_4)_2$	$Mn(MDH)_3-(BF_4)_2$	$Co(MDH)_{3/2}-(BF_4)_2$	$Co(MDH)_3-(BF_4)_2$	$Ni(MDH)_2-(BF_4)_2$	$Ni(MDH)_3-(BF_4)_2$	Tentative Assignments
3180m,br	3120m,br	3184s,br	3250m,br	3240vs,br	3248m,v.br	3230m,br	$\nu_{as}(NH_2)$
3030w	3030m	3100m			3025w	3040w	$\nu(NH)$, $\nu_s(NH_2)$
2848w	3020w 2830w	3018m 2830m	3011w	3019w		2930w	Overtone and combination
1650vs,br 1605s,br	1650s,br 1585m	1650vs 1591vs	1640s 1585m	1645vs 1590m	1660s 1612m	1635s,br 1590m	$\nu C=O$
1515m	1510m	1510m	1512w	1510m	1540m	1530m	$\nu CN + \delta NH_2$
1418m 1388w 1335s	1410w 1353w 1320s	1410m 1358s 1320vs	1405m 1360m	1405s 1350s	1420m,br 1390m	1410m 1340m,br	$\nu C-H$ $\nu C-C$
1282vw	1290w	1285w	1296w	1290w	1291w	1290w	νCH_2
1250w	1260w	1258vs	1250w	1250m	1205w	1250w	$\nu CN + \delta NH_2$
1155w	1155m	1170vs	1104s,br	1100vs,br			νBF_4^-, νCH_2
1110w 1025s,br	1090s,br	1060s,v.br			1100s,br	1100m,br	δHNC, δHNN
950m,br	957w 942w	950w	950w	805m	950w	940m	$\delta C-H$ $\delta C-C$
895m 725s,br 660m,br 590w	900w 725s,br 625w	690w 635m	725m 710m,br	740m 680m	720m 580w	740m,br 640m,br	δNCO δCH_2
550m 415s 378m 318w	519m 468m	518vs 450m	555w 510m 470m 390w 346w	540s 510s 400m,br 350w	520m,br 410w	510m 445w 390m 315w	M - L + ligand vibrational modes

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF MALONIC DIHYDRAZIDE COMPLEXES

MDH	$Cu(MDH)_2-(BF_4)_2$	$Cu(MDH)_3-(BF_4)_2$	$Zn\ MDH-(BF_4)_2$	$Zn(MDH)_3-(BF_4)_2$	$Cd(MDH)_2-(BF_4)_2$	Tentative Assignments
	3280w,br	3280w,br			3250m	
3180m,br			3175w	3170vw	3150m	$\nu_{as}(NH_2)$
3030w	3040w	3008vw	3005vw	3000vw	3000w	$\nu(NH)$, $\nu_s(NH_2)$
2848w			2825vw	2820w		) Overtone and
			2305w	2300w		) combination
1650vs,br	1620m,br	1635m,br	1635s	1637s	1650s,br	$\nu C=O$
			1598m	1605 sh	1605m	
1605s,br		1580m				
	1555m					
1515m	1515w	1515w	1510m	1510m	1518w	$\nu CN + \delta NH_2$
1418m	1400m,br	1430m	1415w,br	1495w	1455w	$\nu C-H$
					1405w	
1388w		1382m	1355s	1385w		$\nu C-C$
				1350m	1350s	
1335s	1325w	1320w			1315m	
1282vw			1290w	1290w	1295w	νCH_2
1250w	1265m,br	1265m	1250w	1250m	1238m	$\nu CN + \delta NH_2$
1155w	1116w	1190w	1170vw	1160w	1180m	
1110w	1075s,v.br	1070s,v.br	1050m,br	1050w,br	1040vs,br	νBF_4^-, νCH_2
1025s,br						δHNC, δHNN
950m,br		925w	965vw	960w	975m	$\delta C-H$
			925w	927vw	819m	$\delta C-C$
895m		795w				
725s,br	725m,br	745w	714m	715m	735m,br	δNCO
660m,br	660s,br		682w	690m,br	675s,br	δCH_2
590w						)
550m	520m,br	510m	529vw	530vw	586w	)
					555m	)
					469s	) M - L + Ligand
415s		430w	480w,br	413vw	415m	) vibrational
378m	350w,br	365w	348vw	352vw	345w	) modes
318w					280w,br.	)

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF MALONIC DIHYDRAZIDE COMPLEXES

MDH	Hg(MDH)$_3$(BF$_4$)$_2$	Hg(MDH)$_2$(BF$_4$)$_2$	Mg(MDH)$_{3/2}$(BF$_4$)$_2$	Mg(MDH)$_2$(BF$_4$)$_2$	Tentative Assignments
3180m,br	3160m,br	3200m,br	3280m 3170m	3270s 3160m	νas(NH$_2$)
3030w	3030vw	3032w	3015w	3030m	ν(NH), νs(NH$_2$)
2848w		2860w	2890w		Overtone and combination
1650vs,br	1650s,br	1645s,br	1630s	1630vs	νC = O
1605s,br	1590s	1590w	1575s	1580s	
1515m	1492m,br	1495m	1520w,br	1520m	νCN + δNH$_2$
1418m		1410m	1480m 1400m	1485m 1404m	νC – H
1388w 1335s	1345m	1350m 1320w	1340m	1350s	νC – C
1282vw	1290w	1295w	1292w	1285w	νCH$_2$
1250w	1230w	1260m	1220m	1228m	νCN + δNH$_2$
1155w				1190m	
1110w	1060s,v.br	1070s,v.br	1070m,br	1080m,br	νBF$_4^-$, νCH$_2$
1025s,br					δHNC, δHNN
950m,br	955m	950 vw	945m,br	950s	δC – H
895m					δC – C
725s,br	740m,br	780m	740w,br	740w	δNCO
660m,br 590w 550m 415s 378m 318w	650m,br 520m 450w 380w,br	685m 525m,br 485w 395w	660w,br 540w 440m,br	660m,br 580w 544m 450m,br 400m	M – L + Ligand vibrational modes

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF SUCCINIC DIHYDRAZIDE COMPLEXES

SDH	$Mn(SDH)_2-(BF_4)_2$	$Mn(SDH)_3-(BF_4)_2$	$Co(SDH)_2-(BF_4)_2$	$Co(SDH)_3-(BF_4)_2$	$Ni(SDH)_{3/2}-(BF_4)_2$	$Ni(SDH)_2-(BF_4)_2$	Tentative Assignments
.3180m,br	3230m,br	3250m,br	3200s,br	3200s,br	3250m,v.br	3200s,v.br	$\nu as(NH_2)$
3020w	3010m	3010m	3040w	3010w	2930w	2920w	$\nu(NH)$, $\nu s(NH_2)$
2630vw	2625w	2620w	2600w		2638w	2640w	Overtone and combination
1630s,br	1645s	1640s	1630s	1635s	1630s,br	1630s,br	$\nu C = O$
	1589s	1589s	1585s	1590m	1580w	1585s	
1510m	1520w	1520w	1535w	1520m	1530w	1520m,br	$\nu CN + \delta NH_2$
1445w	1415w	1415w			1400m,br	1400s,br	
	1398m	1400m	1394m	1380m,br			$\nu C - H$
1335m	1353w	1356w	1345w				$\nu C - C$
		1320w					
1232m	1280m,br	1275w	1280w	1280w	1285m,br	1285m	$\nu CN + \delta NH_2$
		1265w	1247w				
1174s	1116m	1115m	1160s				) νBF_4^-, νCH_2
1112w	1070vs,br	1074s,br	1060s,br	1060s,br	1100s,v.br	1100s,br	) δHNC, δHNN
997s			965m			970w	) $\delta C - H$
940w,br	940w	915w				948w	) $\delta C - C$
	870w	890m	.895m	890m	895w	895m	)
740m			730vs				δNCO
620m,br	630w,br	645w,br	630vw	640w	650w,br	640m,br	
450s	545w	547w		510m	510m	510m	)
	505w	508w					) M - L +
		460w					) ligand
		435w			445w		) vibrational
					390w	390w	) modes
	380w	385w	300vw	350w	345w		)
292w		290w				295w	

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF SUCCINIC DIHYDRAZIDE COMPLEXES (Contd.)

SDH	$Cu(SDH)_2(BF_4)_2$	$Cu(SDH)_3-(BF_4)_2$	$Zn(SDH)_{3/2}-(BF_4)_2$	$Zn(SDH)_2-(BF_4)_2$	$Cd(SDH)_2-(BF_4)_2$	$Cd(SDH)_3-(BF_4)_2$	Tentative Assignments
3180m,br	3200w,br	3230m,br	3175m,br	3105w	3240s,br	3200s,br	$\nu as(NH_2)$
3180m,br	3100w						
3020w			3025m	3035w	3040m	3041vw	ν (NH), $\nu s(NH_2)$
2630vw	2630vw		2905w,br	2885w	2910w		
		2350w	2305w,br	2305m			Overtone and combination
		1690s					
1630s,br	1625w,br	1620m,br	1630s	1630s,br	1640vs	1630s	$\nu C = O$
	1550w,br				1580s	1589s	
1510m	1525w	1515m	1530w	1530m	1530s	1510m	$\nu CN + \delta NH_2$
1445w	1400m,br	1410m	1406w	1405m,br	1450w	1405m	$\nu C - H$
			1395w		1430s		
1335sh					1340s		
1232m	1295w	1295w	1230m		1290 m	1290m	$\nu C - C$
		1270w	1205sh	1228m	1228s	1225m	$\nu CN + \delta NH$
1174s			1155m	1155m	1170s		νBF_4^-, νCH_2
1112w	1100m,v.br	1080m,v.br	1045s,br	1055m,v.br	1050vs,br	1080vs,v.br	δHNC δHNN
997s		970w	973m,br	968w			$\delta C - H$
940w			897m,br	900vw	940w	885m	$\delta C - C$
740m	740w,br	740w,br			730s	700w	δNCO
620m,br	640w,br	640w,br	645m,br		655w		
	510m	520w	525w		630m		M - L + Ligand vibrational modes
450s		460w	455w	515w	580m		
					525m	510m	
	360w	370w	398vw	391vw	476 sh		
292w		325w	349vw	348vw	395w	330w	

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF SUCCINIC DIHYDRAZIDE COMPLEXES

SDH	Hg SDH$(BF_4)_2$	Hg$(SDH)_2(BF_4)_2$	Mg SDH$(BF_4)_2$	Mg$(SDH)_3(BF_4)_2$	Tentative Assignments
3180m,br	3200m,br	3170s,br	3200s,br	3280vs 3190m	$\nu as(NH_2)$
3020w	3024vw	3022vw	3020w	3010m	$\nu(NH)$, $\nu s(NH_2)$
2630vw		1695w	1680s		Overtone and combination
1630s,br	1620s	1615m	1615s 1590vs	1620vs 1580s	$\nu C = O$
1510m	1520m	1525w	1520m	1505s	$\nu CN + \delta NH_2$
1445w	1420m,br	1472m 1390s	1475s 1403vs	1445m	$\nu C - H$
1335m	1295m	1290m	1300w 1275w	1340vs	$\nu C - C$
1232m	1230w	1228w	1210m	1235s	$\nu CN + \delta NH_2$
1174s			1110s,br	1175s,br	νBF_4^-, δCH_2
1112w	1060vs,v.br	1040s,br			δHNC, δHNN
997s		940w	942m	940s	$\delta C - H$
940w	880w	800w,br	860w,br 810w		$\delta C - C$
740w,br	735w	740w	735w,br	740s	δNCO
620m,br		630m,br		625s,br	
	515s	510m	585w		
450s	455w		440s,br	445m	M - L + ligand vibrational modes
	415w	490w	345w	350m	
292w	330w,br			310m	

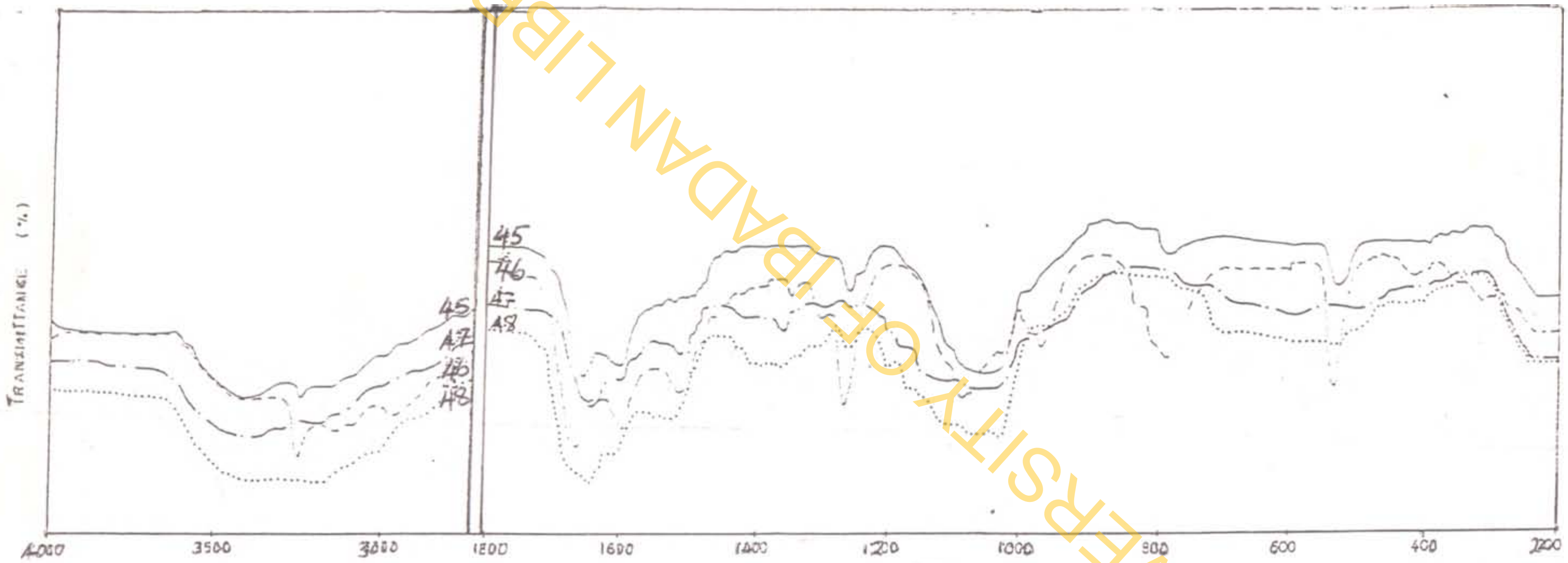


Fig 2.5 IR Spectra of Zinc(II) tetrafluoroborate complexes

Fig. 25

45. $Zn(ODH)_2(BF_4)_2$

46. $Zn(ODH)_3(BF_4)_2$

47. $ZnMDH(BF_4)_2$

48. $Zn(MDH)_3(BF_4)_2$

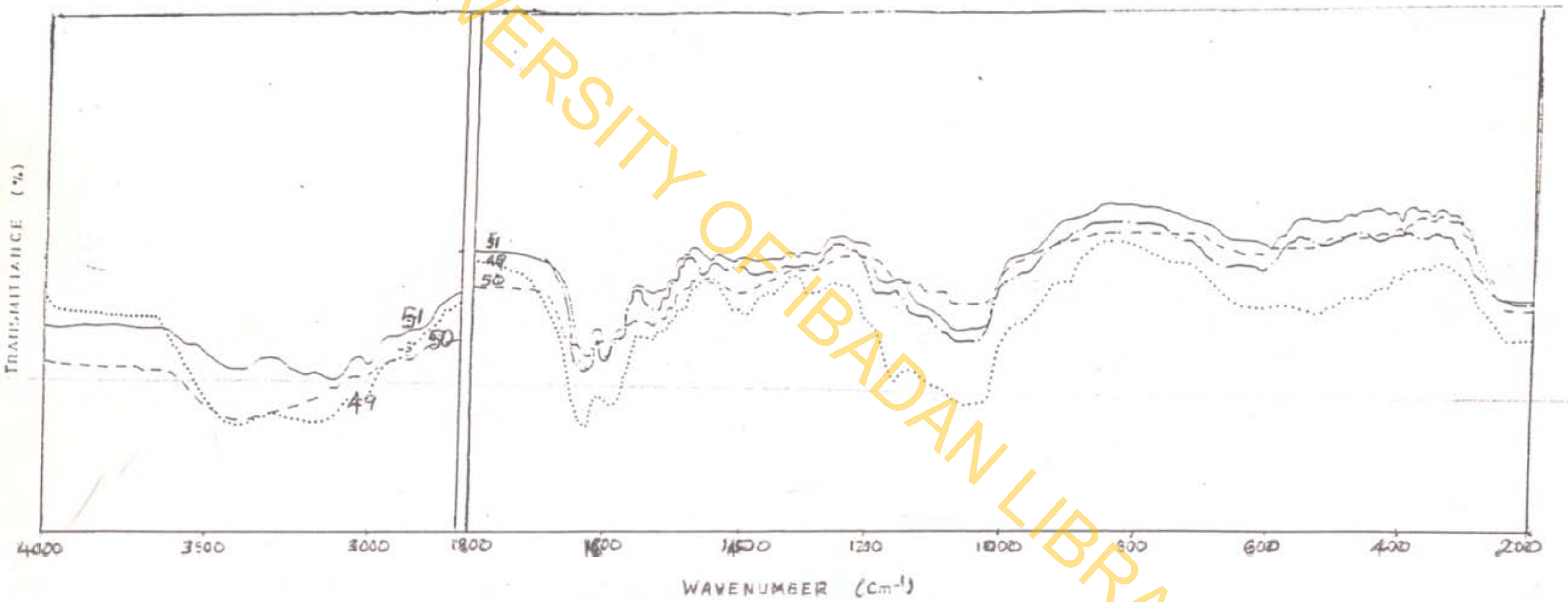


Fig 26. IR. Spectra of Zinc(II) tetrafluoroborate complexes (continued).

