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Metal Complexes of Aroylhydrazones : Preparation and Structural Characterization

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Four aroylhydrazone Schiff bases viz. 2-furaldehyde-p-chlorobenzoylhydrazone (fcbH), p-methoxybenzaldehyde-p-chlorobenzoylhydrazone (mbcbH), *p*-methoxybenzaldehyde salicyloylhydrazone (mbsH) and 2-furaldehyde salicyloylhydrazone (fsH) are prepared, Fifteen complexes of the general formula $[ML_2(H_2O)_2]$ and three of general formula $[ML_2]$ have been synthesised where LH = fcbH; mbcbH, mbsH, fsH and M = a bipositive cation. From the results of chemical analysis, magnetic susceptibility measurements at different current, ir, drs and thermal studies the mode of chelation of the ligand and geometry of the complex molecules are assigned. Consequently Co(II)-mbsH and the diamagnetic Ni(II)-mbsH, Ni(II)-fsH complexes are formulated as square pyramidal whereas an octahedral environment around each metal is proposed in rest of the bispositive aroylhydrazone complexes.

INTRODUCTION

The remarkable biological activity of acid hydrazides, $R{-}CO{-}NH{-}NH_2$, their corresponding aroylhydrazones, $R{-}CO{-}NH{-}N{=}CH{-}R'$ and the dependence of their mode of chelation with transition metal ions present in the living system offer significant interest in recent years[1-4]. It is believed that the $-CO-NH-N{=}C{=}$ moiety of hydrazone imparts biological characteristic[5] to this class of compounds. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors[6] and are useful due to their pharmacological applications[7-9]. Temerk and Ghoneim[10] studied metal complexes with acetophenone salicyloyl- and acetophenone-benzoylhydrazones. Five coordinate complex of bivalent nickel and copper with ligands derived from acid hydrazides and acetylacetone have been synthesised by Teotia and coworkers[11]. Other complexes investigated include the uranyl(VI) and nickel(II) complexes with aroylhydrazones and Ni(II), Cu(II), Zn(II) and Cd(II) metal complexes with diacetyl[12]. The latter complexes are presumed to be polymeric in nature. Salicyloylhydrazone derived from α-oximinobenzoylacetarylamides has been used as gravimetric reagent for determination of Pd(II)[13]. Stereochemical features of Cu(II) and Ni(II) complexes with benzoylhydrazone ligand has been studied by Rastogi *et al.*[14]. The authors have

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also studied tetrahedral and octahedral cobalt complexes with hydrazones derived from salicylaldehyde and 2-hydroxyl-1-naphthaldehyde and benzoyl hydrazide. An oxygen bridged complexes of Zn(II) and Cd(II) with benzoyl hydrazone of *o*-hydroxy aldehydes and ketones have been suggested whereas Co(II) and Ni(II) complexes with ligand derived from oxalyldihydrazide and salicylaldehyde are reported to be octahedral via enolic oxygen coordination[15]. Studies have been extended to isolate complexes formed with tripositive cations, lanthanide complexes of salicylidenebenzoylhydrazone are obtained as yellow crystalline precipitates by refluxing their metal nitrates and the ligand in ethanol[16]. In view of the growing interest in hydrazones on account of structural, analytical and pharmacological importance of their metal complexes the synthesis of four aroyl hydrazones *viz.* 2-furaldehyde-p-chlorobenzoylhydrazone (fcbH), p-methoxybenzaldehyde-p-chlorobenzoylhydrazone (mbcbH), p-methoxybenzaldehyde salicyloylhydrazone (mbsH) and 2-furaldehyde salicyloylhydrazone (fsH) are described. The ligands and their several complexes have been characterised by analytical, spectral, magnetic and thermal properties.

EXPERIMENTAL

Materials and Methods

Salicylic acid (AnalaR), p-chlorobenzoic acid, hydrazine hydrate (both Ranbaxy) were employed. Reagent grade metal acetates, solvents and instruments employed are the same as described earlier[17]. Synthesis of salicyloyl p-chlorobenzoyl hydrazides requires two steps involving the formation of methyl ester of salicylic-p-chlorobenzoic acid and its subsequent reaction with hydrazine hydrate. This has also been reported by the authors[17].

