



Synthesis, Characterization and Thermal Decomposition Studies of Biologically Active Mixed Ligand Complexes Derived from Benzofuran-2-Carboxylic acid (2-Oxo-1,2-dihydro-indol-3-ylidene) Hydrazide and Acetylacetone, 1,10-Phenanthroline and 2,2'-Bipyridyl

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The mixed ligand complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with benzofuran-2-carboxylic acid (2-oxo-1,2-dihydro-indol-3-ylidene)-hydrazide and acetylacetone(acac), 1,10-phenanthroline(1,10-phen) and 2,2'-bipyridyl(2,2'-bipy) have been prepared. All complexes have the general formula. $MLL'X_n$, where $n = 2$, $X = Cl$ and L is the ligand prepared by the reaction of benzofuran-2-carboxy-hydrazide with isatin (indole-2,3-dione) and L' is the secondary ligand such as acetylacetone, 1,10-phenanthroline or 2,2'-bipyridyl. The complexes were characterized on the basis of elemental analysis, spectral, magnetic moment, conductance, X-ray diffraction and thermal decomposition studies. The ligand coordinates to the metal ions through the oxygen of the carbonyl group and the nitrogen of hydrazine group of the primary ligand (L). The probable geometry for all these complexes, have been assigned based on their physico-chemical data.

Key Words: Mixed ligand complexes, Synthesis, Spectral studies.

INTRODUCTION

Benzofuran compounds have created an interest to the chemists because, they occur in nature in a variety of structural forms which is a simple molecule such as 5-methoxy benzofuran to a very complicated molecules like morphine A and B. The seed oil "Egonoki" which is much common in Japan is known to contain a benzofuran derivative called "Egonal". It is an effective synergist for rotenone pyrethrum against house flies, mosquitoes, aphids and many other insects¹. Bakers yeast contains a benzofuran derivative, which acts as an antioxidant and prevents haemorrhagic liver necrosis in rats and haemolysis of red cells in vitamin deficient rats². Benzofurans and furanochromes are known to possess various pharmacological properties³. Khellin a furanochromone is well known for its physiological activity⁴.

Spath and Gruber⁵ have reported that Khellin has a selective antispasmodic effect upon the urater, bronchial muscles, gall bladder and bile duct. Khellin is found to be a potent coronary vasodilator⁶, inhibits gastric ulcers and intestinal activity⁷. It is also useful in the treatment of heart diseases and whooping cough.

The survey of literature on benzofuran compounds reveals the fact that they are biologically and industrially much important and good chelating agents, with many analytical applications both in qualitative and quantitative analysis.

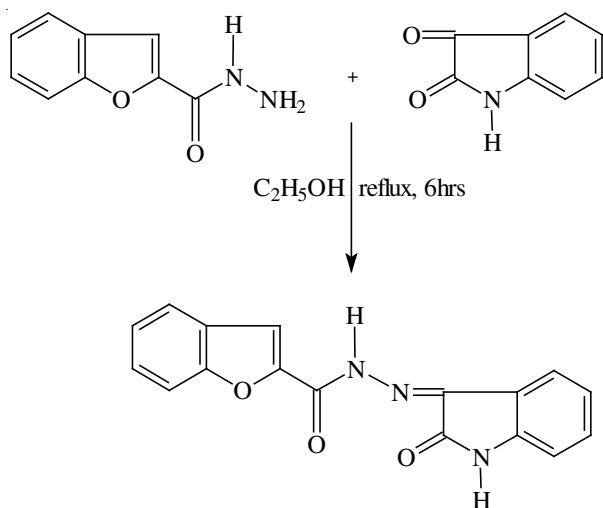
In view of biological importance of the benzofuran derivatives, it is worthwhile to synthesize the mixed ligand complexes derived from the benzofuran Schiff's base as primary ligand obtained by the reaction between benzofuran-2-carbohydrazide and isatin (indole-2,3-dione) [BFIDOPMC] and secondary ligand such as acac, 1,10-phenanthroline and 2,2'-bipyridyl with metal ions such as Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II).

The metal complexes synthesized were characterized on the findings of elemental analysis, conductance, IR, ¹H NMR, ESR, electronic spectra, magnetic property, X-ray diffraction and thermal decomposition studies.