Fig. 26 49. $Zn(SDH)_{3/2}(BF_4)_2$

50. $Zn(SDH)_2(BF_4)_2$

51. $Zn(ADH)_3(BF_4)_2$

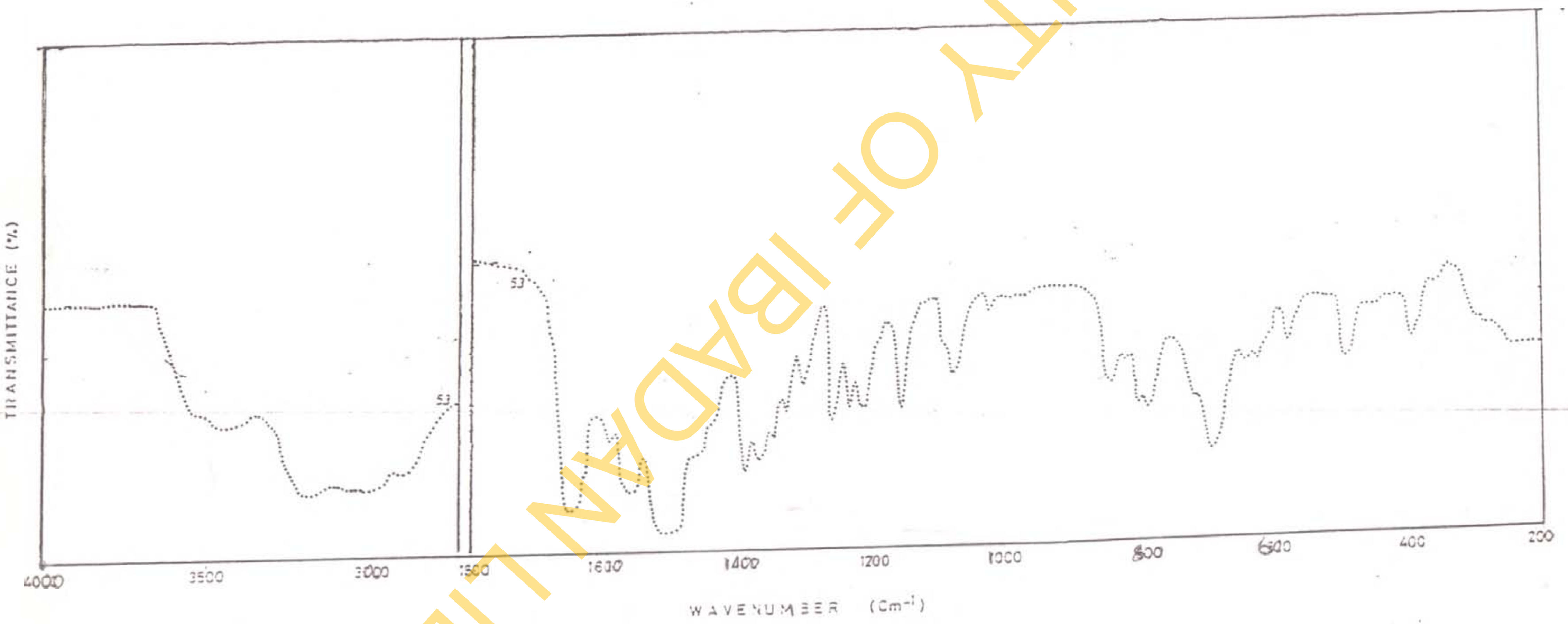


Fig. 27 IR Spectra of Zinc(II) tetrafluoroborate Complexes (continued)

Fig. 27 53. $Zn(PDH)_3(BF_4)_2$

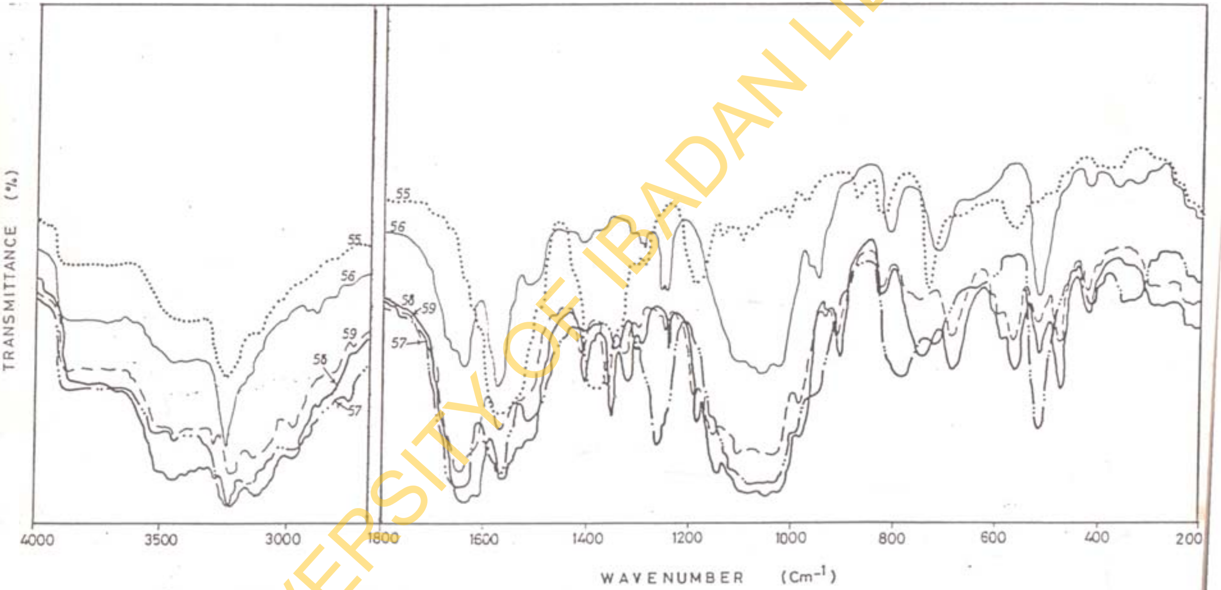


Fig28: IR Spectra of zinc(II) and cadmium(II) tetrafluoroborate Complexes.

Fig.28: 55. $Zn(TDH)_3(BF_4)_2$

56. $Cd(ODH)_2(BF_4)_2$

57. $Cd(ODH)_3(BF_4)_2$

58. $Cd(MDH)_2(BF_4)_2$

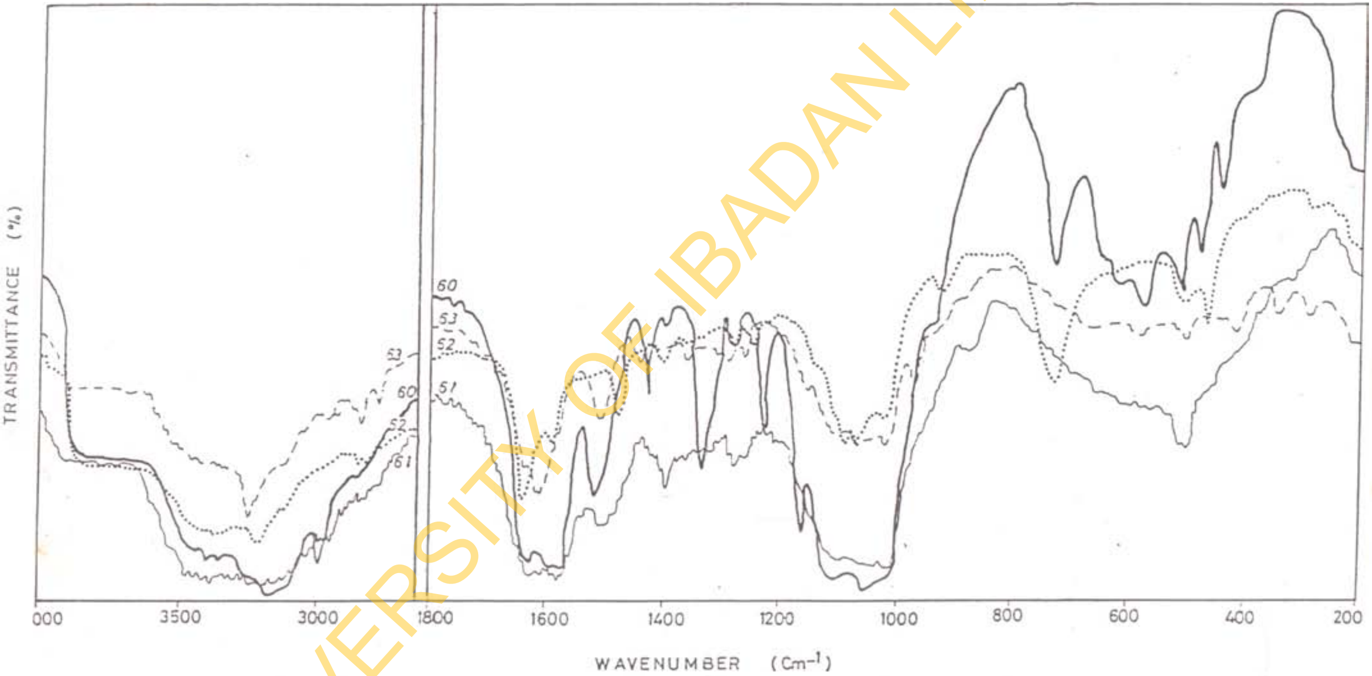


Fig.29. IR Spectra of cadmium(II) tetrafluoborate Complexes.
(continued)

Fig. 29: 60. $Cd(SDH)_2(BF_4)_2$

61. $Cd(SDH)_3(BF_4)_2$

62. $Cd(ADH)_2(BF_4)_2$

63. $Cd(ADH)_3(BF_4)_2$

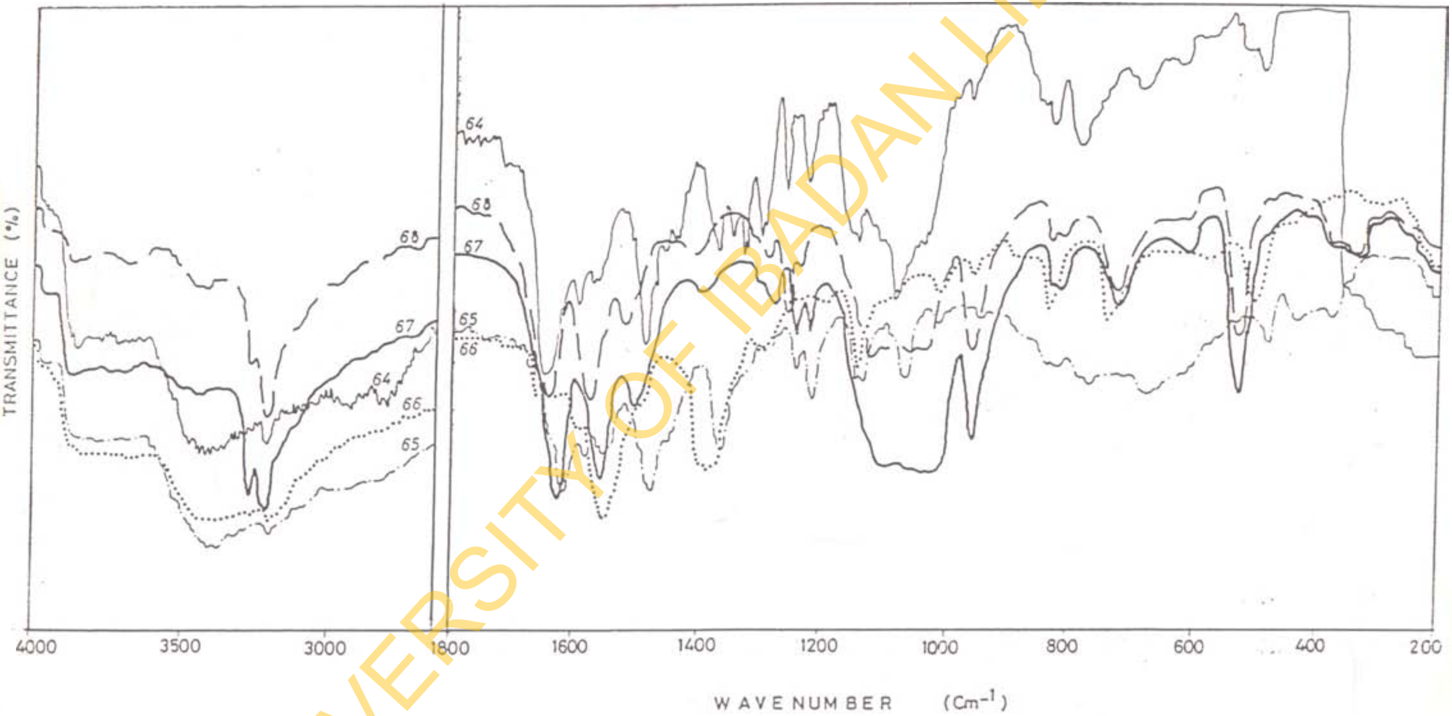


Fig.30: IR Spectra of cadmium(II) and mercury(II) tetrafluoroborate Complexes.

Fig. 30. 64. $Cd(PDH)_2(BF_4)_2$

65. $Cd(PDH)_3(BF_4)_2$

66. $Cd(TDH)_3(BF_4)_2$

67. $Hg(ODH)_3(BF_4)_2$

68. $Hg(ODH)_{3/2}(BF_4)_2$

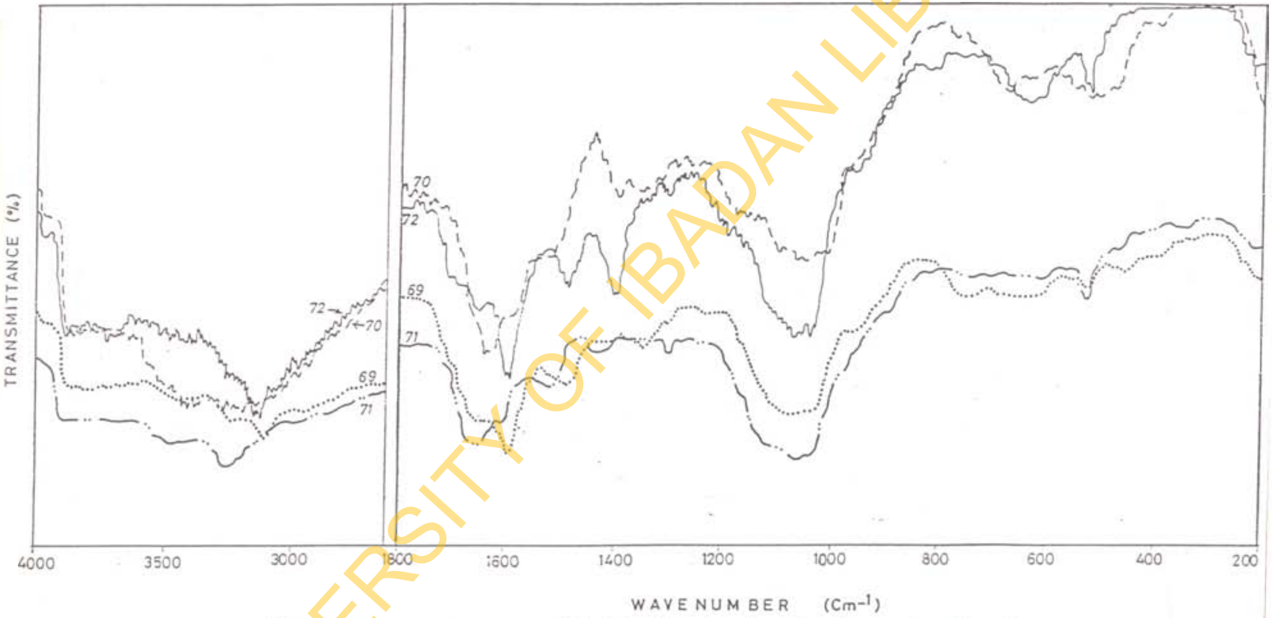


Fig.31 : IR Spectra of mercury(II) tetrafluoroborate Complexes. (continued)