Synthesis of 2-furaldehyde-p-chlorobenzoylhydrazone (fcbH)

Furaldehyde (4.14 cm^3) was added gradually to the solution of p-chlorobenzoyl hydrazide (8.53 g) dissolved in hot ethanol with constant stirring and the mixture was refluxed on a water bath for 2 hrs. On cooling, a light yellow coloured solid separated, which was filtered, washed with ethanol and ether successively and dried over anhydrous $CaCl_2$. The yield of ligand was 80% and its m.pt. 218°C.

Synthesis of p-methoxybenzaldehyde-p-chlorobezoylhydrazone (mbcbH)

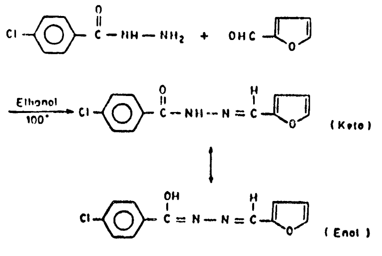
To the solution of p-chlorobenzoyl hydrazide (8.53g) in hot ethanol, p-methoxybenzaldehyde (6 cm^3) was added gradually with stirring and the mixture was refluxed on a water bath for 2 hrs. On cooling, a white crystalline solid was obtained, which was filtered, washed with ethanol and ether successively and then dried over anhydrous $CaCl_2$. Yield was 85% and its m.pt. 215°C.

Synthesis of *p*-methoxybenzaldehyde salicylohydrazone (mbsH)

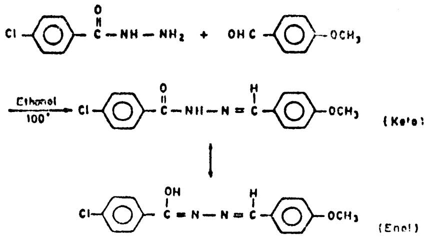
7.6g (.05M) of salicyloyl hydrazide was dissolved in 150 cm^3 of hot ethanol. To this was added 6 cm^3 (.05M) of *p*-methoxybenzaldehyde gradually and the mixture was refluxed on a water bath for 2 hrs. On cooling, a white crystalline solid separated which was filtered and isolated as above (yield 85%, m.pt. 205°C).

Synthesis of 2-furaldehyde salicyloyl hydrazone (fsH)

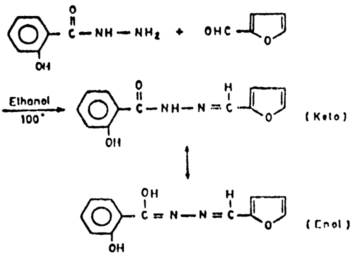
An ethanolic solution of salicyloyl hydrazide (7.6g, 0.05M) was treated with furaldehyde (4.14 cm^3) and the mixture was refluxed on water bath for 3 hrs. A light yellow mass separated on cooling and collected as above (yield 80%, m.pt. 160°C). The reactions involved in the synthesis of hydrazones and their tautomeric forms are shown below.



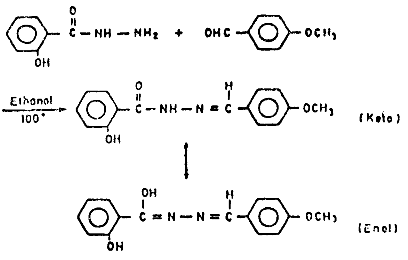
Tautomeric forms of FCBH



II : Tautomeric forms of MBCBH



III: Tautomeric forms of FSH



IV: Tautomeric forms of MBSH

Synthesis of Metal Complexes

Complexes of fcbH, mbcbH, mbsH and fsH were synthesised by refluxing an ethanolic solution of the ligand and an aqueous ethanolic solution of different metal acetates in 2 : 1 molar ratio on water bath for 2–3 hrs. A 0.02M of metal salt solution containing 0.49g of $Mn(CH_3COO)_2 \cdot 4H_2O$, 0.50g of $Co(CH_3COO)_2$ $4H_2O$, 0.50g of $Ni(CH_3COO)_2 \cdot 4H_2O$, 0.40g of

$Cu(CH_3COO)_2 \cdot H_2O$ or 0.44g of $Zn(CH_3COO)_2 \cdot 2H_2O$ was reacted with 1.00g of fcbH, 1.15g mbcbh, 1.08 of mbsH or 0.92g of fsH (0.004M). The insoluble complex thus prepared were filtered off, washed with ethanol and dried over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The analytical data of the complexes reveal that the complexes have 1 : 2 stoichiometry having the general formula $(ML_2(H_2O)_2]$ where, HL=fcbH, mbcH, mbsH, and fsH; M=bipositive cation. The general formula of Co—mbsH, Ni—mbsH and Ni—fsH complex is ML_2 which do not contain water molecules. The physical and analytical data are summarised in Table 1.