EXPERIMENTAL

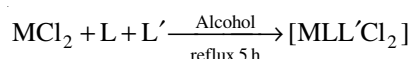
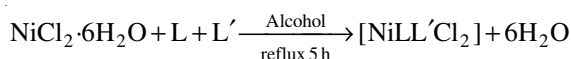
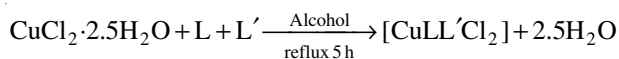
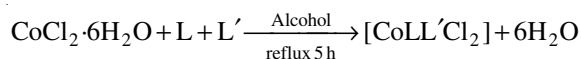
All the chemicals used were of analytical grade benzofuran-2-carboxyhydrazide was prepared by the literature methods⁸. The estimation of metal and chloride were done by standard method⁹.

Preparation of benzofuran [indole-2,3-dione phenylmethine]carbohydrazone [BFIDOPMC]: A mixture of benzofuran-2-carbohydrazone (0.1 mol) and isatin (indole-2,3-dione) (0.1 mol) in ethanol (30 mL) were refluxed on water bath for *ca.* 6 h in presence of few drops of glacial acetic acid. The product which was separated was filtered out on cooling to room temperature washed with alcohol and crystallized from alcohol. m.f. $C_{17}H_{11}N_3O_3$, m.p. 252 °C, yield (%) 70 %, m.w. 305.



Synthesis of ligand [benzofuran[indole-2,3-dione phenylmethine]carbohydrazone]

Preparation of mixed ligand complexes with benzofuran[indole-2,3-dione phenylmethine]carbohydrazone and secondary ligands: The ligand benzofuran[indole-2,3-dione phenylmethine]carbohydrazone (0.1 mol) and secondary ligand such as acetyl acetone (acac) or 1,10-phenanthroline (1,10-phen) or 2,2'-bipyridyl (2,2'-bipy), were mixed with alcoholic solution of respective metal salts (0.1 mol) in 1:1:1 molar ratio. The reaction mixtures were refluxed on water bath for *ca.* 5 h. The reaction mixture was concentrated and cooled to room temperature; separated light coloured complexes were filtered out, washed with alcohol and water successively then dried over anhydrous $CaCl_2$. The formation of the mixed ligand complexes is represented by the following equations.



where $M = Cd, Zn$ or Hg , $L = BFIDOPMC$ and $L' = acac$ or 1,10-phen or 2,2'-bipy.

The magnetic susceptibility of the complexes was determined by Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant at room temperature. The IR spectra were recorded on Perkin-Elmer 783-FTIR model IR spectrophotometer in the range of 4000-350 cm^{-1} in KBr pellets. The electronic spectra of Co(II), Cu(II) and Ni(II) complexes in DMF (10^{-3} M) solution were

recorded using Elico UV-visible spectrophotometer in the range of 200-1100 nm. The molar conductances were carried out on Equiptronic conductivity bridge type EQ-667 provided with a dip type conductivity cell fitted with platinum electrode. FAB mass spectra were recorded on Jeol-SX 102/DA-6000 mass spectrophotometer using Argon 6 KV, 10 mA as the FAB gas, *m*-nitrobenzyl alcohol was used as matrix and spectra were obtained from CDRI Lucknow. Thermogravimetry (TG) and differential thermal analysis (DTA) studies were made for some of the complexes in the range of 28-800 °C temperature with heating rate of 10 °C/min in nitrogen atmosphere on Perkin-Elmer thermal analyzer. Thermal data were collected from STIC-Cochin University, Kochi.

RESULTS AND DISCUSSION

All the mixed ligand complexes are generally non-hygroscopic, stable solids, insoluble in water with varying solubility in common organic solvents and completely soluble in DMF, DMSO and pyridine and stable at least upto 180 °C indicating a strong metal ligand bond. The analytical data of the complexes show that the complexes of the type $MLL'Cl_2$, where L is [BFIDOPMC] and L' is the secondary ligand, such as acac, 1,10-phen or 2,2'-bipy, where M is bivalent metal ion. The observed molar conductance values for the complexes fall in the range 10-25 $ohm^{-1} cm^2 mol^{-1}$. These values are too low to account for any electrolytic behaviour of the complexes. Therefore, they may be regarded as non-electrolytic in nature¹⁰.