Fig. 31

69. $Hg(MDH)_3(BF_4)_2$
70. $Hg(MDH)_2(BF_4)_2$
71. $HgSDH(BF_4)_2$
72. $Hg(SDH)_2(BF_4)_2$

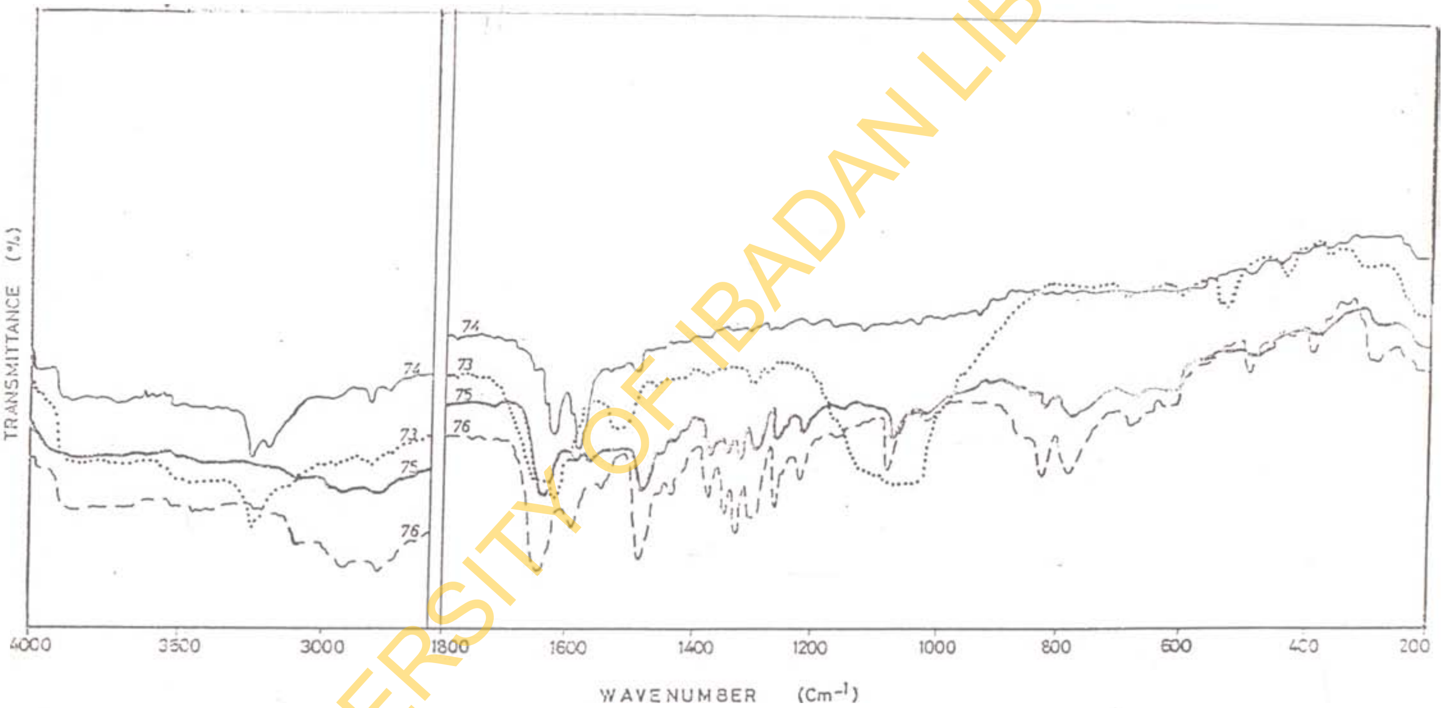


Fig.32 : IR Spectra of mercury(II) and magnesium tetrafluoborate Complexes .(continued)

Fig. 32 73. $Hg(ADH)_2(BF_4)_2$

74. $Hg(ADH)_{3/2}(BF_4)_2$

75. $Hg(PDH)_2(BF_4)_2$

76. $Hg(PDH)_3(BF_4)_2$

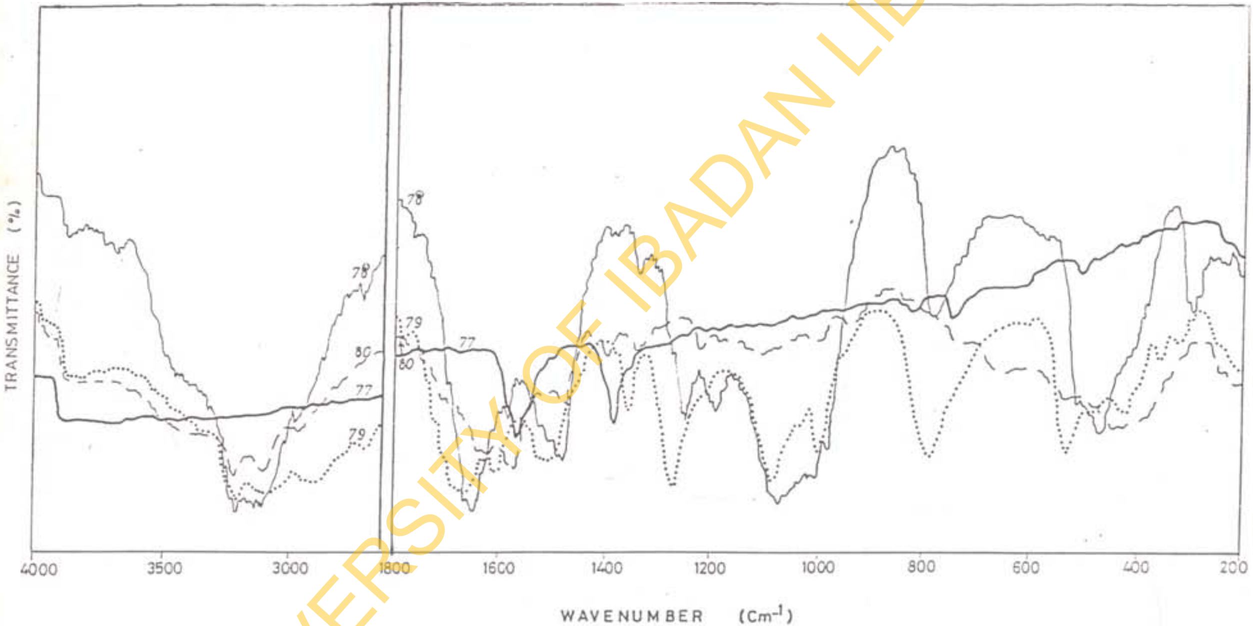


Fig.33 IR Spectra of mercury(II) and magnesium tetrafluoroborate Complexes (continued)

Fig. 33 77. $HgTDH(BF_4)_2$

78. $Mg(ODH)_2(BF_4)_2$

79. $Mg(ODH)_3(BF_4)_2$

80. $Mg(MDH)_{3/2}(BF_4)_2$

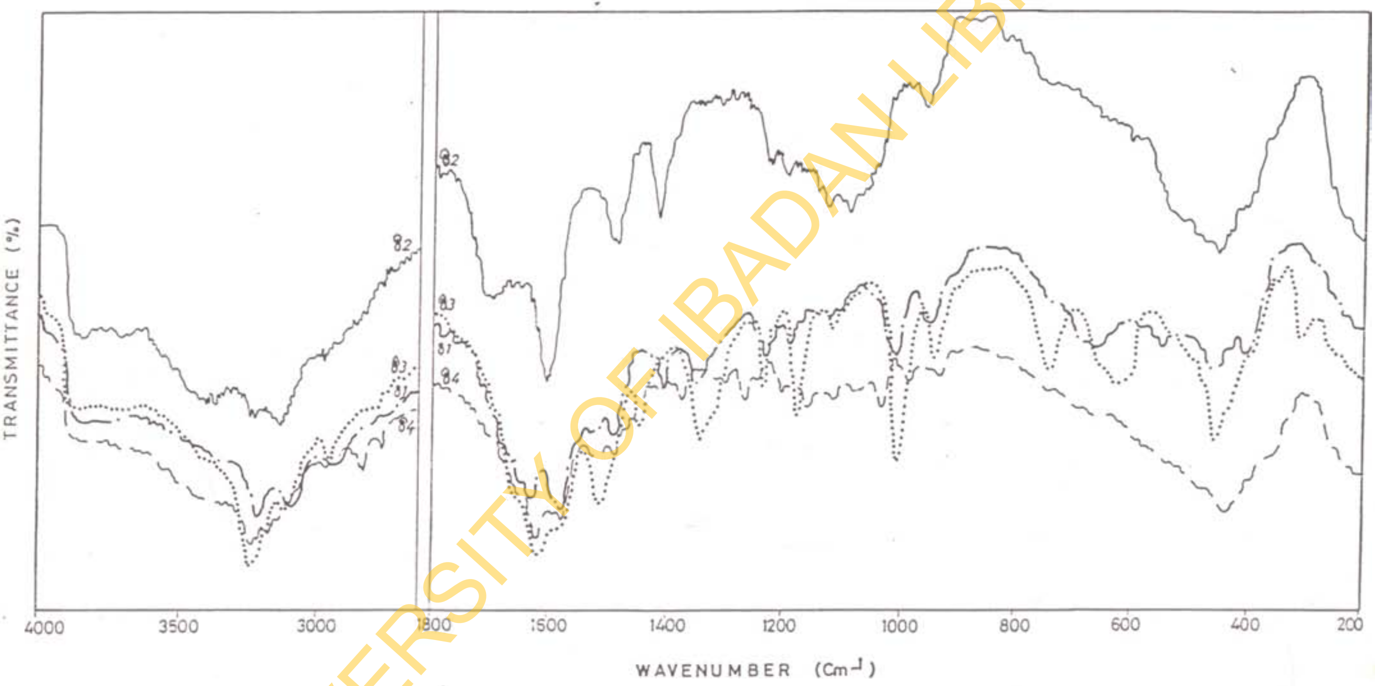


Fig. 34 IR Spectra of magnesium tetrafluoroborate Complexes. (continued)

Fig. 34: 81. $Mg(MDH)_2(BF_4)_2$

82. $MgSDH(BF_4)_2$

83. $Mg(SDH)_3(BF_4)_2$

84. $Mg(MDH)_2(BF_4)_2$

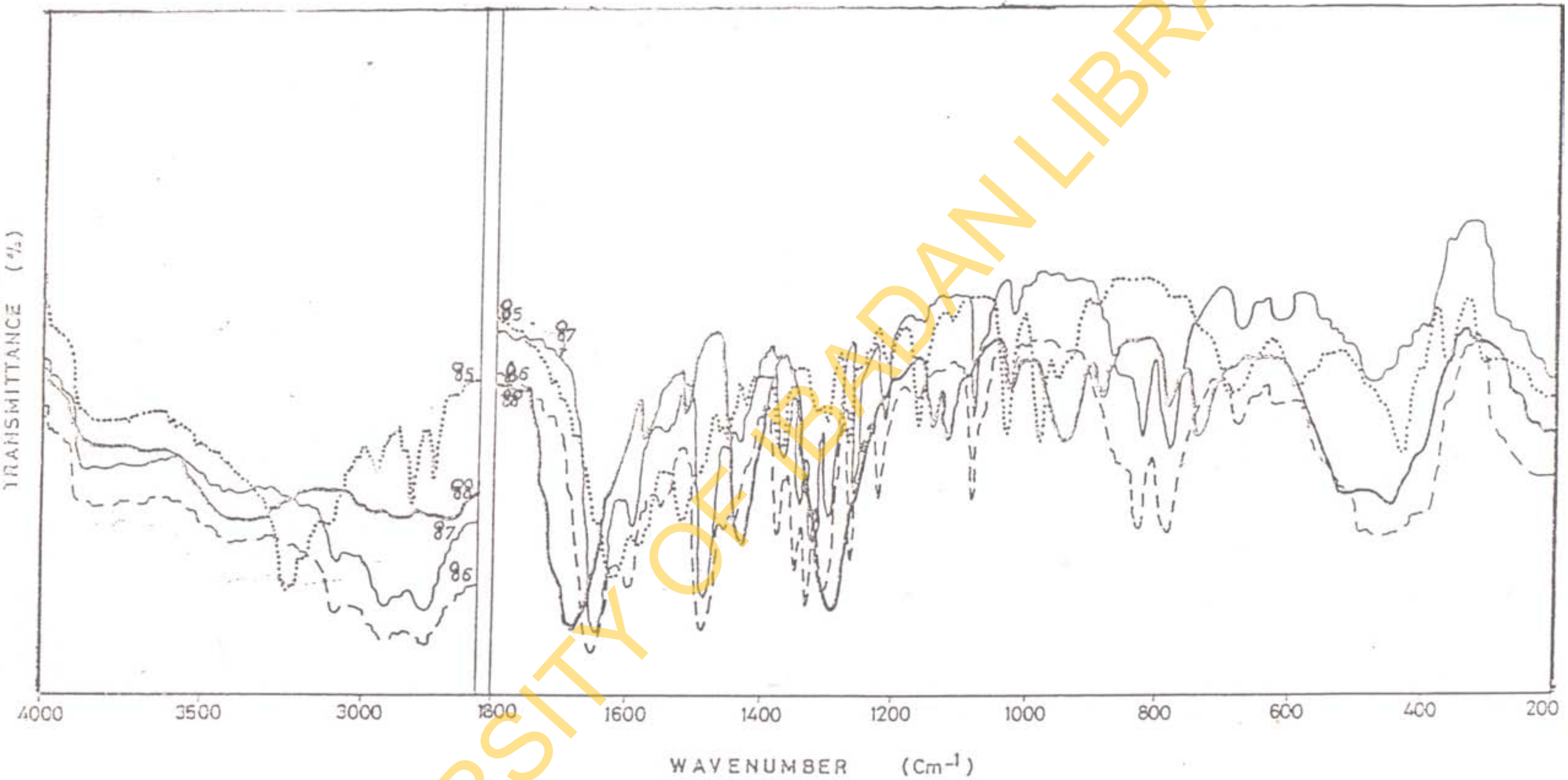


Fig. 35. IR. Spectra of magnesium tetrafluoroborate Complexes. (continued).

Fig. 35

85. $Mg(ADH)_3(BF_4)_2$

86. $Mg(PDH)_2(BF_4)_2$

87. $Mg(PDH)_3(BF_4)_2$

88. $MgTDH(BF_4)_2$

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF ADIPIC DIHYDRAZIDE COMPLEXES

ADH	Mn(ADH)$_{3/2}$-(BF$_4$)$_2$	Mn(ADH)$_3$-(BF$_4$)$_2$	Co(ADH)$_2$-(BF$_4$)$_2$	Co(ADH)$_3$-(BF$_4$)$_2$	Ni(ADH)$_{3/2}$-(BF$_4$)$_2$	Ni(ADH)$_2$-(BF$_4$)$_2$	Tentative Assignments
3270s	3240m,br	3270m,br	3210s	3250s	3200s,br	3200m,br	νas(NH$_2$)
3140w	3149m			3120s,br			ν(NH)
			3030m		3040m		
3019m	3000w	3015w	3020m	3025m	3030w	3015w	νs(NH$_2$)
2930w	2940w		2940w	2940w			
		2890w		2900w	2930m	2940w,br	Overtone and combination
2832m				2850w			
1640 sh	1630s,br	1610s	1640 sh	1645 sh	1630vs	1625s	νC = O
1612vs	1580s	1578w	1625vs	1630vs	1590vs	1580s	
1510s	1510m	1510m	1505w	1505w	1520m	1520m,br	νCN + δNH$_2$
1455m	1430m	1445m	1445m	1455m		1430w,br	)
1419m	1395w		1410m	1420m	1400w,br		)νC - H
1366s	1363m	1365w	1360m,br	1370m	1367w	1372w	)νC - C
1315	1332w	1300w,br	1310m	1312w	1309vw	1312vw	)
1295s	1280m	1265m					
1262m	1280m	1262w	1285w,br	1285w	1290m	1285w	νCN + δNH
1203s		1204m	1220w				
1154vs	1158m	1150m	1180s	1138w		1180w,br	νBF$_4^-$, νCH$_2$
1024vs	1065s,br	1060s,br	1070vs,br	1070vs,br	1090s,br	1050s,v.br	δHNC, δHNN
974vs		970s	970w	975w			
947w	943w	940w	930w	922w	950vw	948vw	
885w	885w	890w	850w	890w			) δC - H
770vw	730vw	770vw	780vw	780vw	730vs,br	720s,br	) δC - C
		730vw	690m	698w			
675s,br		670m	625m	650w			
585 s	540m,br	580m		587m			
417vs	470s	415m	500m	500m,br	506m	510m	)
			410m	420m	470m	465m	) M - L + Ligand
345s	320 w	345 w	390w	390w	390m,br	380w,br	) vibrational
290m		295 w	350w	350w		342w	) modes

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF ADIPIC DIHYDRAZIDE COMPLEXES

ADH	$Cu(ADH)_2-(BF_4)_2$	$Cu(ADH)_3-(BF_4)_2$	$Zn(ADH)_3-(BF_4)_2$	$Cd(ADH)_2-(BF_4)_2$	$Cd(ADH)_3-(BF_4)_2$	Tentative Assignments
3270s	3200m,br	3200m,br	3205m,br	3260m,br	3298s	ν_{as} NH_2
3140w			3115m	3160w	3150w	$\nu(NH)$, $\nu_s(NH_2)$
3019m	3020m,br	3030w	3005m		3035w	
2930w	2920w	2930w		2920w	2950m	Overtone and
2832m	2850w	2860w	2845w,br	2890w	2850w	combination
			2305s,br			
1640sh	1630s,br	1630w	1630vs	1620s	1632s	$\nu C = O$
1612vs	1580m	1590s	1600s	1595m		
			1577w			
1510s	1500s	1506m	1515m	1513w,br	1513s	$\nu CN + \delta NH_2$
1455m	1465w		1447m	1480s	1450m	)
1419m	1410m	1400m	1408w	1405s	1420w	) $\nu C - H$
1366s	1370m			1365w	1370m	) $\nu C - C$
1315s	1320m		1310m	1340w	1300w	)
1295s						
1262m	1262m	1270m,br	1225w	1224m	1215m	$\nu CN + \delta NH$
1203s	1190w	1189m,br				
1154vs			1175m		1115s	νBF_4^-, νCH_2
1024vs	1050s,v.br	1080m,v.br	1065s,br	1074s,br	1060s,br	δHNC, δHNN
974vs	980w	980w	955m,br		978m	)
947w		950w		935m		) $\delta C - H$
885w				923m	890w	) $\delta C - C$
770vw	740vw	730vw				
			665m,br			δNCO
675s,br	600w	650w,br			588w	)
585s	510m	520w	532w	510m	510m	) M - L + Ligand
417vs				470s		) vibrational
380sh	380m,br	370m,br	397m	410w	425m	) modes
345s			353m	385w	356m	)
290m		298w		295w	300m	)