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Compd. No.	Empirical Formulae of compounds	Colour (m.pt.°C)*	Elemental Analyses Found (Calc.)%			
			M	C	H	H
1.	$C_{12}H_9O_2N_2Cl$	Light Yellow (218)	—	58.10 (57.94)	3.42 (3.62)	11.42 (11.26)
2.	$[Mn(C_{12}H_8O_2N_2Cl)_2(H_2O)_2]$	Yellowish brown (280)	9.25 (9.37)	49.46 (49.15)	3.70 (3.41)	9.63 (9.55)
3.	$[Co(C_{12}H_8O_2N_2Cl)_2(H_2O)_2]$	Brown (280)	9.96 (9.99)	49.02 (48.81)	3.51 (3.39)	9.71 (9.49)
4.	$[Ni(C_{12}H_8O_2N_2Cl)_2(H_2O)_2]$	Orange (360)	9.75 (9.95)	48.78 (48.83)	3.58 (3.39)	9.39 (9.49)
5.	$[Cu(C_{12}H_8O_2N_2Cl)_2(H_2O)_2]$	Green (200)	10.54 (10.68)	48.76 (48.44)	3.60 (3.36)	9.35 (9.41)
6.	$C_{15}H_{13}O_2N_2Cl$	White	—	62.37 (62.39)	4.52 (4.50)	9.25 (9.70)
7.	$[Mn(C_{15}H_{12}O_2N_2Cl)_2(H_2O)_2]$	Light Yellow (300)	8.15 (8.24)	54.24 (54.05)	4.43 (4.20)	8.24 (8.40)
8.	$[Co(C_{15}H_{12}O_2N_2Cl)_2(H_2O)_2]$	Brown (300)	8.40 (8.79)	53.96 (53.73)	4.29 (4.17)	8.04 (8.35)
9.	$[Ni(C_{15}H_{12}O_2N_2Cl)_2(H_2O)_2]$	Orange (320)	8.37 (8.76)	53.69 (53.75)	4.41 (4.17)	8.05 (8.35)
10.	$[Cu(C_{15}H_{12}O_2N_2Cl)_2(H_2O)_2]$	Green (240)	9.00 (9.41)	53.54 (53.36)	3.94) (4.15)	8.09 (8.30)

TABLE 1 (contd.)

Compd. No.	Empirical Formulae of compounds	Colour (m.pt. °C)*	Elemental Analyses Found (Calc.)%			
			M	C	H	N
11.	$[Zn(C_{15}H_{12}O_2N_2Cl)_2(H_2O)_2]$	Dirty brown (280)	9.52 (9.69)	53.96 (53.22)	4.13 (4.13)	8.56 (8.27)
12.	$C_{15}H_{14}O_3N_2$	White (205)	—	66.98 (66.66)	5.38 (5.18)	10.34 (10.37)
13.	$[Mn(C_{15}H_{13}O_3N_2)_2(H_2O)_2]$	Light Yellow (240)	8.61 (8.73)	57.57 (57.23)	4.53 (4.76)	8.98 (8.90)
14.	$[Co(C_{15}H_{13}O_3N_2)_2]$	Brown (300)	9.70 (9.87)	59.83 (60.30)	4.34 (4.35)	9.48 (9.38)
15.	$[Ni(C_{15}H_{13}O_3N_2)_2]$	Orange (320)	9.78 (9.83)	60.07 (60.33)	4.39 (4.35)	9.11 (9.38)
16.	$[Cu(C_{15}H_{13}O_3N_2)_2(H_2O)_2]$	Green (200)	9.82 (9.96)	56.32 (56.46)	4.39 (4.70)	8.53 (8.78)
17.	$[Zn(C_{15}H_{13}O_3N_2)_2(H_2O)_2]$	Gream (300)	10.10 (10.22)	56.32 (56.30)	4.34 (4.69)	8.49 (8.75)
18.	$C_{12}H_{10}O_3N_2$	Light Yellow (160)	—	62.15 (62.60)	4.57 (4.34)	12.06 (12.17)
19.	$[Mn(C_{12}H_9O_3N_2)(H_2O)_2]$	Brown (120)	10.25 (10.00)	52.86 (52.46)	3.92 (4.00)	10.01 (10.20)
20.	$[Ni(C_{12}H_9O_3N_2)]$	Orange (280)	11.42 (11.36)	55.76 (55.73)	3.46 (3.48)	10.68 (10.83)
21.	$[Cu(C_{12}H_9O_3N_2)_2(H_2O)_2]$	Green (200)	11.30 (11.39)	51.60 (51.65)	3.82 (3.94)	9.69 (10.04)
22.	$[Zn(C_{12}H_9O_3N_2)_2(H_2O)_2]$	Light Yellow (240)	11.65 (11.68)	51.35 (51.48)	3.20 (3.93)	10.00 (10.01)