The mixed ligand complexes of $[Co(BFIDOPMC)(acac)Cl_2]$, $[Co(BFIDOPMC)(1,10-phen)Cl_2]$ and $[Co(BFIDOPMC)(2,2'-bipy)Cl_2]$ shows magnetic moments 4.89, 4.85 and 5.05 BM (Table-1), respectively at room temperature. Usually Co(II) complexes in an octahedral environment are orbitally degenerate, this causes an orbital angular momentum contribution to the magnetic moment and experimental magnetic moment values lie between spin only $\mu_{SO} = [4S(S+1)]^{1/2} = 3.88$ BM and $\mu_{S+L} = [4S(S+1) + L(L+1)]^{1/2} = 5.2$ BM. The present values lying in the range between μ_{SO} and μ_{S+L} suggesting octahedral geometry around Co(II) ion^{11,12}. The measured magnetic moments at room temperature for the Ni(II) complexes are in the range 3.05-3.55 BM. In almost all its six coordinated complexes Ni(II) has an octahedral stereochemistry with spin triplet ground state in high spin configuration. The magnetic properties¹³ of copper(II), are in the range 1.87-1.92 BM suggesting the distorted octahedral geometry.

Electronic spectra: The electronic spectra of Co(II) complexes exhibit two absorption bands in the region 15856-16298 and 19875-20735 cm^{-1} in DMF (10^{-3} M) solutions. These two bands can be assigned to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transition, respectively, in an octahedral geometry^{14,15}. However, the ν_1 band could not be observed due to limited range of the instrument and these values were calculated using band fitting procedure¹⁶ are found to be in the range of 7295-7448 cm^{-1} . The spectral band positions in DMF solution are presented in the Table-2. The ligand field parameters Dq , B' , β , $\beta\%$, ν_2/ν_1 ratio and LFSE have been calculated by using the equation derived from Secular determination^{17,18} and are given in the Table-2. All these data suggestive of octahedral geometry for Co(II) complexes.

TABLE-1
ANALYTICAL, MOLAR CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA OF
MIXED LIGAND COMPLEXES OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II)

Ligand/complexes	m.w.	m.p. (°C)	Analysis % found/(calcd.)					μ_{eff} (BM)	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	M	Cl		
BFIDOPMC.acac C ₂₂ H ₁₉ O ₅ N ₃	405.120	–	64.92 (65.16)	4.23 (4.66)	10.12 (10.30)	–	–	–	–
[Co(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	535.243	>300	49.16 (49.37)	3.29 (3.58)	7.62 (7.85)	10.86 (11.00)	13.10 (13.25)	4.89	13.35
[Ni(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	535.003	315	49.13 (49.39)	3.31 (3.58)	7.62 (7.85)	10.78 (10.97)	13.09 (13.25)	3.55	11.55
[Cu(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	539.855	309	48.64 (48.95)	3.32 (3.55)	7.57 (7.78)	11.52 (11.77)	12.82 (13.13)	1.90	12.21
[Zn(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	541.699	320	48.65 (48.79)	3.12 (3.54)	7.54 (7.75)	11.89 (12.07)	12.86 (13.11)	–	18.95
[Cd(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	588.720	338	44.52 (44.78)	3.12 (3.25)	6.89 (7.14)	18.89 (19.09)	11.91 (12.04)	–	17.09
[Hg(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	676.899	345	38.72 (39.01)	2.65 (2.83)	6.05 (6.21)	29.22 (29.63)	10.21 (10.48)	–	19.52
BFIDOPMC.1,10-phen C ₂₉ H ₁₉ O ₃ N ₅	485.000	–	71.54 (71.75)	3.78 (3.91)	14.21 (14.43)	–	–	–	–
[Co(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	614.930	350	56.32 (56.61)	2.92 (3.11)	11.16 (11.38)	9.23 (9.58)	11.25 (11.52)	4.85	18.32
[Ni(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	615.092	350	56.28 (56.63)	2.89 (3.11)	11.05 (11.39)	9.32 (9.54)	11.19 (11.53)	3.05	16.25
[Cu(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	619.945	310	55.92 (56.18)	2.83 (3.09)	11.09 (11.30)	10.06 (10.25)	11.17 (11.44)	1.92	10.85
[Zn(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	621.789	295	55.89 (56.02)	2.78 (3.08)	11.12 (11.26)	10.23 (10.52)	11.15 (11.40)	–	14.02
[Cd(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	668.110	335	51.79 (52.08)	2.63 (2.86)	10.35 (10.47)	16.78 (16.81)	10.31 (10.60)	–	19.52
[Hg(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	756.989	350	45.72 (46.01)	2.23 (2.53)	9.01 (9.25)	26.32 (26.50)	9.08 (9.37)	–	24.50
BFIDOPMC.2,2'-bipy C ₁₇ H ₁₉ O ₃ N ₅	461.190	–	69.82 (70.25)	3.96 (4.11)	14.96 (15.17)	–	–	–	–
[Co(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	591.311	350	54.58 (54.84)	3.08 (3.24)	11.46 (11.84)	9.51 (9.97)	11.82 (12.00)	5.05	16.69
[Ni(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	591.071	315	54.55 (54.86)	3.12 (3.24)	11.51 (11.85)	9.71 (9.93)	11.79 (12.01)	3.32	17.51
[Cu(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	595.923	335	54.12 (54.42)	3.04 (3.21)	11.54 (11.75)	10.37 (10.66)	11.59 (11.75)	1.87	18.82
[Zn(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	597.767	298	54.09 (54.25)	2.96 (3.20)	11.43 (11.72)	10.41 (10.94)	11.51 (11.86)	–	20.25
[Cd(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	644.788	300	50.01 (50.29)	2.68 (2.97)	10.59 (10.86)	17.29 (17.43)	10.89 (11.01)	–	17.32
[Hg(C ₁₇ H ₁₉ O ₃ N ₅)Cl ₂]	732.967	350	44.11 (44.24)	2.35 (2.61)	9.27 (9.55)	27.19 (27.37)	9.29 (9.67)	–	19.56