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF ADIPIC DIHYDRAZIDE COMPLEXES

ADH	$Hg(ADH)_2(BF_4)_2$	$Hg(ADH)_{3/2}(BF_4)_2$	$Mg(ADH)(BF_4)_2$	$Mg(ADH)_3(BF_4)_2$	Tentative Assignments
3270s	3295m	3290m	3290m	3290s	$\nu_{as}(NH_2)$
3140w	3190w	3230m	3230m	3160m	$\nu(NH)$, $\nu_s(NH_2)$
3019m			3030m	3012m	
2930w	2912vw	2910w	2900m	2910s	Overtone and combination
2832m			2840w	2850s	
1640sh	1635m	1636m	1620s	1620s	$\nu C=O$
1612vs	1612vs	1613s	1572s	1579m	
1512s	1512m,br	1525s	1512m	1512m	$\nu CN + \delta NH_2$
1455m	1470w	1485w	1480m	1450m	
1419m			1410w	1420m	$\nu C-H$
1366s	1366m	1370m	1373m	1370s	
1315s	1308w	1310w	1300m,br	1315m	$\nu C-C$
1295s	1290w			1300s	
1262m	1265w	1265w	1245m	1250m	$\nu CN + \delta NH$
1203s		1200w			
1154vs		1155w	1155m	1120w	
1024s	1080s,m.br	1070w,br	1070w,br	1060w,br	νBF_4^-, νCH_2, δHNC, δHNN
974vs	920vw	925w	980m	976s	
			928m	950s	$\delta C-H$
947w	892w	890w	890w	890m	$\delta C-C$
885w					
770vw			730vw		δNCO
675s,br	680m,br		650w	675m	
585s	590w	560m		585m	
	515m	480m			
417vs	425m		440m	428s	M - L + Ligand vibrational modes
345s	350w	350w	390w	390 sh	
		325w	340w	350s	
290m	295w			300w	

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF PHTHALIC DIHYDRAZIDE COMPLEXES

PDH	$Mn(PDH)_2(BF_4)_2$	$Mn(PDH)_3(BF_4)_2$	$Co(PDH)_3(BF_4)_2$	$Ni(PDH)_3(BF_4)_2$	Tentative Assignments
3350m,br	3250m,br	3350m,br	3288m	3258m	$\nu_{as}(NH_2)$,
				2880w	$\nu_s(NH_2)$, $\nu(NH)$
1625vs	1625s	1630s	1640vs	1628m	$\nu C = O$
1589m					
1558s	1550s	1550s	1565m	1550w	$\nu CN + \delta NH_2$
1540sh	1525sh	1540sh			
1457s	1468s	1470s	1478s	1470s	
	1423s	1430s	1430m	1432m	$\nu C - H$
	1350s	1355s	1304m	1360m	$\nu C - C$
				1340m	
1245m	1250s	1250m	1225w	1248m	
1230s	1210s	1208s	1210s	1200m,br	$\nu CN + \delta NH$
1149m	1150m	1150m	1159m	1176m	
1117w	1085m	1070s	1110w	1145w	νBF_4^-, δHNC
1060s	1065s		1074s	1074m	δHNN
1018m	1015m	1012m	1015m	1018w	
942m	980w	955w	945w	950w	
	955w				
921w	925w	925w	920w		$\delta C - H$
858w	858w			860vw	$\delta C - C$
820s	830s	830s	832m	820m	
		812m	817m		
760m,br	760m	770s	770s	770m,br	δNCO
670m,br	650m,br	674m	674m	680m	
		615w	615m,br	620w	
536w	550w	545w			
480s	470m	470m	480m	480w	M - L + Ligand vibrational modes
430vs,br	435w	440w	430w		
370m	370m	370m	368m	390m,br	
342w	340w	340w	340w		
		275w	295m		

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF PHTHALIC DIHYDRAZIDE COMPLEXES

PDH	$Cu(PDH)_2$ — $(BF_4)_2$	$Cu(PDH)_3$ — $(BF_4)_2$	$Zn(PDH)_3$ — $(BF_4)_2$	$Cd(PDH)_2$ — $(BF_4)_2$	$Cd(PDH)_3$ — $(BF_4)_2$	Tentative Assignments
3350m,br	3220s	3220m	3165m,br	3250m,br	3250m,br	$\nu_{as}(NH_2)$
				2980m,br		$\nu_s(NH_2)$, $\nu(NH)$
			2325w	2870w		Overtone and combination
1625vs	1635vs	1645vs	1649s	1640vs	1620s	$\nu C = O$
			1613s			
1589m	1595s	1590m		1587m	1585m	Overtone and combination
1558s	1550vs	1555s	1553s	1550m	1555m	$\nu_{CN} + \delta_{NH_2}$
1540sh	1510m	1510w	1505vs,br	1498sh		
1457s	1484vs	1483vs	1480in	1475vs	1475vs	) $\nu C - H$
	1455w	1370m	1448w	1445w	1450 sh	)
	1375s	1350m	1360w	1430w	1368s	) $\nu C - C$
		1325m		1319s	1290w	)
1245m	1248s	1250m,br	1250m	1250s	1244m	$\nu_{CN} + \delta_{NH}$
1230s	1212s	1215m	1225m	1216s	1218s	
1149m	1155m	1150w,br	1147s	1133m	1149s	) νBF_4^-, δ_{HNC}
1117w					1135s	)
1060s	1068s	1060m	1065m,br	1070s	1065s	) δ_{HNN}
				1025m	1010w	)
1018m	1015m	1025w	1017w			
942m						
921w				950m	948w	) $\delta C - H$
858w	840m		840s	830w	825w,br	) $\delta C - C$
820s		820w,br	800m	816m		)
760m,br	780m,br	770m,br	785w	770s	770w,br	δ_{NCO}
	720m	720w	685s			
670m,br	670w	650w,br		670m	675m,br	)
536w	520m	595w	604s	607m		)
480s	490m			560w,br		) M - L + ligand
430vs,br	435m	428w	480m	470s	480s	) vibrational
370m	365w		385w		435w,br	) modes
342w	320m		354w	320w	370m	)

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF PHTHALIC DIHYDRAZIDE COMPLEXES

PDH	$Hg(PDH)_2(BF_4)_2$	$Hg(PDH)_3(BF_4)_2$	$Mg(PDH)_2(BF_4)_2$	$Mg(PDH)_3(BF_4)_2$	Tentative Assignments
3350m,br	3000w,br	3140m	3120m	3120m	$\nu as(NH_2)$
		3000w	3000m	3000m	
			2880m	2380m	$\nu(NH)$ $\nu s(NH_2)$
1625vs	1645s	1645s	1645vs	1645vs	$\nu C=O$
1589m	1588m	1590sh	1590s	1590s	Overtone and combination
1558s	1555w	1542w	1540m	1540m	$\nu CN + \delta NH_2$
1540sh					
1457s	1480m	1448w	1475vs	1480vs	)
	1365m	1430w	1445w	1448w	) $\nu C-H$
	1342m		1430w	1430w	) $\nu C-C$
	1322m	1370s	1365s	1346s	)
	1295m,br	1342s	1340s	1340s	)
1245m	1255m	1257s	1258vs	1255s	$\nu CN + \delta NH$
1230m	1215m	1218m	1215s	1215s	
1149m		1160w	1155m	1158w	)
1117w	1075m	1075s	1074vs	1080vs	) νBF_4^-, δHNC
1060s	1055w	1045w			
1018m	1020w	1018m,br	1015s	1015vs	δHNN
942m				940w	)
921w					) $\delta C-H$
858w		860w	855sh	850sh	) $\delta C-C$
820s	820m	820s	820s	818s	)
760m,br	775m,br	775s	775s	775s	δNCO
670m,v.br	670w,br	675m,br	670m	670m	
		615w,br	610m,br	618m,br	
536w	550w				
480s	475m,br	485m		470m,br	)
		415w	450vs,br	415w	) M - L + Ligand
430vs,br					) vibrational
370m	375w,br	390s	385s	380w	) modes
342w				345w	)
	275m	280m,br		299w	)

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF TEREPHTHALIC DIHYDRAZIDE COMPLEXES

TDH	Mn(TDH)$_3$-(BF$_4$)$_2$	Co(TDH)$_3$-(BF$_4$)$_2$	Ni(TDH)$_3$-(BF$_4$)$_2$	Cu(TDH)$_3$-(BF$_4$)$_2$	Zn(TDH)$_3$-(BF$_4$)$_2$	Tentative Assignments
3280m	3325s	3270s	3278s			
3200m,br	3250m	3225m	3230m	3280vw	3250s,br	$\nu_{as}(NH_2)$
3010m,br	3140w	3020w	3150w	3050w		$\nu(NH)$, $\nu_s(NH_2)$
1705s		1915w				
1640m	1635s	1600vs	1615vs	1665m,br	1625m,br	$\nu C=O$
1603s	1598s		1595vs			
1545m	1558vs	1530s	1555w	1550m,br	1570vs,br	$\nu CN + \delta NH_2$
	1500w					
1490m,br	1455vs	1460w	1410 sh	1490w	1490sh	$\nu C-H$
1400s						$\nu C-C$
1365sh	1370vs	1367vs	1370vs	1380vs	1385vs,br	
					1307m	
1285m	1285m	1300w	1204m	1280m	1285m	$\nu CN + \delta NH$
1175m	1200w		1140s	1200w	1185s	
1110s	1125m	1187s				νBF_4^-, δHNC
		1136s	1105w	1155w	1135m	
	1000s	1005s	1005s	1030m	1100m	δHNN
					1008m	
990m	880m	964m	974m		975m	
		875m	930m	930m,br		$\delta C-H$
865m,br	845m		870m	870m	875m	$\delta C-C$
820w,br	825w	815s	820m		830m	
	810s			765w	820m	
735m	745s	736s	730s	720s	735vs	δNCO
	720s					
680m,br	570m,br	655w	680w			
		587m	615m			
500m	500s	530m,br	540w	515m	560m	M - L + ligand
			490m			vibrational
400m,br	420m	377s	405w		520w	modes
330m,br	320s	335w	340w	298m	380w	
				235s	290w	

TABLE 11 (Contd.): INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF TEREPHTHALIC DIHYDRAZIDE COMPLEXES

TDH	$Cd(TDH)_3(BF_4)_2$	$Hg\ TDH(BF_4)_2$	$Mg\ TDH(BF_4)_2$		Tentative Assignments
3280m	3250s,br	3200vw			
3200m,br		3195vw	3000m,br		$\nu_{as}(NH_2)$
			2850m,br		
1705s			2650m		$\nu(NH)$, $\nu_s(NH_2)$
1640m	1635m	1618w	1665vs		$\nu C = O$
	1625w				
1603s	1585w	1570sh			
1545m	1545s	1560s	1558s		$\nu CN + \nu NH_2$
1490m,br			1495s	)	$\nu C - H$
1400s			1415vs	)	$\nu C - C$
1365sh	1380s	1378s		)	
1285m	1275m,br	1270w	1275vs		$\nu CN + \delta NH$
1175m	1185w		1130s	)	
1110s	1135s	1080w,br	1105s	)	νBF_4^-, δHNC
1096s	1000m	1010w,br	1075m	)	δHNN
			1007s	)	
990m	945m				
			930s,br	)	$\delta C - H$
865m,br			870m	)	$\delta C - C$
820w,br	826s	815m	770s	)	
735m	735s	735m	730s		δNCO
680m,br	570w	600vw		)	
500m	495s		510s,br	)	M - L + Ligand
400m,br	440w	490vw		)	vibrational
		410w	440s	)	modes
330m,br	300m,br	295w	385w	)	
			310w	)	

INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE ASSIGNMENTS OF THE TETRAFLUOROBORATE SALTS

$Mn(BF_4)_2\cdot 6H_2O$	$Co(BF_4)_2\cdot 6H_2O$	$Ni(BF_4)_2\cdot 6H_2O$	$Cu(BF_4)_2\cdot 6H_2O$	$Zn(BF_4)_2\cdot 6H_2O$	$Cd(BF_4)_2\cdot 7H_2O$	$Hg(BF_4)_2\cdot 6H_2O$	$Mg(BF_4)_2\cdot 6H_2O$	Tentative Assignments
3406s,v.br	3400s,v.br	3450s,v.br	3420s,br	3480s,br	3400s,br	3435s,v.br	3500s,v.br	$\nu(OH)$
1614m	1605m	1614m	1612s	1608s	1618s	1610m	1612m	$\nu(H_2O)$
1306m	1290w	1310m	1285m	1300m	1300m	1304m	1310m	$\delta(OH) + \delta(H_2O)$
1108s,br	1100m,br	1102s,br	1106s,br	1100s,br	1100s,br	1110s,br	1112s,br	νBF_4^-
765m,br	750m	740m	756m	760s	740m	750m	742m	$\nu M\text{-}OH_2$
530s	540m	530m	540s	535w	535s	535s	540s	$\delta\ BF_4^-$
520s	525w	525m	520w	525m	520s	518s	522s	

s = strong, m = medium, w = weak, br = broad, v.br = very broad, sh = shoulder

ν = stretching frequency δ = bending frequency

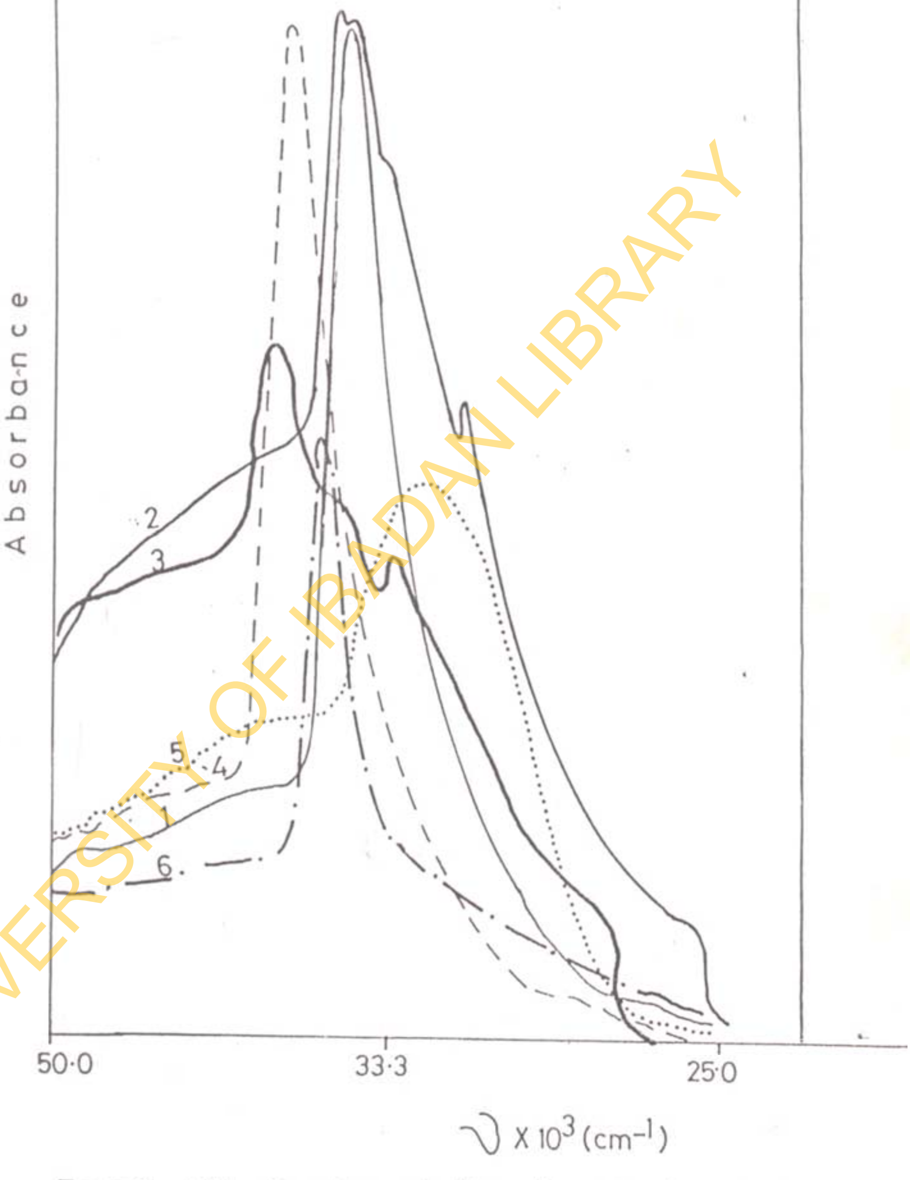


Fig. 36: UV Spectra of the ligands in water

Fig.36 :
1. Oxalic dihydrazide
2. Malonic dihydrazide
3. Succinic dihydrazide
4. Adipic dihydrazide
5. Phthalic dihydrazide
6. Terephthalic dihydrazide