*With decomposition

$C_{12}H_9O_2N_2Cl$ = 2-Furaldehyde-p-chlorobenzoylhydrazone[fcbH]

$C_{15}H_{13}O_2N_2Cl$ = p-Methoxybenzaldehyde-p-chlorobenzoylhydrazone[mbcbH]

$C_{15}H_{14}O_3N_2$ = p-Methoxybenzaldehyde salicyloylhydrazone[mbsH]

$C_{12}H_{10}O_3N_2$ = 2-Furaldehyde salicyloylhydrazone[fsH]

Infrared Spectral Studies

The infrared absorption bands further confirm the presence of water of coordination[18] in mbsH, fsH, fcbH and mbcbH complexes. The bands due to —OH stretching deformation and rocking[19] modes are observed at 3550–3600, 1600–1650 and 740–780 cm^{-1} respectively in above complexes. No such bands are observed in case of Co—mbsH, Ni—mbsH and Ni—fsH complexes evidently showing the absence of water molecules.

The aroylhydrazone chelating ligands mbsH, fsH, fcbH and mbcbH exhibit fairly intense bands at 1600, 1610, 1620 and 1595 cm^{-1} due to C=N stretching, indicating the formation of hydrazones by the condensation of carbonyl groups with amido groups of hydrazides[20]. A downward shift in case of complexes shows the participation of azomethine nitrogen on complexation. This is consistent with the low frequency shift of ν(C=N) observed by Patil and Kulkarni[21] at 1600–1620 cm^{-1}, Ali *et al*[22] at 1595–1618 cm^{-1}; 1580–1610 cm^{-1}, Leovac *et al*[23] at 1600 ± 10 cm^{-1} and other investigators[24]. The occurrence of ν(N—N) band at a higher frequency in their spectra of the complexes compared to the ligand suggests a reduction of the repulsion between the lone pairs of the nitrogen atoms as a result of coordination via azomethine nitrogen[25].

The absorption bands for C=O and N—H stretchings observed between 1680–1730 and 3220–3260 cm^{-1} respectively for the above hydrazones disappear in the complexes[26]. The chelation occurs via enolic form through deprotonation which finds support from the fact that (i) The ir spectra of the complexes do not contain the (N—H) band of the free ligand *ca* 3240 cm^{-1} (ii) C=O stretching bands disappear on complexation (iii) New bands characteristic of azine $>C=N-N=C<$ group appear in the range of *ca* 1505–1575 cm^{-1} in hydrazone complexes[27]. (iv) The C—O stretching (enolic) vibration in mbsH, fsH, fcbH and mbcbH occurs as a strong band at 1255, 1235, 1230 and 1250 cm^{-1} respectively. These bands are raised by 15–50 cm^{-1} in their metal complexes. The high frequency shift of enolic ν(C—O) on complexation is inconsistent with oxygen coordination through —OH group[28,29] to metal as also observed by Pardhy *et al*[30] in the case of penta-coordinated Ru(II) hydrazone complexes.