TABLE-2
ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF Co(II), Ni(II)
AND Cu(II) MIXED LIGAND COMPLEXES IN DMF (10⁻³ M) SOLUTION

Complexes	Transitions (cm ⁻¹)			Dq (cm ⁻¹)	B' (cm ⁻¹)	β	β (%)	v ₂ /v ₁	LFSE (k cal)
	v ₁ *	v ₂	v ₃						
[Co(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	7448	16298	20735	885	954	0.953	4.737	2.188	15.17
[Co(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	7376	15856	20145	848	925	0.952	4.735	2.149	14.53
[Co(C ₂₇ H ₁₉ O ₃ N ₅)Cl ₂]	7295	15675	19875	838	911	0.938	6.179	2.148	14.36
[Ni(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	10210	16125	25771	1021	750	0.721	27.880	1.579	35.00
[Ni(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	10260	16165	25758	1026	742	0.714	28.650	1.575	35.17
[Ni(C ₂₇ H ₁₉ O ₃ N ₅)Cl ₂]	10360	16255	25815	1036	731	0.703	29.710	1.569	35.52
[Cu(C ₂₂ H ₁₉ O ₅ N ₃)Cl ₂]	13053-17685			1520	–	–	–	–	26.14
[Cu(C ₂₉ H ₁₉ O ₃ N ₅)Cl ₂]	12392-18105			1585	–	–	–	–	27.17
[Cu(C ₂₇ H ₁₉ O ₃ N ₅)Cl ₂]	13652-16785			1510	–	–	–	–	25.88

*Calculated values.

The electronic spectra of hexa coordinated Ni(II) complex exhibits two bands in the region 16125-16255 and 25758-25815 cm^{-1} in DMF solution. The transitions are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. These bands are characteristic of octahedral geometry. However ν_1 band can be calculated using band fitting procedure and found to be in the range 10210-10360 cm^{-1} . The ligand field parameters have been calculated according to the Under Hill and Billing¹⁷ which supports the octahedral geometry of Ni(II) complexes.

The Cu(II) complexes exhibit a single broad asymmetric band in the region 12392-13652 cm^{-1} the asymmetry being in the lower energy side. These observations suggest that all the complexes have tetragonally distorted octahedral structure. The broadness of the band may be due to dynamic Jahn-Teller distortion.

ESR spectra: The ESR spectrum of the Cu(II) complexes at room temperature displayed a poorly resolved broad asymmetric signal with Hamiltonian parameters range $g_{\parallel} = 2.1322$ - 2.2072 and $g_{\perp} = 2.0319$ - 2.0452 . These values are in agreement with values for distorted octahedral structure¹⁸ with no hyperfine splitting in the parallel features. It is difficult to interpret quantitatively this broad band. The exchange interaction parameters G in all the complexes are less than 4, indicating that, the absence of copper-copper exchange coupling interaction between copper(II) centers in the solid state.