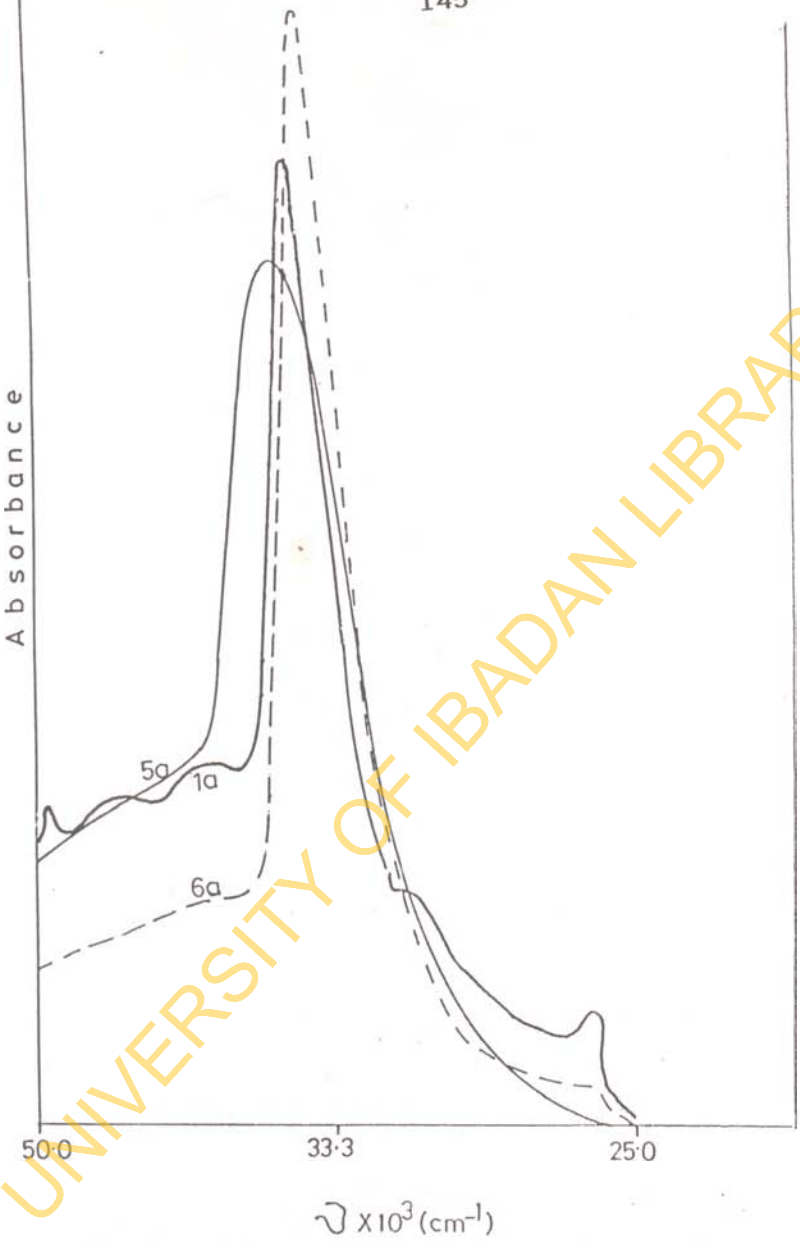


Fig.37 UV Spectra of ligands in methanol

Fig. 37:

1a.	Oxalic dihydrazide
5a.	Phthalic dihydrazide
6a.	Terephthalic dihydrazide

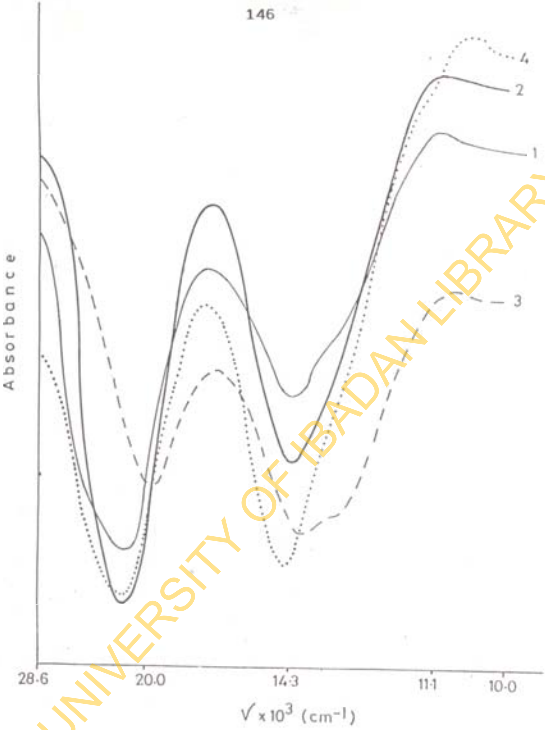


Fig.38: Reflectance Spectra of nickel(II) tetrafluoroborate dihydrazides.

Fig.38: 1. $Ni(ODH)_2(BF_4)_2$

2. $Ni(ODH)_3(BF_4)_2$

3. $Ni(MDH)_2(BF_4)_2$

4. $Ni(MDH)_3(BF_4)_2$

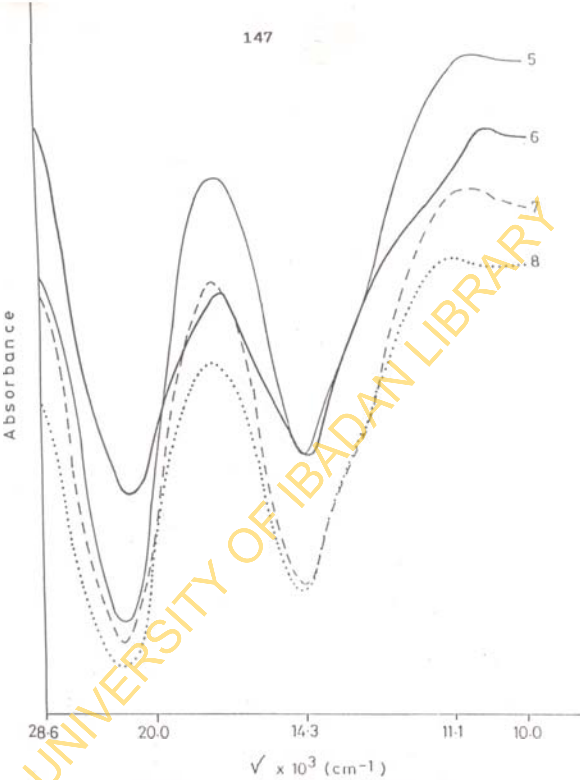


Fig.39: Reflectance Spectra of nickel(II) tetrafluoroborate dihydrazides Contd.

Fig. 39: 5. $Ni(SDH)_{3/2}(BF_4)_2$

6. $Ni(SDH)_2(BF_4)_2$

7. $Ni(ADH)_{3/2}(BF_4)_2$

8. $Ni(ADH)_2(BF_4)_2$

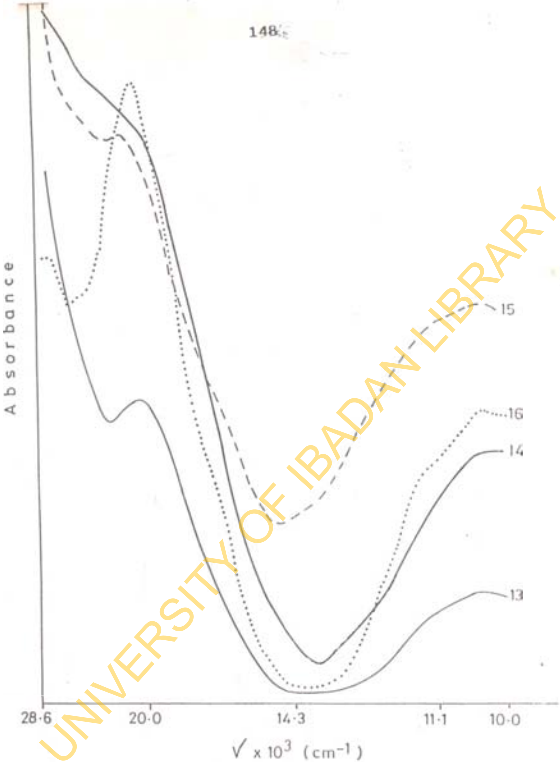


Fig. 40 Reflectance Spectra of Cobalt(II) tetrafluoroborate dihydrazides.

Fig. 40

13. $Co(ODH)_3(BF_4)_2$

14. $Co(MDH)_{3/2}(BF_4)_2$

15. $Co(MDH)_3(BF_4)_2$

16. $Co(SDH)_2(BF_4)_2$

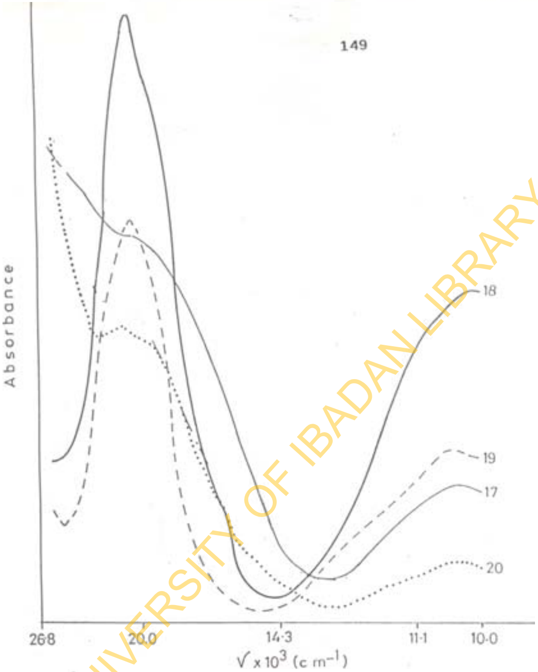


Fig.4 I. Reflectance Spectra of Cobalt(II) tetrafluoroborate dihydrazides Contd.

Fig. 41 : 17. $Co(SDH)_3(BF_4)_2$

18. $Co(ADH)_2(BF_4)_2$

19. $Co(ADH)_3(BF_4)_2$

20. $Co(PDH)_3(BF_4)_2$

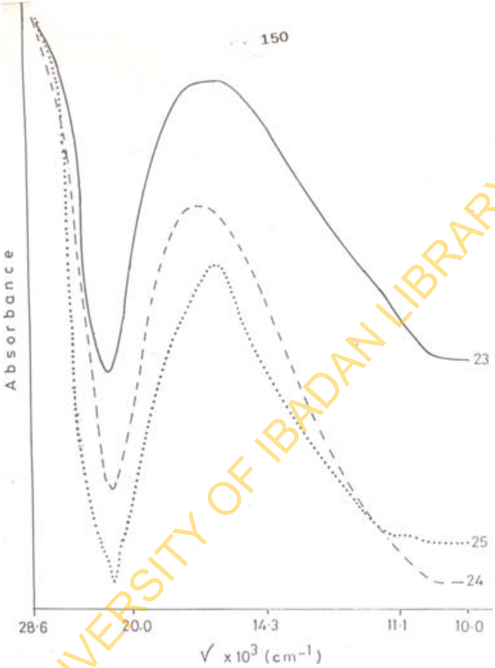


Fig.42 Reflectance Spectra of Copper (II) tetrafluoroborate dihydrazides.

Fig.42. 23. $Cu(ODH)_{3/2}(BF_4)_2$

24. $Cu(ODH)_3(BF_4)_2$

25. $Cu(MDH)_3(BF_4)_2$

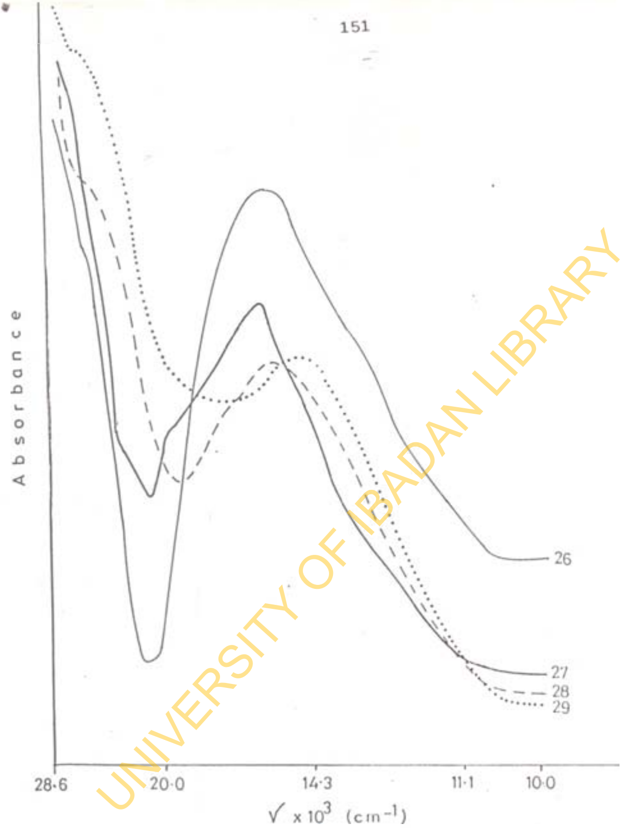


Fig.43 Reflectance Spectra of Copper(II) tetrafluoroborate dihydrazides Contd.

Fig. 43

26. $Cu(MDH)_3(BF_4)_2$

27. $Cu(SDH)_2(BF_4)_2$

28. $Cu(SDH)_3(BF_4)_2$

29. $Cu(ADH)_{3/2}(BF_4)_2$

TABLE 12: ELECTRONIC SPECTRAL DATA OF THE LIGANDS AND COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) TETRAFLUOROBORATE

Compound	Wavelength x $10^3 cm^{-1}$	Tentative Assignments
ODH	33.9^a, 34.5	$\pi \rightarrow \pi^*$
MDH	35.0	$\pi \rightarrow \pi^*$
SDH	35.1	$\pi \rightarrow \pi^*$
ADH	35.0	$\pi \rightarrow \pi^*$
PDH	33.9^a, 32.6	$\pi \rightarrow \pi^*$
TDH	34.5^a, 35.1	$\pi \rightarrow \pi^*$
$Co(ODH)_2(BF_4)_2$	20.4	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	10.3	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$Co(ODH)_3(BF_4)_2$	20.4	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	10.4	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$Co(MDH)_{3/2}(BF_4)_2$	20.0	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	10.2	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$Co(MDH)_3(BF_4)_2$	21.3	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	10.3	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$

TABLE 12 (Contd.)

Compound	Wavelength x $10^3 cm^{-1}$	Tentative Assignments
$Co(SDH)_2(BF_4)_2$	20.5	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.3	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Co(SDH)_3(BF_4)_2$	20.4	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.3	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Co(ADH)_2(BF_4)_2$	20.4	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.1	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Co(ADH)_3(BF_4)_2$	20.4	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.4	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Co(PDH)_3(BF_4)_2$	20.6	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.3	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Co(TDH)_3(BF_4)_2$	20.4	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	10.3	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$
$Ni(ODH)_2(BF_4)_2$	17.1	${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	11.0	${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(ODH)_3(BF_4)_2$	17.2	${}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.8	${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$

TABLE 12 (Contd.)

Compound	Wavelength $\times 10^3 cm^{-1}$	Tentative Assignments
$Ni(MDH)_2(BF_4)_2$	16.8	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.7	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(MDH)_3(BF_4)_2$	17.2	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.5	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(SDH)_{3/2}(BF_4)_2$	17.1	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.6	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(SDH)_2(BF_4)_2$	16.9	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.5	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(ADH)_{3/2}(BF_4)_2$	17.2	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.7	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(ADH)_2(BF_4)_2$	17.2	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	11.0	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
$Ni(PDH)_3(BF_4)_2$	18.2	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.5	$^3A_{2g}(F) \longrightarrow {}^3A_{2g}(F)$
$Ni(TDH)_3(BF_4)_2$	17.7	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	10.3	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$

TABLE 12 (Contd.)

Compound	Wavelength x $10^3 cm^{-1}$	Tentative Assignments
$Cu(ODH)_{3/2}(BF_4)_2$	25.0sh	CT band
	15.7	d → d
$Cu(ODH)_3(BF_4)_2$	25.3sh	CT band
	16.5	d → d
$Cu(MDH)_2(BF_4)_2$	25.6sh	CT band
	15.9	d → d
$Cu(MDH)_3(BF_4)_2$	24.4sh	CT band
	15.5	d → d
$Cu(SDH)_2(BF_4)_2$	25.6sh	CT band
	15.9	d → d
$Cu(SDH)_3(BF_4)_2$	24.4sh	CT band
	15.5	d → d
$Cu(ADH)_2(BF_4)_2$	25.0sh	CT band
	14.6	d → d
$Cu(ADH)_3(BF_4)_2$	24.1sh	CT band
	15.5	d → d

TABLE 12 (Contd.)

Compound	Wavelength x $10^3 cm^{-1}$	Tentative Assignments
$Cu(PDH)_2(BF_4)_2$	23.3sh	CT band
	15.6	d→d
$Cu(PDH)_3(BF_4)_2$	23.8sh	CT band
	16.4	d→d
$Cu(TDH)_3(BF_4)_2$	25.0sh	CT band
	15.4	d→d

Notes: a = Solution spectra of ligands in methanol, the rest in water; spectra of complexes were taken as solids

CT = Charge-transfer sh = shoulder

4.6 Magnetic susceptibility data

The results of the magnetic susceptibility measurements at room temperature are given in Tables 13 and 14 respectively.