The phenolic —OH group of salicyloylhydrazone does not take part in coordination[31] as C—O (phenolic) stretching frequency remains unaltered from their original positions at *ca.* 1500 cm^{-1} in mbsH and fsH. Mn(II) Cu(II) and Zn(II) complexes formed by mbsH and fsH exhibit bands due to —OH stretching, deformation and rocking modes. These bands are observed at 3550–3610, 1610–1645 and 755–760 cm^{-1} respectively, in mbsH complexes. Similar bands are observed at 3550–3600, 1610–1640 and 750–780 cm^{-1} in the case of fsH metal complexes. Coordination through oxygen and nitrogen[32–34] donor atoms of the hydrazones which is substantiated by the occurence of new bands in the low frequency region assignable to M—O and M—N stretchings. These are not observed in all the four hydrazones alone. Selective ir spectral bands are shown in Table 2. In the case of fsH, fcbH chelating ligands, lowering of vibrations due to furan ring does not occur showing that oxygen atom to furan ring does not take part in coordination. Moreover, the ir spectra of fsH complexes do not contain any band attributable to M—O stretching in far ir region; further supports the above proposition (Table 2). Additional

TABLE 2

CHARACTERISTIC IR SPECTRAL DATA OF COMPLEXES, (cm^{-1})

Compd.	ν(OH),H_2O	ν(NH)	ν(C=N)	ν(C=N—N=C)	ν(N—N)	ν(M—O)	ν(M—N)
1.	—	3220(s)	1620(s)	—	1065(s)	—	—
2.	3550(m),1640(w),750(d)	—	1580(m)	1545(m)	1010(s)	520(s)	415(m)
3.	3580(m),1650(m),750(s)	—	1580(s)	1575(m)	1030(s)	525(s)	400(m)
4.	3560(m),1620(s),750(s)	—	1580(s)	1505(m)	1015(s)	525(s)	415(s)
5.	3600(m),1610(m),750(s)	—	1575(m)	1505(m)	1020(s)	525(s)	420(s)
6.	—	3220(s)	1595(s)	—	1025(s)	—	—
7.	3560(s),1610(m),760(s)	—	1590(s)	1560(s)	1025(s)	535(s)	390(m)
8.	3550(m),1600(m),750(s)	—	1580(s)	1560(s)	1020(s)	530(s)	410(m)
9.	3560(s),1600(m),745(s)	—	1580(s)	1515(s)	1020(s)	530(s)	415(s)
10.	3575(s),1610(m),755(s)	—	1580(s)	1515(s)	1020(s)	535(s)	420(s)
11.	3580(w),1610(m),740(s)	—	1590(s)	1555(s)	1030(s)	525(s)	410(m)
12.	—	3240(s)	1600(s)	—	1030(s)	—	—
13.	3550(m),1645(m),755(s)	—	1595(s)	1575(s)	1035(s)	525(s)	425(m)
14.	—	—	1590(s)	1545(s)	1030(m)	530(s)	445(m)
15.	—	—	1585(s)	1555(w)	1030(s)	530(s)	410(m)
16.	3580(m),1610(m),755(s)	—	1585(s)	1555(w)	1030(s)	530(s)	420(s)
17.	3610(m),1645(m),760(s)	—	1590(s)	1570(m)	1035(s)	535(s)	445(m)
18.	—	3260(s)	1610(m)	—	1015(s)	—	—
19.	3550(m),1610(s),750(s)	—	1595(s)	1535(s)	1020(m)	530(s)	420(s)
20.	—	—	1600(s)	1530(s)	1030(s)	540(s)	435(s)
21.	3600(s),1620(s),760(s)	—	1600(m)	1525(s)	1040(s)	525(s)	425(s)
22.	3580(m),1600(s),780(s)	—	1590(s)	1540(m)	1020(s)	530(s)	425(m)

Abbreviations: w = weak, m = medium, s = sharp, d =doublet.

band due to ν(C—Cl) is observed at *ca.* 800 cm^{-1} in fcbH and mbcbH and at *ca.* 2820 cm^{-1} due to $\nu(CH_3)$ of methoxy group in mbcbH, mbsH practically remains unaltered on their metal complexes indicating their non-involvement in coordination.