Infrared spectra: The important IR stretching frequencies of the IR spectra of the free ligand [BFIDOPMC] and its mixed ligand complexes with acac, 1,10-phen or 2,2'-bipy, secondary ligand are taken in KBr pellets. A common feature of the IR spectra of the free ligand exhibited a broad band at 3234 and 3185 cm^{-1} due to $\nu(\text{NH})$ stretching vibrations of indole moiety and due to amide group, respectively.

In case of all the metal complexes, these bands remains almost unaffected indicating non-involvement of 'N' of indole ring in bonding to metal ions.

The band due to $\nu(\text{C}=\text{O})$ stretching vibrations in free ligand appeared at 1700 and 1678 cm^{-1} are due to $\nu(\text{C}=\text{O})$ in indole moiety and amide, respectively. The indole ($\text{C}=\text{O}$) remains unaffected indicating non-involvement of oxygen of $\nu(\text{C}=\text{O})$ ring in bonding to metal ion. The $\nu(\text{C}=\text{O})$ due to amide, band is shifted to lower frequency side in all the complexes and appears in the region 1665-1619 cm^{-1} in the spectra of complexes, indicating the coordination of oxygen atom of carbonyl group^{19,20}.

The $\nu(\text{C}=\text{N})$ stretching vibrations due to isatin moiety is observed at 1600 cm^{-1} in free ligand. In case of all the metal complex these bands shifts to lower frequency side and appears in the region 1585-1575 cm^{-1} . The shift towards lower frequency about 15-25 cm^{-1} indicating the bonding of the nitrogen of ($\text{C}=\text{N}$) ring²¹.

In view of the earlier reports²², in present study the band observed at 1110 cm^{-1} is assigned to $\nu(\text{N}-\text{N})$ stretching vibration of the hydrazine residue. This band shifted to higher wave number side in the case of complexes indicating involvement of one of the nitrogen atom in bonding to metal ion²³.

The ring $\nu(\text{C}=\text{N})$ stretching vibration, of secondary ligand 1,10-phenanthroline, 2,2'-bipyridyl is observed around 1645

cm^{-1} . In the metal complexes this band is observed in the region 1538-1591 cm^{-1} , shift towards lower wave number side, suggesting coordination through ring nitrogen to the metal ion²⁴⁻²⁶ in all the complexes.

The vibrational frequencies of $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{Cl})$ bands for the complexes can be carefully assigned in far-IR region. The appearance of a new set of bands in the case of all the complexes under study due to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ vibrations are the direct evidence for complexation. In most of the reports²⁷ the higher absorption values are reported for $\nu(\text{M}-\text{O})$ vibration than the $\nu(\text{M}-\text{N})$ vibration.

The weak to medium intensity bands in the region 565-510 and 473-416 cm^{-1} in the spectra of the metal complexes may be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibration, respectively. It may be noted that these bands are not present in the spectra of the ligand. The broad and weak intensity bands observed in the region 390-360 cm^{-1} are assigned to $\nu(\text{M}-\text{Cl})$ stretching vibrations in view of the earlier reports.

${}^1\text{H}$ NMR spectrum: ${}^1\text{H}$ NMR spectrum of the primary ligand BFIDOPMC gave characteristic signal at δ 11.35 (s, 1H) for the amide proton as a singlet. The signal due to NH proton of the indole ring is observed at δ 9.75 (s, 1H). The nine aromatic proton signals are observed in the range δ 6.75-7.85 (m, 9H) as multiplet.

The signals due to amide proton CONH in the primary ligand appeared at δ 11.35 and these signals shifted to down field in the spectra of Zn(II) and Cd(II) complexes and appear at δ : 11.80 and 11.95, this indicates the coordination of primary ligand through oxygen atom of CONH group.

FAB Mass: The FAB mass spectrum of ligand BFIDOPMC shows a molecular ion peak at m/z 306, 307 which is equivalent to its molecular weight. The molecular ion on subsequent loss of H_2O gave rise to a intense peak at m/z 289 (75 %). The loss of one of the aromatic moiety has taken place giving rise to a fragment ions at m/z 218 (85 %) and m/z 215 (75 %). This fragmentation pattern supports the structure of the ligand.