4.6.1 Calibration of sample tube

Weight of empty tube, field off = 1.2561 g

Weight of empty tube, field on = 1.2548 g

Weight of tube + water, field off = 1.5158 g

Weight of tube + calibrant, field off = 1.7079 g

Weight of tube + calibrant, field on = 1.7372 g

Temperature = 304 K

Density of water at 29°C (304 K) = 0.995976 g/cm^3

x (volume susceptibility of air) = 0.029×10^{-6}

Mass of water in tube = 0.2597 g

Volume of water in tube (V) = 0.2607 cm^3

Weight of calibrant (W) = 0.4518 g

Diamagnetic correction of glass (x) = 0.0013 g

Paramagnetic pull on $Hg[Co(CNS)_4]$ (y) = 0.0293 g

Actual change in weight under magnetic field: w = y+x = 0.0306 g

$$\text{But } \chi = \frac{xV + \beta w}{W}$$

$$\therefore \beta = \frac{\chi W - xV}{w}$$

$$= \frac{(15.99\times10^{-6}\times0.4518) - (0.029\times10^{-6}\times0.2607)}{0.0306}$$

$$\beta = 235.0\times10^{-6}.$$

4.6.2 Calculation of the magnetic moment of $Ni(ODH)_2(BF_4)_2$

Weight of sample tube, field off (X_o) = 1.2561 g

Weight of sample tube, field on (X_1) = 1.2548 g

Weight of sample tube + sample, field on (X_2) = 1.3598 g

Weight of sample tube + sample, field off (X_3) = 1.3571 g

Paramagnetic pull on sample (X_2-X_3) (x) = 0.0027 g

Diamagnetic correction of glass (X_1-X_o) (y) = 0.0013 g

Weight of sample (W) = 0.1010 g

Actual change in weight under magnetic field(w) = 0.004 g
w=y+x

Temperature = 304 K

Molecular mass of the sample = 468.7 g

$$\chi = \frac{xV + \beta w}{W}$$

$$\chi = 9.0\times10^{-6} \text{ c.g.s. unit}$$

$$\chi_M = \chi \times \text{molecular mass} = 4397\times10^{-6} \text{ c.g.s. unit}$$

$$\chi_A = \chi_M - \chi_L$$

The calculation of the diamagnetic ligand correction (χ_L) is from the Pascal's constants[87].

$$\chi_L = -177\times10^{-6} \text{ c.g.s. unit}$$

$$\chi_A = 4397\times10^{-6} + 177.10^{-6} \text{ c.g.s. unit}$$

$$= 4574\times10^{-6} \text{ c.g.s. unit}$$

$$\mu_{eff} = 2.828\sqrt{\chi_A T} \text{ B.M.}$$

$$= 3.34 \text{ B.M.}$$

Calculations for the other transition metal complexes were similarly made.

4.6.3 Calculation of the magnetic moment of $Zn(SDH)_2(BF_4)_2$

Weight of sample tube, field off = 1.2561 g

Weight of sample tube, field on = 1.2548 g

Weight of sample tube + sample, field off = 1.5031 g

Weight of sample tube + sample, field on = 1.5016 g

Paramagnetic pull on sample (x) = -0.0015 g

Diamagnetic correction of glass (y) = 0.0013 g

Weight of sample (W) = 0.2470 g

Temperature = 302 K

Molecular mass of sample = 530.98 g

$$\chi = \frac{xV + \beta w}{W}$$

$$\chi = -0.160\times10^{-6} \text{ c.g.s unit}$$

χ_M calculated, $\chi_{Mc.}$

Diamagnetic correction of $Zn(BF_4)_2$ = -93×10^{-6} c.g.s. unit

Diamagnetic correction of $(SDH)_2$ = -146.64×10^{-6} c.g.s. unit

χ_{Mc} = -240×10^{-6} c.g.s. unit

χ_M experimental, χ_{Me}

$\chi = -0.160\times10^{-6}$ c.g.s unit

$\chi_{Me} = (-0.160\times10^{-6}) \times 530.98$ c.g.s unit

$= -85\times10^{-6}$ c.g.s. unit

But

$\Delta\chi_M = \chi_{Me} - \chi_{Mc}$

$= (-85+240) \times 10^{-6}$

$= +\ 155\times10^{-6}$ c.g.s. unit

$\chi_A = \chi_M - \chi_L$ and $\Delta\chi_M = \chi_{Me} - \chi_c$; hence

$\chi_A = \Delta\chi_M$

$\therefore\ \mu_{eff} = 2.828\sqrt{\Delta\chi_M . T}$ B.M.

$= 0.61$ B.M.

Calculations for the other non-transition metal complexes were similarly made.

TABLE 13: MAGNETIC DATA OF MANGANESE(II), COBALT(II), NICKEL(II), AND COPPER(II), TETRAFLUOROBORATE COMPLEXES OF THE DIHYDRAZIDES

Compound	Temp. (K)	$\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_L \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\chi_A \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff} (B.M.)
$Mn(ODH)_2(BF_4)_2$	306	13414	177	13591	5.77
$Mn(ODH)_3(BF_4)_2$	306	13954	227	14181	5.90
$Mn(MDH)_2(BF_4)_2$	306	13532	201	13733	5.80
$Mn(MDH)_3(BF_4)_2$	306	14002	262	14264	5.91
$Mn(SDH)_2(BF_4)_2$	304	14239	225	14464	5.93
$Mn(SDH)_3(BF_4)_2$	304	14384	298	14682	5.98
$Mn(ADH)_{3/2}(BF_4)_2$	304	14708	224	14931	6.03
$Mn(ADH)_3(BF_4)_2$	304	14871	369	15240	6.09
$Mn(PDH)_2(BF_4)_2$	304	14525	303	14828	6.01
$Mn(PDH)_3(BF_4)_2$	304	14506	415	14922	6.03
$Mn(TDH)_3(BF_4)_2$	304	14745	415	15160	6.08
$Co(ODH)_2(BF_4)_2$	304	7723	177	7900	4.39

TABLE 13 (Contd.)

Compound	Temp. (K)	$\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_L \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\chi_A \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff} (B.M.)
$Co(ODH)_3(BF_4)_2$	305	8519	227	8746	4.62
$Co(MDH)_{3/2}(BF_4)_2$	301	9471	170	9641	4.82
$Co(MDH)_3(BF_4)_2$	300	10892	262	11154	5.18
$Co(SDH)_2(BF_4)_2$	304	8045	225	8270	4.49
$Co(SDH)_3(BF_4)_2$	304	10061	298	10359	5.02
$Co(ADH)_2(BF_4)_2$	304	9484	272	9756	4.87
$Co(ADH)_3(BF_4)_2$	301	10254	369	10623	5.06
$Co(PDH)_3(BF_4)_2$	301	9375	415	9790	4.85
$Co(TDH)_3(BF_4)_2$	299	10282	415	10697	5.06
$Ni(ODH)_2(BF_4)_2$	304	4397	177	4574	3.34
$Ni(ODH)_3(BF_4)_2$	299	4329	227	4556	3.30
$Ni(MDH)_2(BF_4)_2$	301	3945	201	4146	3.16
$Ni(MDH)_3(BF_4)_2$	303	4269	262	4532	3.31
$Ni(SDH)_{3/2}(BF_4)_2$	301	3709	188	3897	3.07
$Ni(SDH)_2(BF_4)_2$	303	3804	225	4029	3.13

TABLE 13 (Contd.)

Compound	Temp. (K)	$\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_L \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\chi_A \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff} (B.M.)
$Ni(ADH)_{3/2}(BF_4)_2$	299	4212	224	4436	3.26
$Ni(ADH)_2(BF_4)_2$	301	4111	272	4383	3.25
$Ni(PDH)_3(BF_4)_2$	303	4106	415	4521	3.31
$Ni(TDH)_3(BF_4)_2$	299	3088	415	3503	2.90
$Cu(ODH)_{3/2}(BF_4)_2$	304	1233	152	1385	1.84
$Cu(ODH)_3(BF_4)_2$	299	1758	227	1984	2.18
$Cu(MDH)_2(BF_4)_2$	299	1589	201	1790	2.07
$Cu(MDH)_3(BF_4)_2$	303	1463	262	1725	2.05
$Cu(SDH)_2(BF_4)_2$	299	1450	225	1674	2.00
$Cu(SDH)_3(BF_4)_2$	301	1288	298	1586	1.96
$Cu(ADH)_2(BF_4)_2$	303	1575	272	1847	2.12
$Cu(ADH)_3(BF_4)_2$	300	1307	369	1677	2.01
$Cu(PDH)_2(BF_4)_2$	304	1021	303	1324	1.80
$Cu(PDH)_3(BF_4)_2$	299	1503	415	1918	2.14
$Cu(TDH)_3(BF_4)_2$	299	1575	415	1991	2.18

TABLE 14: MAGNETIC DATA OF ZINC(II), CADMIUM(II), MERCURY(II) AND MAGNESIUM TETRAFLUOROBORATE COMPLEXES

Compound	Temp. (K)	$-\chi_g \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(exp.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(calc.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\Delta\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff}(B.M.)
$Zn(ODH)_2(BF_4)_2$	302	0.118	56	192	136	0.57
$Zn(ODH)_3(BF_4)_2$	302	0.371	220	242	22	0.23
$ZnMDH(BF_4)_2$	302	0.366	136	154	19	0.21
$Zn(MDH)_3(BF_4)_2$	302	0.246	156	277	121	0.54
$Zn(SDH)_{3/2}(BF_4)_2$	302	0.116	76	203	127	0.55
$Zn(SDH)_2(BF_4)_2$	302	0.160	85	240	155	0.61
$Zn(ADH)_3(BF_4)_2$	302	0.362	276	384	109	0.51
$Zn(PDH)_3(BF_4)_2$	302	0.407	334	430	96	0.48
$Zn(TDH)_3(BF_4)_2$	302	0.470	386	430	44	0.33
$Cd(ODH)_2(BF_4)_2$	304	0.197	103	199	96	0.48
$Cd(ODH)_3(BF_4)_2$	303	0.115	74	249	175	0.65
$Cd(MDH)_2(BF_4)_2$	303	0.249	137	223	86	0.46
$Cd(SDH)_2(BF_4)_2$	306	0.175	101	247	146	0.60

TABLE 14 (Contd.)

Compound	Temp. (K)	$-\chi_g \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(exp.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(calc.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\Delta\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff}(B.M.)
$Cd(SDH)_3(BF_4)_2$	306	0.375	272	320	48	0.34
$Cd(ADH)_2(BF_4)_2$	305	0.270	171	294	123	0.55
$Cd(ADH)_3(BF_4)_2$	303	0.382	309	391	82	0.45
$Cd(PDH)_2(BF_4)_2$	303	0.271	183	325	142	0.59
$Cd(PDH)_3(BF_4)_2$	303	0.212	184	437	253	0.78
$Cd(TDH)_3(BF_4)_2$	303	0.169	147	437	290	0.84
$Hg(ODH)_3(BF_4)_2$	306	0.256	186	264	78	0.44
$Hg(ODH)_{3/2}(BF_4)_2$	304	0.275	152	190	38	0.30
$Hg(MDH)_3(BF_4)_2$	303	0.274	211	299	88	0.46
$Hg(MDH)_2(BF_4)_2$	303	0.171	109	238	129	0.56
$HgSDH(BF_4)_2$	305	0.202	105	188	83	0.45
$Hg(SDH)_2(BF_4)_2$	303	0.169	113	262	149	0.60
$Hg(ADH)_2(BF_4)_2$	303	0.167	120	309	189	0.68
$Hg(ADH)_{3/2}(BF_4)_2$	305	0.231	147	261	114	0.53
$Hg(PDH)_2(BF_4)_2$	304	0.189	144	340	196	0.69

TABLE 14 (Contd.)

Compound	Temp. (K)	$-\chi_g \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(exp.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$-\chi_{M(calc.)} \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	$\Delta\chi_M \times 10^{-6}$ (erg gauss^{-2} mole^{-1})	μ_{eff} (B.M.)
$Hg(PDH)_3(BF_4)_2$	303	0.204	195	452	257	0.79
$Hg\ TDH(BF_4)_2$	303	0.168	95	227	132	0.57
$Mg(ODH)_2(BF_4)_2$	304	0.304	132	180	48	0.34
$Mg(ODH)_3(BF_4)_2$	305	0.363	200	230	30	0.27
$Mg(MDH)_{3/2}(BF_4)_2$	304	0.180	71	173	102	0.50
$Mg(MDH)_2(BF_4)_2$	303	0.218	101	204	103	0.50
$Mg\ SDH(BF_4)_2$	302	0.179	62	155	93	0.47
$Mg(SDH)_3(BF_4)_2$	305	0.317	202	301	99	0.49
$Mg\ ADH(BF_4)_2$	304	0.264	98	178	80	0.44
$Mg(ADH)_3(BF_4)_2$	302	0.404	291	372	81	0.44
$Mg(PDH)_2(BF_4)_2$	304	0.356	140	194	54	0.36
$Mg(PDH)_3(BF_4)_2$	303	0.471	367	418	51	0.35
$Mg\ TDH(BF_4)_2$	303	0.233	91	193	102	0.50

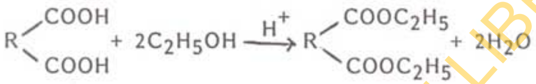
$\Delta\chi_M = \chi_{M(exp.)} - \chi_{M(calc.)}$.

CHAPTER FIVE

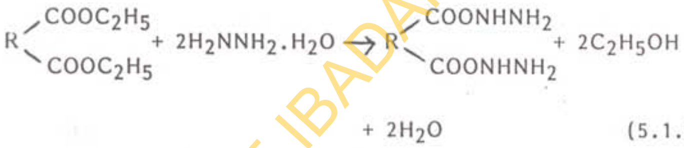
DISCUSSION OF RESULTS

5.1 The ligands

The preparation of the ligands from their acids may be represented by the following equations:



$$\mathrm{R}\begin{matrix}\diagup \mathrm{COOH}\\ \diagdown \mathrm{COOH}\end{matrix} + 2C_2H_5OH \xrightarrow{H^+} \mathrm{R}\begin{matrix}\diagup \mathrm{COOC_2H_5}\\ \diagdown \mathrm{COOC_2H_5}\end{matrix} + 2H_2O \qquad (5.1.1)$$



$$\mathrm{R}\begin{matrix}\diagup \mathrm{COOC_2H_5}\\ \diagdown \mathrm{COOC_2H_5}\end{matrix} + 2H_2NNH_2.H_2O \rightarrow \mathrm{R}\begin{matrix}\diagup \mathrm{COONHNH_2}\\ \diagdown \mathrm{COONHNH_2}\end{matrix} + 2C_2H_5OH + 2H_2O \qquad (5.1.2)$$

where

$R = (CH_2)_n$ (n = 0,1,2,4) or C_6H_4.

In cases where the diethyl esters were available commercially, only equation (5.1.2) applies. The melting points and analytical data of the ligands given in Table 8 agree with the expected or literature values[5-6,8-9,11].

5.1.1 Electronic spectra of the ligands

The bands observed in the spectra of the ligands (Table 12) around 32,600-35,100 cm^{-1} may be assigned to internal $\pi \rightarrow \pi^*$ transitions. There was little variation in band positions in going from ODH to ADH.

5.2 Complexes of manganese(II) tetrafluoroborate dihydrazides

5.2.1 Colour of compounds

All the complexes are dirty white powdery solids (Table 8) which are expected of octahedral high spin manganese(II) complexes[60].

5.2.2 Analytical data

The analytical result for the complexes (Table 8) indicates that the reactions involving 1:2 metal to ligand reactant ratios yielded complexes having a 1:3 metal to ligand stoichiometry, whereas, the use of a 1:1 metal to ligand reactant ratios gave mostly complexes with 1:2 metal to ligand stoichiometry. However, the complex of ADH prepared using the 1:1 molar ratio of ligand to metal salt contained one and a half moles of ADH. This phenomenon has been observed before[10,11].

5.2.3 Melting points/Decomposition temperatures

The ODH, PDH and TDH complexes melted/decomposed (Table 8) at temperatures above 300°C, whereas, the melting points/decomposition temperatures of the MDH, SDH and ADH complexes were generally between 135-273°C.

5.2.4 Percentage yields

The yields obtained for the complexes ranged between 62% and 84% (Table 8).

5.2.5 Solubility

The solubilities of the complexes in various polar and non-polar solvents are shown in Table 9. Most of the complexes were slightly soluble in these solvents, while some were found to be soluble in water and DMSO.

5.2.6 Molar conductance

The molar conductances of the ODH, MDH, SDH and ADH complexes that were soluble in water and DMSO are shown in Table 10. These values reveal a 1:2 type of electrolytes[11], and indicate that the anions are probably not coordinated in the complexes. Nonetheless, water as a solvent for conductance purposes is not popular because of problems of occasional hydrolysis.[89]

5.2.7 Infrared spectra

The infrared spectra of the complexes and those of other complexes studied (Table 11) were assigned by comparison with those of the ligands and related compounds[3,10-12,33]. The bands in the region 3300-300 cm^{-1} in both the ligands and Mn(II) tetrafluoroborate complexes and the others, that is complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Mg were complicated by splittings thereby making the assignment of the ν(NH) and $\nu(NH_2)$ in this region unreliable. This complication has been observed by other workers[3,47]. Changes in the frequencies in this region could not therefore be used to infer the coordination of the amino nitrogen. However, changes in the amide I, amide II and amide III have been used in this work to interprete the IR spectra of all the complexes studied.

The amide I band (νC=O) is displaced to lower frequencies in the ODH, ADH and TDH complexes. This suggests the coordination of the carbonyl group. The behaviour of these complexes resembles those observed for some transition metal complexes of these and related ligands[4,10,11]. The amide I band remains practically unchanged in the MDH complexes and $Mn(PDH)_2(BF_4)_2$, while it increased in $Mn(PDH)_3(BF_4)_2$ and the succinic dihydrazide complexes. These observations suggest the non-involvement of the carbonyl oxygen in coordination.