Diffused Reflectance Spectral Studies

Cobalt(II) Complexes

Under the influence of the octahedral field the ground state ^4F of Co(II) ion splits up into three levels. The three spin-allowed transitions for octahedral Co(II) complexes are expected which may be assigned as:

$$\nu_1 = {}^4T_{1g} \rightarrow {}^4T_{2g}(F),\ \nu_2 = {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \text{ and } \nu_3 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$$

Since the transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ is essentially a 2-electron transition from $t_{2g}^5eg^2$ to $t_{2g}^3eg^4$ it is expected to be weak by about a factor of 10^{-2} than the other transitions. It is not observed in most of the cases but can be calculated. In the drs of Co(II) complexes these bands occur at 11363 cm^{-1}, 23809 cm^{-1} for fcbH and 10869 cm^{-1}, 24390 cm^{-1} for mbcbH chelating ligands respectively. However, the complex formed with mbsH exhibits one band at 14705 cm^{-1} and the other one at near infrared which could not be located. The ligand field parameters are calculated and shown in Table 3. The energy ratio ν_2(Calcd)/ν_1 (obsd) lies in the range 2.1–2.2 for octahedral complexes. The ratio is found well within the range for three Co(II) complexes and assigned octahedral geometry.

TABLE 3

LIGAND FIELD PARAMETERS OF COMPLEXES

Complex	10 Dq (cm^{-1})	B′ (cm^{-1})	β	β°(%)	ν_2(cm^{-1})	ν_2/ν_1[a] $\sigma_1\sigma_2$[b]
Co(II)–fcbH	11363	829.50	0.854	14.57	22726	2.00[a]
Co(II)–mbcbH	12292	996.26	1.020	2.60	23161	2.10[a]
Ni(II)–fcbH	11363	411.26	0.389	61.05	18518	1.62[a]
Ni(II)–mbcbH	10869	565.30	0.535	46.46	18518	1.70[a]
Cu(II)–mbcbH	6270	—	—	—	—	1.11[b]
Cu(II)–fsH	4009	—	—	—	—	—

Nickel(II) Complexes

Ni(II) ion splits in an octahedral field to exhibit three bands assigned as :

$$\nu_1 = {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) = 10\ Dq,\ \nu_2 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \text{ and}$$

$$\nu_3 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$$

Ni(II) complexes of fcbH and mbcbH show three transition bands in about the same range as expected for octahedral complexes and are observed at 11363, 18518 and 24390 cm^{-1} for fcbH and at 10869, 18518 and 25000 cm^{-1} for mbcbH complexes. The value of ν_2/ν_1 ratio which is found to be 1.62 and 1.70 fcbH and mbcbH complexes, respectively, provides an additional support to the octahedral geometry of complexes[35]. Nickel(II) complexes formed by mbsH and fsH are different, they are diamagnetic and exhibit square planar geometry. Diamagnetism is a consequence of eight electrons being paired in the four lower lying d orbitals. If a monodentate ligand is used, the upper orbital is $x^2 = y^2(b_{1g})$. In case of bidentate ligand, the upper orbital is $xy(b_{2g})$. The four lower orbitals are often so close together in energy that individual transitions from these orbitals to the upper d level cannot be distinguished, hence a single absorption band is expected. Therefore, it is assumed that for monodentate ligands, empty orbital is $x^2 - y^2(b_{1g})$ and for other $xy(b_{2g})$. Thus E_g, B_{2g} and A_{2g} are three excited states and the following transitions are expected for square planar Ni(II) complexes:

$$^1A_{1g} \rightarrow {}^1B_{2g}(^1B_{1g}),\ ^1A_{1g} \rightarrow {}^1A_{2g} \text{ are } ^1A_{1g} \rightarrow {}^1E_g$$

Square planar complexes typically have a single band at 17000–22000 cm^{-1}, which corresponds to the yellow to blue region of spectra and hence is responsible for the reddish colour. A second more intense band near the ultraviolet region observed around 23000–30000 cm^{-1} is often charge transfer in origin.