X-Ray powder diffraction: The X-ray diffraction pattern of the primary ligand BFIDOPMC, shows six reflections in the range 5-75° (2θ). The interplanar distance 'd' calculated from the positions of the peak. All important peaks have been indexed and observed values of interplanar distance were compared with the calculated one. The unit cell calculations have been made for cubic symmetry of the ligand. The characteristic of the cubic system is that $\sin^2 \theta$ values have common factor²⁸. The cell parameter have been calculated using equation,

$$\sin^2 \theta = \left[\frac{\lambda^2 (h^2 + k^2 + l^2)}{4a^2} \right]$$

where $\lambda^2/4a^2$ is common factor. There is no presence of forbidden peaks indicates the cubic system of the primary ligand.

X-Ray powder diffraction of [Cu(BFIDOPMC acac)Cl₂], [Cd(BFIDOPMC)bipy)Cl₂] (Fig. 1) and [Cu(BFIDOPMC)bipy)Cl₂] have been taken. The 2θ values with maximum intensity of peak for the compounds were found to be 11.4564°, 10.8662° and 11.10590° (2θ) values corresponding to d: 7.7174, 8.1355 and 7.9602 Å, respectively. In all the spectra there is forbidden peaks such as 15, 23, 28, 31 *etc.*, indicate the absence of cubic system in these complexes.

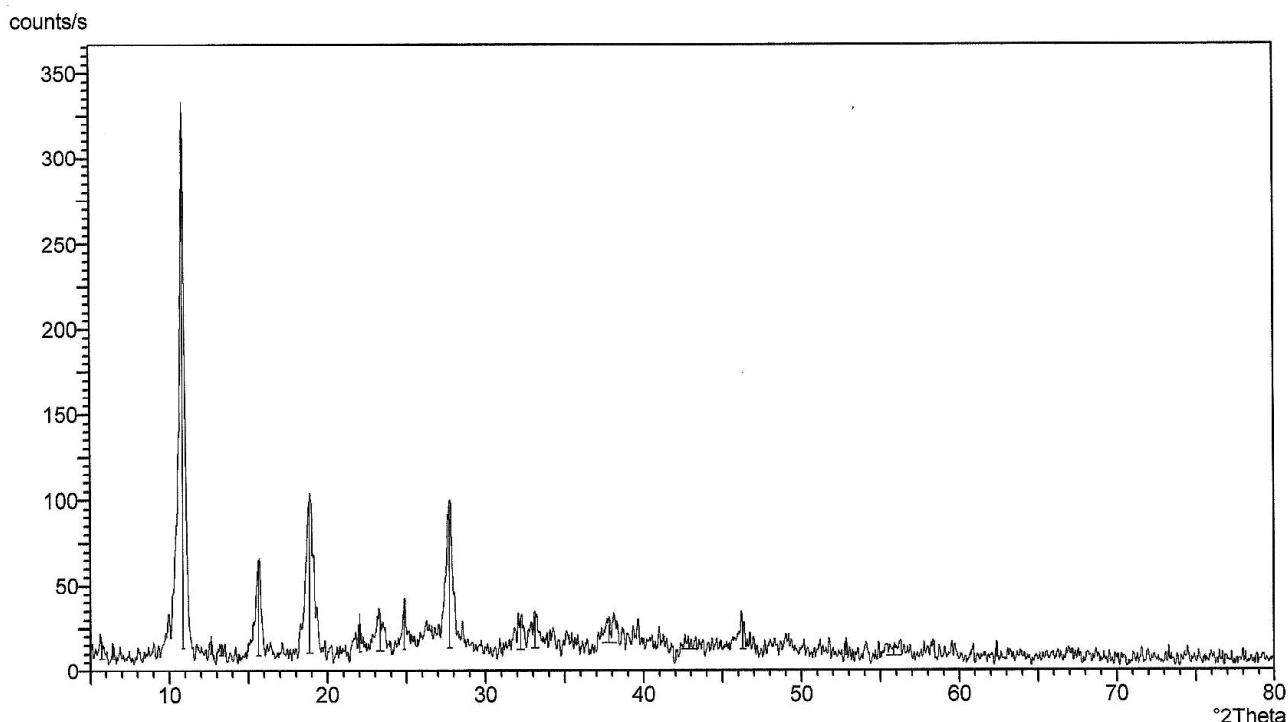
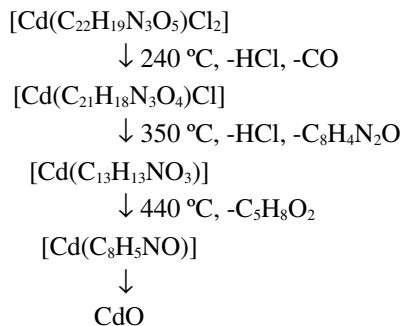