The amide II band ($\nu CN + \delta NH_2$) is lowered in frequency in the ODH, MDH and PDH complexes, and suggest the involvement of the amino nitrogen in coordination in accord with previous studies[3,34]. Whereas the band rose on complex formation in $Mn(SDH)_2(BF_4)_2$, $Mn(SDH)_3(BF_4)_2$ and $Mn(TDH)_3(BF_4)_2$, but remains stationary in the adipic dihydrazide complexes.

The amide III band ($\nu CN + \delta NH$) rose on complex formation in the succinic dihydrazide complexes, whereas the δNCO band disappears, an indication that the amide nitrogen is coordinated[11]. In the spectra of the ODH and TDH complexes as well as $Mn(ADH)_3(BF_4)_2$ there is a shift to higher frequencies of the amide III band. The δNCO band is lowered in the oxalic dihydrazide and $Mn(MDH)_3(BF_4)_2$ complexes but remains stationary in $Mn(MDH)_2(BF_4)_2$ and $Mn(TDH)_3(BF_4)_2$. This band is however very weak in the adipic dihydrazide complexes and adipic dihydrazide as a result no meaningful deductions could be made. Observations involving shifts in the amide (III) and δNCO bands preclude the involvement of the amide nitrogen in the formation of ODH, MDH, ADH, PDH and TDH complexes.

A broad band between 1200-1000 cm^{-1} in the spectra of ODH, MDH, SDH and ADH complexes has been assigned to the νBF_4^- mode[92]. This band is taken as an envelope of νBF_4^- and some ligand vibrational modes which occur in this region. Though there is some weak splitting of this band, the presence of ligand modes makes it difficult to associate the splitting with the coordination of the BF_4^- ion. In the PDH and TDH complexes, like in similar complexes of the other metals studied, the broad band was not observed. Other bands between 1000-1150 cm^{-1} similar to those in the ligand spectra were observed. The bands in the region below 580 cm^{-1} in the complexes are assigned to metal-ligand stretching modes[93].

Because of the effect of H-bonding in hydrazides and their complexes[11-12,44], these assignments and those of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II) and magnesium discussed later in this work are tentative. And the factors which determine whether N or O bonding is obtained are not yet clear[10-12].

5.2.8 Electronic spectra

The complexes showed no d→d transitions as would be expected of a high spin d^5 configuration since there is no excited state of the same spin multiplicity as the ground term ($^6A_{1g}$)[79].

5.2.9 Magnetic properties

The magnetic moments of the complexes (Table 13) are in the range 5.77-6.08B.M. High spin octahedral or tetrahedral Mn(II) complexes with an $^6A_1$ ground term is expected to give a spin-only temperature independent moment,[60, 90,91] of 5.92B.M. The observed deviations could be attributed to magnetic interactions in the complexes[60,91].

5.3 Complexes of cobalt(II) tetrafluoroborate dihydrazides

5.3.1 Colour of compounds

The colours of the complexes are indicated in Table 8, they are typical of octahedral cobalt(II) complexes[60, 90].

5.3.2 Analytical data

The analytical results shown in Table 8 shows that the cobalt(II) complexes have metal to ligand stoichiometries similar to those of manganese(II) discussed above.

5.3.3 Melting points/Decomposition temperatures

Some of the complexes did not melt or decompose up to 300°C while the others melted in the range 140-247°C (Table 8).

5.3.4 Percentage yields

The yields are in the range 63% - 90% (Table 8).

5.3.5 Solubility

The complexes are slightly soluble in the polar and non-polar organic solvents used. They are, however, soluble in water except the PDH and TDH complexes (Table 9).

5.3.6 Molar conductance

The molar conductances of the complexes that were soluble in water are presented in Table 10. These values reveal a 1:2 type of electrolytes[11].

5.3.7 Infrared spectra

In the spectra of the oxalic dihydrazide complexes the amide I band around 1660 cm^{-1} shifted to lower frequency, an indication of carbonyl group coordination. The amide II band around 1510 cm^{-1} rose to higher frequencies in both complexes. This suggests that the amino nitrogen is not coordinated. But the amide III and δNCO bands at 1265 cm^{-1} and 795 cm^{-1} respectively were lowered on coordination. These observations suggest the involvement of the amide group in coordination.

The bands in the region below 575 cm^{-1} in all the complexes are assigned to metal-ligand stretching modes[93].

The amide I band around 1650 cm^{-1} shifted to a lower frequency in $Co(MDH)_{3/2}(BF_4)_2$ and $Co(MDH)_3(BF_4)_2$ and this suggests the involvement of the carbonyl group in complexation[10,11]. Similarly, the amide II band around 1515 cm^{-1} decreased in frequency in both complexes, an indication that the amino nitrogen is also involved in coordination. The amide III band around 1250 cm^{-1} remained unchanged in the complexes, while the δNCO band around 725 cm^{-1} remained stationary in $Co(MDH)_{3/2}(BF_4)_2$ but rose to a higher frequency in $Co(MDH)_3(BF_4)_2$. These observations suggest the non-involvement of the amide nitrogen in coordination.

In the spectra of $Co(SDH)_2(BF_4)_2$ and $Co(SDH)_3(BF_4)_2$, the amide I, II and III bands around 1630 cm^{-1}, 1510 cm^{-1} and 1232 cm^{-1} respectively rose to higher frequencies. But the δNCO band around 740 cm^{-1} decreased to a lower frequency in $Co(SDH)_2(BF_4)_2$ and disappeared in $Co(SDH)_3(BF_4)_2$ thus indicating coordination through the amide nitrogen[11,12].

The amide I band around 1640 cm^{-1} in the complexes of ADH remained unchanged in $Co(ADH)_2(BF_4)_2$ but rose slightly on coordination in $Co(ADH)_3(BF_4)_2$, this probably suggests the non-involvement of the carbonyl oxygen in complex formation. On the other hand, the amide II band around 1510 cm^{-1} was lowered on coordination in both complexes while the amide III band increased in frequency in both complexes. The δNCO band was very weak in the ligands and complexes hence no meaningful deductions could be made. These observations suggest that coordination is via the amino group.

In the spectrum of $Co(PDH)_3(BF_4)_2$, the amide I and II bands at around 1625 cm^{-1} and 1558 cm^{-1} bands respectively increased in frequency showing that the carbonyl and amino groups are not coordinated. The δNCO band also shifted to a higher frequency in the complex. The frequency of the amide III band at 1245 cm^{-1} in the free ligand was lowered in the complex. It is suggested that this compound bond through the amide nitrogen.

The amide I and II bands around 1640 cm^{-1} and 1545 cm^{-1}, respectively were lowered in $Co(TDH)_3(BF_4)_2$, indicating the coordination of the carbonyl and amino groups. The δNCO band remained practically unchanged, whereas the amide III band around 1285 cm^{-1} shifted to a higher frequency on complexation.

5.3.8 Electronic spectra

The electronic spectra of the complexes (Table 12) exhibited two bands in the region 10,100 - 10,400 cm^{-1} and 20,000 - 21,300 cm^{-1} respectively. The lower bands (10,100 - 10,400 cm^{-1}) may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, while the second band is due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. The electronic spectra indicates that the complexes are octahedral[59-60, 90, 94].

5.3.9 Magnetic properties

The magnetic moments of the cobalt(II) tetrafluoroborate complexes (Table 13) are in the range 4.39-5.18 B.M. This agrees with the values reported in the literature[59-60, 90] for octahedral cobalt(II) complexes. The magnetic moments are higher than the spin only value of 3.87 B.M. for cobalt(II) high configuration with three unpaired electrons. In octahedral cobalt(II) the ground term is $^4T_{1g}$ and orbital contribution to the magnetic moment is expected being a T term[60,90]. This explains the high values observed.

5.4 Complexes of nickel(II) tetrafluoroborate dihydrazides

5.4.1 Colour of compounds

The colours of the complexes are shown in Table 8. These colours are typical of octahedral nickel(II) complexes[59, 60], with a d^8 configuration.

5.4.2 Analytical data

The analytical results (Table 8) shows that most of the complexes have 1:2 and 1:3 metal to ligand stoichiometry and a few with 1:$^{3}/_{2}$ stoichiometry.

5.4.3 Melting points/Decomposition temperatures

The melting points/decomposition temperatures (Table 8) were quite high in most cases ranging between 214 and above 300°C, except the MDH complexes and $Ni(SDH)_2(BF_4)_2$ which melted below 200°C.

5.4.4 Percentage yields

The yields ranged between 67% and 88% (Table 8).

5.4.5 Solubility

The complexes have poor solubilities in the range of solvents used except a few that were water soluble (Table 9).

5.4.6 Molar conductance

The molar conductances (Table 10) revealed that the MDH and SDH complexes are conductors in water[11].

5.4.7 Infrared spectra

The amide I band ($\nu C{=}O$) around 1660 cm^{-1} was lowered in frequency in $Ni(ODH)_2(BF_4)_2$ and $Ni(ODH)_3(BF_4)_2$. This shift in frequency suggests that the carbonyl oxygen is one of the bonding sites in the complexes. Similarly, the amide II band ($\nu CN + \delta NH_2$), around 1510 cm^{-1} was lowered in frequency on complexation, an indication that the amino nitrogen is probably coordinated[11]. However, the amide III (νCN + δNH) and δNCO bands around 1265 cm^{-1} and 795 cm^{-1} respectively rose to higher frequencies in both complexes. These observations suggest the non-involvement of the amide nitrogen in coordination[58]. The bands in the region below 680 cm^{-1} in the complexes may be assigned to metal-ligand stretching modes[93].

In the spectra of the complexes of malonic dihydrazide, the amide II band around 1650 cm^{-1} shifted to a higher frequency on coordination in $Ni(MDH)_2(BF_4)_2$, but is lowered in the spectrum of $Ni(MDH)_3(BF_4)_2$. This suggests the non-involvement of the carbonyl group in bonding in $Ni(MDH)_2(BF_4)_2$. The amide II band around 1515 cm^{-1} rose to a higher frequency in both complexes suggesting that the amino group is not coordinated. The spectrum of $Ni(MDH)_2(BF_4)_2$ reveals that the amide III and δNCO bands are lowered in frequencies on coordination. This presupposes the coordination of the amide nitrogen. The amide III band around 1250 cm^{-1} remained stationary, while the δNCO band around 725 cm^{-1} rose to a higher frequency in the spectrum of $Ni(MDH)_3(BF_4)_2$. This may preclude the amide group in bonding in the complex.

In the spectra of the SDH complexes, the amide I band around 1630 cm^{-1} remained unshifted in the complexes. Whereas the amide II and III bands around 1510 cm^{-1} and 1232 cm^{-1}

respectively rose to higher frequencies in $Ni(SDH)_{3/2}(BF_4)_2$ and $Ni(SDH)_2(BF_4)_2$ complexes. The δNCO band around 740 cm^{-1} in the ligand disappeared in the spectra of the complexes. Bonding in these complexes is presumed to be through the amide nitrogen[11].

In the spectra of the ADH complexes, the amide I band around 1640 cm^{-1} decreased on complexation suggesting that the carbonyl oxygen is involved in bonding. The amide II and III bands rose on complex formation; these observations suggest that the amino and amide groups are not involved in bonding in these complexes. The spectra of these compounds indicate that the molecules of the dihydrazide are bonded to the nickel(II) ion through the carbonyl oxygen.

The amide I band around 1625 cm^{-1} rose to higher frequencies in the PDH complex, whereas the amide II band around 1558 cm^{-1} decreased in frequency on complex formation. The amide III and δ NCO bands rose to higher frequencies in the complex. The bonding in this compound is through the amino nitrogen[34].

The spectrum of $Ni(TDH)_3(BF_4)_2$ revealed that the amide I band around 1640 cm^{-1} is lowered in frequency on coordination. Likewise, the amide III and δNCO bands. Whereas, the amide II band around 1545 cm^{-1} rose to a higher frequency on coordination. The general features of the TDH spectrum suggests that coordination is via the carbonyl and amide groups.

5.4.8 Electronic spectra

Octahedral nickel(II) complexes with $^3A_{2g}$ ground state are expected to have three spin allowed transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$; and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively[60]. Some workers[58-60] have reported two or three of these spin-allowed transitions. The nickel(II) complexes studied exhibit two bands in the regions 10,300-11,000 cm^{-1} and 16,800-18,200 cm^{-1} which may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively (Table 12)[95]. Sutton[96], also reported that for octahedral nickel(II) complexes the ratio of the first and second bands should be ≤ 1.8, whereas, for tetrahedral complexes it should be close to 2.2. In this study, this ratio lies between 1.6 and 1.7 indicating that the complexes assume octahedral geometry.

5.4.9 Magnetic properties

The magnetic moments of the nickel(II) tetrafluoroborate complexes studied are in the range 2.90-3.34 B.M. For octahedral nickel(II) complexes with two unpaired electrons, magnetic moments ranging from 2.9 to 3.4 B.M. is expected depending on the magnitude of orbital contribution[60]. The complexes are presumed to be octahedral and free from magnetic interactions (Table 13).

5.5 Complexes of copper(II) tetrafluoroborate dihydrazides

5.5.1 Colour of compounds

The colours of the complexes are typical of compounds of Cu(II) with a d^9 configuration[60] (Table 8).

5.5.2 Analytical data

The metal to ligand stoichiometries (Table 8) are similar to those obtained in the complexes of Mn(II), Co(II) and Ni(II) respectively.

5.5.3 Melting points/Decomposition temperatures

The melting points/decomposition temperatures were generally $\geq$ 200°C, except $Cu(MDH)_3(BF_4)_2$ which melted between 106-108°C.

5.5.4 Percentage yields

The experimental yields were quite high (Table 9), ranging from between 63-82% (Table 8).

5.5.5 Solubility

The complexes were slightly soluble in most of the solvents used, while the MDH and SDH complexes were soluble in water (Table 9).

5.5.6 Molar conductance

Molar conductances of the MDH and SDH complexes in water suggests that they are conductors and 1:2 type electrolytes (Table 10)[11].

5.5.7 Infrared spectra

Infrared spectra of the complexes were assigned by comparison with those of the ligands and related compounds[10-12] (Table 11).

The amide I band around 1660 cm^{-1} is lowered in $Cu(ODH)_{3/2}(BF_4)_2$ and $Cu(ODH)_3(BF_4)_2$ complexes, showing coordination through the carbonyl group. Whereas, the amide II band around 1510 cm^{-1} rose to higher frequencies in both complexes, this suggests that the amino group is not coordinated. The amide III band around 1265 cm^{-1} remained practically unchanged in the $Cu(ODH)_3(BF_4)_2$ complex but rose on coordination in the $Cu(ODH)_{3/2}(BF_4)_2$ complex. The δNCO decreased slightly in frequency on complexation. These observations suggest the non-involvement of the amide nitrogen in coordination[12].

In the spectra of the MDH complexes, the amide I band around 1650 cm^{-1} experience a negative shift to lower frequencies in both, this suggests the involvement of the carbonyl oxygen in coordination. But the amide II band around 1515 cm^{-1} remained unchanged in the complexes, whereas the amide III band rose to a higher frequency in both $Cu(MDH)_2(BF_4)_2$ and $Cu(MDH)_3(BF_4)_2$. The band due to δNCO around 725 cm^{-1} remained also unchanged in $Cu(MDH)_2(BF_4)_2$ but rose in $Cu(MDH)_3(BF_4)_2$ complex. Bonding in these complexes is presumed to be through the carbonyl group[4,11].

In the SDH complexes, the amide I band around 1630 cm^{-1} decreased on complexation suggesting that the carbonyl oxygen is involved in bonding. Whereas, the amide II and III bands rose on complex formation and δNCO band unaffected, these observations suggest that the amino and amide groups are not bonded in these compounds.

In the spectra of the complexes of ADH, the amide I and II bands were lowered in frequencies in both complexes. While the amide III band rose slightly in $Cu(ADH)_3(BF_4)_2$ but remained unaltered in $Cu(ADH)_2(BF_4)_2$ complex, the spectra of these compounds indicate that the molecules of the hydrazide are bonded to the copper ion through the amino and carbonyl groups in agreement with previous studies[3,34].

The amide I band (Table 11) around 1625 cm^{-1} rose to higher frequencies in the PDH complexes, whereas the amide II band decreased in frequency on complex formation. The frequencies of the amide III and δNCO bands rose in the complexes. It is presumed that these complexes bond through the amino group.

In the spectrum of the TDH complex, the amide I band around 1640 cm^{-1} shifted to a higher frequency, likewise, the amide II band around 1545 cm^{-1} and δNCO band around 735 cm^{-1} rose on complexation. However, the amide III band decreased on coordination. It is suggested that coordination is via the amide nitrogen[11,12].

5.5.8 Electronic spectra

The reflectance spectra of the complexes (Table 12) show a broad band between 14,600 - 16,500 cm^{-1} assigned to $d \rightarrow d$ transitions. The asymmetric nature of the bands indicates distorted octahedral geometry resulting from Jahn-Teller distortion of the ^3e_g state[58,94]. The weak shoulders in the range 23,300-25,600 cm^{-1} in the electronic spectra of the complexes resemble those found in binuclear Cu(II) compounds[58,97]. This band is now known to be a charge-transfer band[98].