Ni(II) complexes of mbsH and fsH orange in colour and show bands within the above quoted range at 19230 cm^{-1} and 18518 cm^{-1} respectively, which is consistent with square planar geometry in each case. The complexes are found to be diamagnetic, which further complements square planar geometry.[36,37]

Copper(II) Complexes

The bivalent copper has a ^2D ground state which splits into two terms under the influence of an octahedral field.[38,39] Cu(II) ion is characterised by large distortions from octahedral symmetry and the band is unsymmetrical. The Jahn-Teller effect leads to appreciable tetragonal distortion of copper(II) complexes in general, they are regarded as distorted octahedral or approximately square planar complexes. Undistorted octahedral complexes of Cu(II) are rare. The majority of Cu(II) complexes are blue or green because of a single absorption band in the region 11000 to 16000 cm^{-1}. Owen[40] has given the following expressions, for the three transitions, which may be expected for distorted octahedral geometry in rare cases.

$$\sigma_1 = \frac{10}{21}K + \frac{2}{7}T_2 + \frac{20}{105}T_4; \ \sigma_2 = \frac{10}{21}K + \frac{8}{7}T_2 + \frac{20}{105}T_4 \text{ and}$$

$$\sigma_3 = \frac{8}{7}T_2 + \frac{40}{105}T_4$$

These values correspond to the transitions,

$$^2B_{1g} \rightarrow {}^2A_{1g},\ {}^2B_{1g} \rightarrow {}^2B_{2g} \text{ and } {}^2B_{1g} \rightarrow {}^2E_g$$

The value of K can be evaluated by the expression 10 Dq = K/2.1, using the above equations. The metal complexes formed by fcbH and mbcbH are consistent with the distorted octahedral geometry as shown by the bands observed in each case. Their respective positions are: a weak band at 17241 and a sharp one at 10638 for fcbH; 18518, 16666 and 14285 for mbcbH and at 17241, 14705 and 12500 cm^{-1} for mbsH complexes. The three bands observed in the latter complexes may be assigned to the transitions as shown above. However, the complexes formed by mbsH, fsH exhibit a single broad band corresponding to the transition $^2E_g \rightarrow {}^2T_{2g}$. This is observed at 14705 cm^{-1} which may be due to the distortion of the Cu(II) complexes enveloping smaller bands. The ratio σ_1/σ_2 is close to 1.0 in all the complexes supporting octahedral geometry.

Magnetic Susceptibility Measurements

The measurements were carried out at 5, 10 and 15 amp current and the detailed data are incorporated in Table 4. The Co(II) complexes formed by fcbH, mbcbH and mbsH in the present studies are subjected to magnetic susceptibility measurements and their respective magnetic moments are found to be 4.93, 4.82 and 4.72 B.M., indicating spin free octahedral nature. The magnetic moments of Ni(II) octahedral complexes generally lie between 2.9 and 3.4 B.M., depending on the magnitude of the orbital contribution. The μ_{eff} values are found to be 2.91 and 3.05 B.M. respectively for fcbH and mbcbH complexes which is typical of octahedral Ni(II) ion. Contrary to them, Ni(II) complexes formed with mbsH and fsH are diamagnetic which compliments square planar geometry. The observed magnetic moments of Cu(II) complexes formed with fcbH, mbcbH, mbsH and fsH are 1.84, 1.86, 1.86 and 1.90 B.M., respectively which lie within the range 1.73–2.2 B.M. and is in consonance with octahedral geometry.

The high-spin d^5 configuration of Mn(II) gives an essentially spin only magnetic moment of *ca.* 5.9 B.M. Since complexes have orbitally non-degenerate ground term, spin only magnetic moment independent of temperature is expected. The magnetic moments of the complexes in above order of the ligands are found to be 5.94, 5.98, 5.85 and 6.02 B.M.

respectively, which is in the expected range of high-spin octahedral Mn(II) complexes.