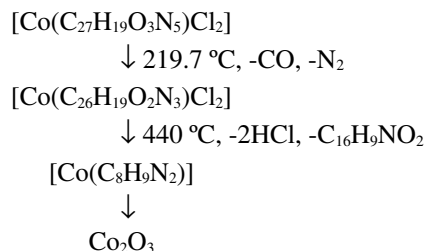
Fig. 1. Powder X-ray diffraction spectrum of Cd(II) complex of the ligand [BFIDOPMC bipy]

Thermal analysis: The $[\text{Cd}(\text{BFIDOPMC acac})\text{Cl}_2]$ is thermally decomposed in three successive decomposition steps. The first estimated weight loss of 10.80 % corresponds to loss of one HCl and one CO molecule at the temperature 240 °C. This observed weight loss of 10.80 % is in accordance with the theoretical weight loss 10.86 %. In the second step the complex underwent further decomposition and gave another break at 350 °C with a weight loss of 35.38 % which corresponds to the decomposition of the complex to expel one molecule of HCl and $\text{C}_8\text{H}_4\text{N}_2\text{O}$. The practical weight loss 35.38 % is in accordance with the theoretical weight 34.32 %. The third inflection occurred at 440 °C with weight loss 28.52 % which corresponds to the loss of $\text{C}_5\text{H}_8\text{O}_2$ species. Finally the compound showed a gradual decomposition upto 800 °C and onwards. The thermal decomposition data of Cd(II) complex with probable assignments given as below.

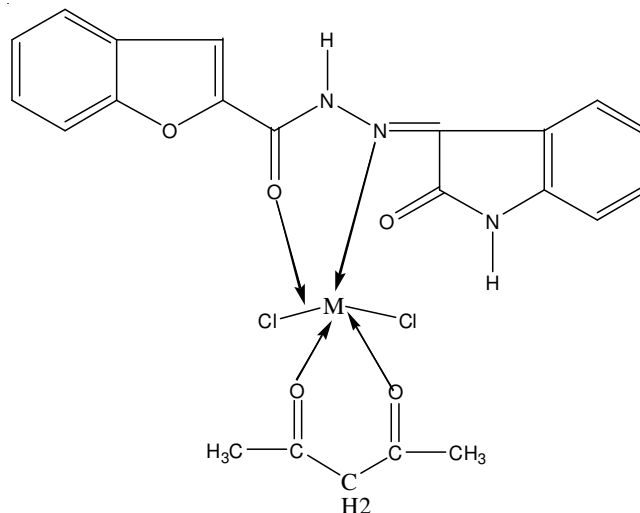


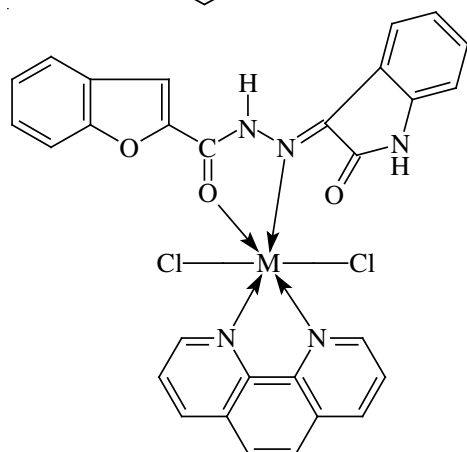
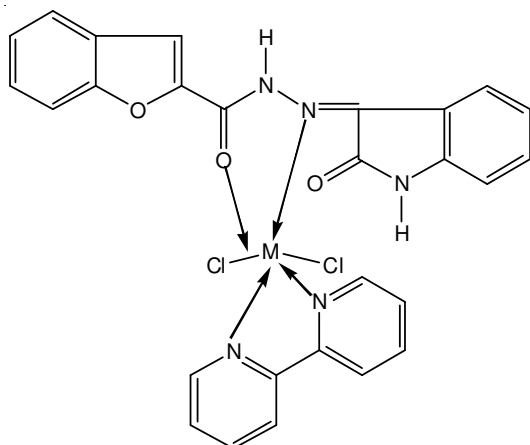
The $[\text{Co}(\text{BFIDOPMC bipy})\text{Cl}_2]$ complex is thermally decomposed in two successive stages. The first stage estimated weight loss 8.77 % corresponds to loss of one CO and one N_2 molecule at 219.7 °C. This practical weight loss is in accordance with the theoretical weight loss of 9.47 %. In second step the complex undergone further decomposition and gave another peak at 440 °C with weight loss of 58.78 % which corresponds