5.5.9 Magnetic properties

The magnetic moments of the complexes (Table 13) are in the range 1.80-2.18 B.M. The magnetic moments of copper(II) complexes excluding those with Cu-Cu interactions are usually in the range 1.75-2.20 B.M. regardless of stereochemistry, and they are independent of temperature except at extremely low temperatures (<5°K)[60]. The complexes can be regarded therefore as being magnetically dilute with no metal-metal interaction[60,90].

5.6 Complexes of zinc(II) tetrafluoroborate dihydrazides

5.6.1 Colour of compounds

Table 8 indicates the colours of the complexes, and are as expected of Zn(II) ion with d^{10} configuration.

5.6.2 Analytical data

Analytical results for the complexes are presented in Table 8. The stoichiometries are similar to those discussed earlier.

5.6.3 Melting point/Decomposition temperatures

The melting points/decomposition temperatures were quite high in most cases ranging between 173 and above 300°C (Table 8).

5.6.4 Percentage yields

As shown in Table 8, the yields are in the range 55-85%.

5.6.5 Solubility

Solubilities in the solvents used were poor except the ODH, MDH and ADH complexes that were soluble in water (Table 9).

5.6.6 Molar conductance

Table 9 indicates the molar conductances of the ODH, MDH and ADH complexes in water. It revealed that they are conductors with 1:2 type electrolytes[11].

5.6.7 Infrared spectra

The amide I band remained practically unchanged in the spectrum of $Zn(ODH)_2(BF_4)_2$ but rose to a higher frequency in $Zn(ODH)_3(BF_4)_2$ showing that the carbonyl group is not involved in coordination. Similarly, the amide III band around 1265 cm^{-1} and the δNCO band remained either unchanged or rose slightly in going from the ligand to the complexes (Table 11). This may indicate the non-involvement of the amide nitrogen in coordination[11,12].

The amide II band around 1510 cm^{-1} was lowered in frequency compared to the free ligand in the spectrum of

$Zn(ODH)_2(BF_4)_2$ and $Zn(ODH)_3(BF_4)_2$. It is suggested that bonding in these complexes is probably through the amino nitrogen.

In the MDH complexes, the carbonyl absorption around 1650 cm^{-1} (amide I band) was lowered in frequency on complex formation in both complexes. This may be taken as evidence for coordination through the carbonyl group. The amide II band decreased slightly in frequency on complex formation, while the amide III and δNCO bands remained invariant in the complexes. It is presumed that these complexes bond through the carbonyl and amino groups[34].

The amide I band remained unshifted in the complexes of SDH, but the amide II band rose to a higher value in the complexes. The amide III band was slightly lowered whereas the δNCO band disappeared on complex formation, probably indicating coordination through the amide nitrogen[12].

The spectrum of the ADH complex has the amide I band lowered in frequency on complex formation, while the amide II band increases in frequency on coordination. However, the amide III band shifted from around 1262 cm^{-1} in the ligand to about 1225 cm^{-1} in the complex.

In the spectrum of $Zn(PDH)_3(BF_4)_2$ amide I band at 1625 cm^{-1} in the ligand was shifted to 1649 cm^{-1}. This is an indication that the C=O bond is not coordinated. Likewise, the amide II and III bands rose to a higher frequency. The δNCO disappeared in the spectrum of the complex, an indication that the hydrazide moiety coordinated through the amide nitrogen[12].

In the spectrum of the TDH complex, the amide I band is lowered on coordination indicating carbonyl group participation in bonding. However, the amide II band rose to a higher frequency on coordination, likewise the amide III and δNCO bands remained unshifted on complexation.

5.6.8 Magnetic properties

The magnetic susceptibilities of the Zn(II) complexes are in the range 0.21-0.57 B.M. These values revealed that they are nearly diamagnetic as expected of Zn(II) with a d^{10} configuration. However, comparison of the experimental susceptibilities with the calculated values (Table 14) reveals a large deviation from the additivity law in most of the complexes. This behaviour has been explained before[99], in terms of polarization paramagnetism. It is suggested that they are probably asymmetric[99-100].

5.7 Complexes of cadmium(II) tetrafluoroborate dihydrazides

5.7.1 Colour of compounds

The colours of the complexes (Table 8) were as expected of cadmium(II) with a d^{10} configuration[90].

5.7.2 Analytical data

The analytical results of the cadmium(II) tetrafluoroborate complexes (Table 8) revealed that the 1:1 and 1:2 metal to ligand reactant ratios gave different metal to ligand stoichiometry in most cases.

5.7.3 Melting points/Decomposition temperatures

All the complexes have sharp melting points (Table 8) ranging between 211 and above 300°C, except for $Cd(SDH)_2$-$(BF_4)_2$ and $Cd(ADH)_3(BF_4)_2$ which melted below 200°C.

5.7.4 Percentage yields

Yields obtained were between 62% and 80% (Table 8).

5.7.5 Solubility

The complexes have poor solubilities in the solvents used. Nonetheless, the ODH, MDH, SDH and ADH were soluble in water (Table 9).

5.7.6 Molar conductance

Presented in Table 10 are the molar conductances of the ODH, MDH, SDH and ADH complexes in water and DMSO. The values indicate that they are conductors with a 1:2 type electrolytes[11].

5.7.7 Infrared spectra

The infrared spectra of the complexes (Table 11) revealed that the amide I band was lowered in $Cd(ODH)_3(BF_4)_2$, $Cd(PDH)_3(BF_4)_2$, ADH and TDH complexes suggesting that the carbonyl group is involved in bonding in these complexes. While the amide I band shifted to higher frequencies in $Cd(ODH)_2(BF_4)_2$, $Cd(SDH)_2$ and $Cd(PDH)_2(BF_4)_2$. This band remained almost stationary in $Cd(MDH)_2(BF_4)_2$ and $Cd(SDH)_3(BF_4)_2$. The IR features suggest the non-involvement of the carbonyl oxygen in coordination in these compounds.

The amide II band was lowered in frequency in the PDH complexes, whereas the complexes of ODH,MDH, ADH and $Cd(SDH)_3(BF_4)_2$ experienced a shift to higher frequency. This band remained unchanged in $Cd(SDH)_3(BF_4)_2$ and $Cd(TDH)_3(BF_4)_2$.

The amide III band was lowered in $Cd(ODH)_2(BF_4)_2$, MDH, SDH and ADH complexes. These complexes also either have the δNCO band lowered or absent in their spectra except for the MDH complex where the δNCO band rose to a slightly higher frequency. The shifts associated with the amide III and δNCO bands are indications that the amide nitrogen is probably involved in bonding. On the other hand, the amide III band rose on complexation in $Cd(PDH)_2(BF_4)_2$ and $Cd(TDH)_3(BF_4)_2$ but remained practically unchanged in $Cd(ODH)_3(BF_4)_2$ and $Cd(PDH)_2(BF_4)_2$.

5.7.8 Magnetic properties

The room temperature magnetic moments of the complexes (Table 14) show that they are diamagnetic as expected. But the experimental and calculated molar susceptibilities differ significantly and probably indicate the presence of polarisation paramagnetism[99-100] in the complexes.

5.8 Complexes of mercury(II) tetrafluoroborate dihydrazides

5.8.1 Colour of compounds

The colours of the complexes are typical of Hg(II) complexes (Table 8)[90].

5.8.2 Analytical data

The analytical results are indicated in Table 8.

5.8.3 Melting points/Decomposition temperatures

Phthalic and terephthalic dihydrazide complexes melted/decomposed at temperatures above 300°C. The other complexes have either melting/decomposition temperatures between 117-269°C (Table 8).

5.8.4 Percentage yields

The yields were between 66% and 82%.

5.8.5 Solubility

A summary of the solubilities of the complexes in various polar and non-polar solvents is presented in Table 9. A few of them were soluble in water, while all of them have poor solubilities in the organic solvents used.

5.8.6 Molar conductance

The molar conductivities of Hg SDH$(BF_4)_2$ and Hg$(ADH)_2(BF_4)_2$ (Table 10) revealed that they are conductors and a 1:2 type electrolytes. The molar conductivities of the other complexes could not be taken because of poor solubility.

5.8.7 Infrared spectra

The IR spectra of the complexes of ODH, SDH, ADH, TDH as well as Hg$(MDH)_2(BF_4)_2$ have their amide I band lowered in frequency on complex formation. This may be taken as evidence for coordination through the carbonyl oxygen. The amide I band in $Hg(MDH)_3(BF_4)_2$ remained invariant, whereas there was a shift to higher frequencies in the PDH compounds.

The amide II band was lowered in frequency in the MDH and PDH complexes, an indication of amino group participation in coordination in the complexes. Nevertheless, the ODH, SDH, ADH and TDH complexes experienced shift to higher frequencies, an observation which suggest the non-involvement of the amino nitrogen in complexation in this group of compounds.

The amide III band was lowered in ODH, SDH and TDH in addition to $Hg(MDH)_3(BF_4)_2$. This band however rose to higher frequencies in the ADH and PDH complexes as well as $Hg(MDH)_2(BF_4)_2$.

5.8.8 Magnetic properties

The magnetic susceptibilities of the complexes (Table 14) show that they are diamagnetic as would be expected of mercury(II) with d^{10} configuration. Nonetheless, the experimental and calculated molar susceptibilities differ significantly and probably indicate the presence of polarisation paramagnetism in the complexes[99-100].

5.9 Complexes of magnesium tetrafluoroborate dihydrazides

5.9.1 Colour of compounds

The colours of the complexes are indicated in Table 8. Magnesium complexes are expected to be colourless, magnesium being a non-transitional element[90].

5.9.2 Analytical data

The analytical results indicate different ligand to metal stoichiometries (Table 8).

5.9.3 Melting points/Decomposition temperatures

All the magnesium complexes have melting/decomposition temperatures above 300°C (Table 8).

5.9.4 Percentage yields

Yields were between 71% and 85%.

5.9.5 Solubility

The complexes were slightly soluble in the polar and non-polar organic solvents used. They also have poor solubility in water except $Mg(ADH)_{3/2}(BF_4)_2$ that was soluble in water (Table 8).

5.9.6 Molar conductance

The molar conductance of $Mg(MDH)_{3/2}(BF_4)_2$ in water (Table 10) reveals a 1:2 type electrolyte[11].

5.9.7 Infrared spectra

In the IR spectra of the magnesium complexes (Table 11) the amide I band was lowered in MDH, SDH and ADH complexes. It is suggested that these compounds bond through the amide nitrogen. However, the amide I band rose on complexation in PDH and TDH complexes, but remained practically unchanged in $Mg(ODH)_2(BF_4)_2$ and $Mg(ODH)_3(BF_4)_2$. These observations suggest the non-involvement of the carbonyl oxygen in the compounds.

The amide II band in $Mg(ODH)_3(BF_4)_2$, $Mg(SDH)_3(BF_4)_2$ and PDH complexes shifted to lower frequencies, whereas it rose to higher frequencies in $Mg(ODH)_2(BF_4)_2$, $Mg(MDH)_{3/2}(BF_4)_2$, $Mg(MDH)_2(BF_4)_2$, $MgSDH(BF_4)_2$, ADH and TDH complexes.

The lowering in frequency probably indicates that the amino nitrogen is involved in bonding while the rise in frequency may be taken as an indication of the non-involvement of the amino group in bonding in the complexes involved.

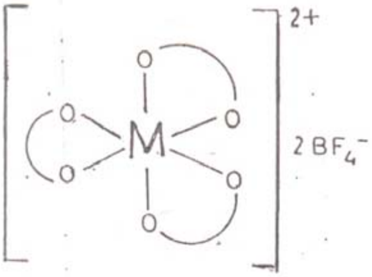
The complexes of $Mg(ODH)_2(BF_4)_2$, $MgSDH(BF_4)_2$ MDH, ADH and TDH have their amide III band lowered in frequency on complexation. Except for the MDH complexes which have the δNCO band slightly increased in complexation, the others, that is, $Mg(ODH)_2(BF_4)_2$, $Mg\,SDH(BF_4)_2$, ADH and TDH complexes have their δNCO band either lowered or absent on coordination. But the amide III band in $Mg(ODH)_3(BF_4)_2$, $Mg(SDH)_3(BF_4)_2$ and PDH complexes shifted to higher frequencies on coordination. The corresponding δ NCO band also rose to higher frequencies.

5.9.8 Magnetic properties

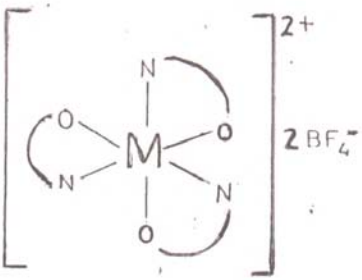
As would be expected, the room temperature magnetic susceptibilities of the Mg complexes (Table 14) shows that they are diamagnetic with some evidence of polarisation paramagnetism[99,100].

5.10 Proposed structures for the complexes

Based on the analytical data and physicochemical data discussed above, structures I-V are suggested for some of the complexes. The proposed structures are only tentative in the absence of X-ray data.



I



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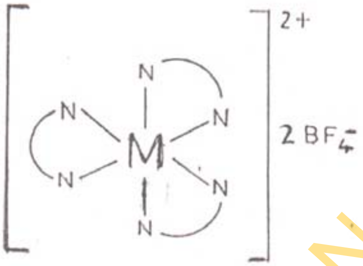

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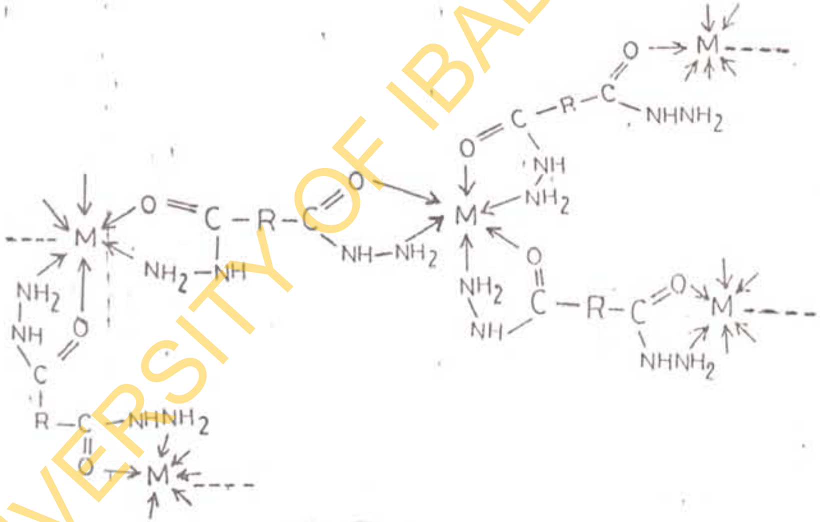

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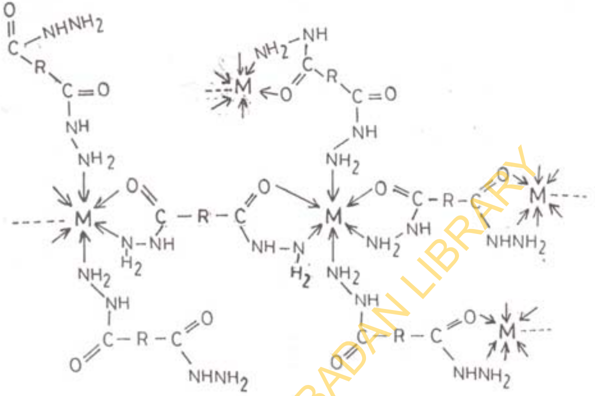

V

Where,

M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Mg

R = $(CH_2)n$ (n = 0, 1, 2, 4) or C_6H_4

Fig. 44 Proposed Structures of the Complexes

5.11 Conclusion and suggestions for further work

Reactions involving 1:1 and 1:2 metal to ligand reactant ratios, yielded complexes with different metal to ligand stoichiometry in most cases. This is an indication that the ligand to metal stoichiometry depends to some extent on the ratio of the reactants used during their preparations.

The infrared studies based on the interpretation of changes in the amide I ($\nu C{=}O$), II ($\nu CN + \delta NH_2$) III ($\nu CN + \delta NH$) and δNCO bands revealed that coordination in the complexes was via the carbonyl, amide or amino groups.

The magnetic moments and electronic spectra of the complexes of manganese(II), cobalt(II), nickel(II), and copper(II) indicated that they assume octahedral geometry. Whereas the magnetic moments of the complexes of zinc(II), cadmium(II), mercury(II) and magnesium indicated that they are diamagnetic as expected with some evidence of polarisation paramagnetism.

The molar conductances of the complexes which were soluble in water and DMSO indicated 1:2 type electrolytes, which is an indication that the BF_4 anion is probably not coordinated in the complexes. The coordination of the tetrafluoroborate anion is rare$^{60,100-104}$, and there are no evidence from this study to suggest "semi-coordinated" BF_4^- anion$^{100-104}$.

The complexes with 1:1, 1:3/2 and 1:2 metal to ligand stoichiometries are probably dimeric or polymeric[10-12,33,34]. The effect of H-bonding in hydrazides and their complexes[11,12,44] makes the IR assignments tentative.

Suggestions for further work

(1) X-ray structural studies of the complexes to confirm some of the proposed structures.

(2) Industrial and biological applications of these complexes could also be exploited.

(3) Characterisation of complexes formed using 1:3 and 1:4 metal to ligand reactant ratios for comparative purposes.

(4) Variable temperature magnetic measurements between 320 and 80K could be carried out to estimate the extent of magnetic interactions, if any, in the complexes of manganese(II), cobalt(II), nickel(II) and copper(II) respectively.

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