TABLE 4

MAGNETIC SUSCEPTIBILITY MEASUREMENT DATA OF THE COMPLEXES AT 0, 5, 10, 15 AMP CURRENT

Complex	χ_{g1} $\times 10^{-6}$	χ_{g2} $\times 10^{-6}$	χ_{g3} $\times 10^{-6}$	Mean $\times 10^{-6}$	χ_m $\times 10^{-6}$	μ_{eff} B.M.
Co(II)–fcbH	15.4	13.5	20.3	16.4	9704.1	4.93 5.00*
Co(II)–mbcbH	31.0	14.8	13.1	(13.9)	9312.1	4.82 4.75*
Co(II)–mbsH	14.1	15.0	14.1	14.4	8595.9	4.62
Ni(II)–fcbH	4.1	5.7	6.7	5.5	3262.1	2.91 2.85*
Ni(II)–mbcbH	5.6	6.0	4.3	5.3	3549.9	3.05
Cu(II)–fcbH	0.7	3.1	14.9	(1.9)	1129.6	1.81
Cu(II)–mbcbH	1.1	1.7	2.3	1.7	1146.7	1.86
Cu(II)–mbsH	0.9	1.8	2.7	1.8	1147.5	1.83
Cu(II)–fsH	0.7	3.5	2.7	2.3	1282.3	1.89
Mn(II)–fcbH	26.5	23.7	22.9	24.4	14296.9	5.94
Mn(II)–mbcbH	20.3	20.9	23.8	21.7	14450.8	5.98
Mn(II)–mbsH	20.8	22.9	22.2	22.0	13836.6	5.85
Mn(II)–fsH	26.0	28.3	27.0	27.1	14876.2	6.05

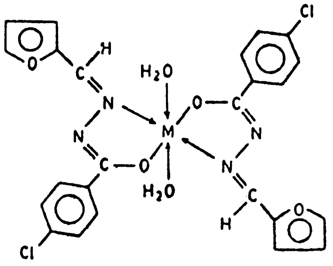
Note 1. Values in parentheses are the mean of two χ_g values

2. *denotes the values obtained by Faraday's method; other values are obtained by Gouy's method:

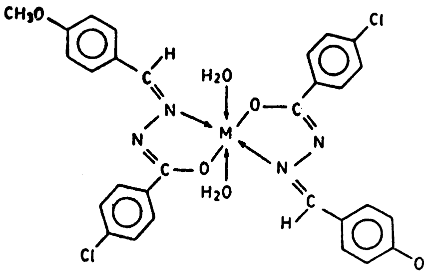
Thermogravimetric Studies

The association of two molecules of water within coordination sphere of the metal is further supported by thermogravimetric data. The observed percentage weight loss of 5.80, 5.92, 6.25 and 6.27 are approximately equal to the calculated values of 6.14, 6.10, 6.10 and 6.05 for Mn(II), Co(II), Ni(II), Cu(II) fcbH complexes respectively. This weight loss occurs between temperature range of 120–320°C, corresponding to the presence of two water molecules. Similarly Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mbcbH complexes show 5.20, 5.31, 5.14, 5.39 and 5.39 percentage weight loss upto the temperature 320°C, which is almost equal to the calculated value of 5.40, 5.37, 5.37, 5.33 and 5.32 respectively. The loss of water molecules at quite a high temperature suggests that the water is present in coordinated form with the metal ion.[41,42] Similar TG data are obtained for other metal complexes having two molecules of coordinated water. Their thermal stabilities have also been investigated. The absence of water molecules in case of Co(II) and Ni(II) complexes of mbsH, Ni(II) complex of fsH and all the complexes of the chelating ligand fcbH is shown by the percentage weight loss which does not correspond to the calculated values. The order of thermal stability of the complexes has also been investigated.

Thus, the analytical data, spectral (ir and drs), magnetic and thermal data taken together focus upon the conclusion that fcbH and mbebH act as bidentate to yield octahedral metal complexes in 1 : 2 stoichiometry as shown below.

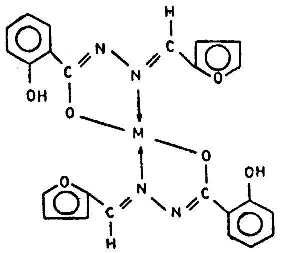


V Proposed structure of FCBH complexes
M : Mn, Co, Ni, Cu

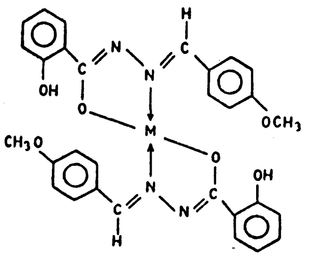


VI : Proposed structure of MBCBH complexes
M = Mn, Co, Ni, Cu, Zn

Similar conclusion is drawn for mbsH and fsH complexes except in few cases where they are 4-coordinate as indicated below:



VII : Proposed structure of FSH complexes M = Ni



VIII : Proposed structure of MBSH complexes M = Co, Ni

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