to the decomposition of complex to expel 2HCl and $\text{C}_{16}\text{H}_9\text{NO}_2$ species. The practical weight loss of 58.78 % is in accordance with theoretical weight loss of 59.61 %. Finally compound showed a gradual decomposition up to 750 °C and onwards. The weight of the residue corresponds to the formation Co_2O_3 . The decomposition pattern is as follows.



On the basis of these studies the structure of the complexes are assigned as follows:





where M = Co, Ni, Cu, Zn, Cd and Hg

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REFERENCES

- H. Mastubara, *Botyok Kogaku*, **19**, 15 (1954).
- M. Forbes, F. Zilliken, G. Robert and P. Gyorgy, *J. Am. Chem. Soc.*, **80**, 385 (1958).
- K.A. Thakur and N.R. Manjaranhar, *J. Indian Chem. Soc.*, **48**, 211 (1971).
- P.F. Wiley, *J. Am. Chem. Soc.*, **74**, 4329 (1952).
- Y. Kawase, M. Nakayama and P. Tamatskuri, *Bull. Chem. Soc. (Japan)*, **35** (1962).
- R.L. Farrand and S.M. Horwath, *Am. J. Physiol.*, **196**, 391 (1959).
- J.J. Desmeroz, *Comp. Rend. Soc., Biol.*, **149**, 1291 (1955); *Chem. Abs.*, **50**, 8107 (1956).
- N. Kawase, M. Yakayama and P.T. Tamatskuri, *Bull. Chem. Soc. (Japan)*, **35**, 149 (1962).
- A.I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, (Longman E.L.B.S. London) edn. 3 (1968).
- W.J. Geary, *J. Coord. Chem. Rev.*, **81**, 7 (1971).
- B.N. Figgis and J. Lewis, in ed.: F.A. Cotton, *In Prog Inorg. Chem.*, Interscience, New York (1967).
- N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth Heimemann, Oxford, edn. 2, 1132 (1997).
- D.W. Smith, *Inorg. Chem.*, **5**, 2236 (1966).
- J. Tian, Gao, E.Q. Liyt and S.X. Lin, *Synth. React. Inorg. Met-Org. Chem.*, **25**, 417 (1995).
- M.M. Mustafa, M.A. Kohattah and K.M. Ibrahim, *Polyhedron*, **2**, 585 (1983).
- A.E. Underhill and D.E. Billing, *Nature*, **210**, 390 (1991).
- C.J. Balhausen, *Introduction of Ligand Field Theory*, McGraw Hill Book Company, New York (1962).
- A.E. Underhill and D.E. Billing, *Nature*, **210**, 834 (1966).
- D.H. Sutaria, J.R. Patel and M.N. Patel, *J. Indian Chem. Soc.*, **73**, 309 (1996).
- J.-S. Huang, Q.-H. Wang, D.-L. Long and Y. Gui, *J. Coord. Chem.*, **49**, 201 (2000).
- K. Mohanan and S.N. Devi, *J. Indian Chem. Soc.*, **83**, 31 (2006).
- B. Singh and T.B. Singh, *J. Indian Chem. Soc.*, **38A**, 355 (1999).
- Marius Andru, M. Augutin, Madalan Damir, Pajie Nicolae and Stapiea, *Inorg. Chem. Acta* (2004).
- N. Raman, A. Kulandaswamy and K.J. Subramaniam, *Indian J. Chem.*, **41A**, 942 (2002).
- P.-Z. Zhang and W. Jun, *J. Indian Chem. Soc.*, **81**, 507 (2004).
- T. Ghosh, *J. Indian Chem. Soc.*, **81**, 957 (2004).
- N.S. Biradar and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).
- B.D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wiley Pub. Co. (1978).