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Synthesis, Characterization, Thermal and Biological Studies of Transitions Metal(II) Complexes with Primary ligand Benzofuran[3,4,5-trimethoxyphenylmethine] Carbohydrazone Schiff's base and Secondary ligand 1,10-Phenanthroline, 2-2^{l}-bipyridyl mixed ligand

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ABSTRACT

The new Mixed ligand complexes of the type MLL′.Cl_2 where M= Cu(II), Co(II), Ni(II), Zn(II),Cd(II) and Hg(II), L= primary ligand derived from Benzofuran [3,4,5–trimethoxyphenyl methine] carbohydrazone [BFTMeOPMC] and L^{l} = Secondary ligands 1, 10-phenantroline (pnthr) and 2,2′-bypyridyl,(bipy) were used. The coordination behavior of mixed ligand complexes have been characterized on the basis of Elemental Analysis, Conductance, Magnetic Susceptibility Measurements, UV-Vis, IR, ^{1}H-NMR and ESR Spectral Studies. Mixed ligands behave as coordinating through the oxygen of the carbonyl group and the nitrogen of the hydrazide group of primary ligand. Based on the results, we have proposed the probable structures for all the metal complexes. Both the Mixed ligands and their complexes have been screened for their biological activities.

Keywords: Benzofurantrimethoxyphenylmethine carbohydrazone, 1, 10-phenantroline and 2, 2′ bypyridyl, Metal(II) Complexes, Spectral Studies and Antimicrobial activities.

Introduction

Benzofuran compounds are abundantly distributed in nature, particularly among plant kingdom often such natural products possessing benzofuran nucleus are endowed with useful pharmacological properties. The enormous interest in synthetic products containing benzofuran nucleus has resulted in the development of benzofuran chemistry in a spectacular fashion during the last several years.

Mixed ligands complexes play an a major role in the storage and transport of additive substance through the membrane and the phenomenon strongly depend on the formation of such species and the nature of the metal ion involved[1]. So it is well known that mixed ligand complexes play a vital role in biological process in which enzymes are known to be activated by metal ions[2]. Mixed chelation appears in biological fluids as millions of potential ligands likely to complete for metal ions found in-vivo i.e., Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn and Mo.

In recent years ternary complexes have gained considerable importance because they provide good models for various biological reactions keeping many of these has been well recognized[3,4].

Mixed ligand complexes in which the metal is simultaneously bonded to two or more different complexing agents are formed in most solutions which contain metal ions and more than one

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kind of ligand and when there are two or more different metal ions present they may exhibit polynuclear complexes. The area of mixed ligand and homo/ hetro binuclear complexation has been extensive growth stimulated by interest in area such as metelloenzymes, homogeneous catalysis, electrical conductance and magnetic exchange processes[5,6].

The complexes in which a metal atom or ion is bound to two or more different ligands are known as mixed-ligand complexes. A mixed ligand complexes in which a metal is bound to two different ligands is called a ternary complexes. Thus a complex species MLL^{I} where L & L^{I} are two different ligands is a 1:1:1 ternary complex. Similarly complexes of the type $MLL^{I}L^{II}$ are quaternary complexes.

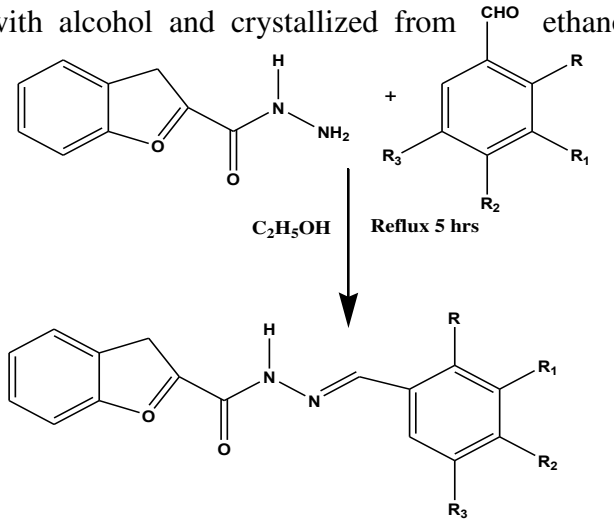
Experimental

All the reagents and solvents were analytical grade benzofuran -2- carbohydrazide was prepared by the literature methods[7]. 1, 10-phenantroline and 2, 2′-bypyridyl were obtained from BDH and used as received. The estimation of metal and chloride were done by standard method[8].

Preparation of Benzofuran [3,4,5–trimethoxyphenylmethine] carbohydrazone [BFTMeOPMC]

A mixture of benzofuran-2-carbohydrazide (0.1mole) and 3,4,5–trimethoxy benzaldehyde (0.1mole) in ethanol (30 ml) were refluxed on water bath for about 6 hrs in presence of few drops of glacial acetic acid. The product which was separated out, was filtered out, washed with alcohol and crystallized from ethanol.

M. P. 272°C, Yield 80%, M. W. 354, Molecular Formula $C_{19}H_{18}O_5N_2$



Synthesis of Primary ligand Benzofuran [3,4,5–trimethoxyphenylmethine] carbohydrazone

Preparation of mixed ligand complexes of Cu(II), Co(II), Ni(II), Zn(II), Cd(II),Hg(II) and Mn(II) with BFTMeOPMC and 1,10–phenanthroline / 2,2^{I} –bipyridyl

An alcoholic solution of BFTMeOPMC and 1,10–phenanthroline / 2,2^{I} –bipyridyl were mixed with alcoholic solution of metal chlorides in 1:1:1 molar ratio. The mixture was refluxed on water bath about 4 hrs. The pH of the solution was adjusted to 7-8 by adding aqueous alcoholic solution of sodium acetate. The reaction mixture was further reflux for one hrs and separated light colored complexes were filtered out washed with alcohol and water successively. Then dried over anhydrous $CaCl_2$.

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$CoCl_2 \cdot 6H_2O + L + L^I \xrightarrow{\text{alcohol, reflux, 2 hrs}} [CoLL^ICl_2] + 5H_2O$ ..1

(L = BTMeOPMC and L^I = 1,10- pnthr / 2,2^I- bipy)

$NiCl_2 \cdot 6H_2O + L + L^I \xrightarrow{\text{alcohol, reflux, 2 hrs}} [NiLL^ICl_2] + 6H_2O$ …2

(L = BTMeOPMC and L^I = 1,10- pnthr / 2,2^I- bipy)

$CuCl_2 \cdot 2H_2O + L + L^I \xrightarrow{\text{alcohol, reflux, 2 hrs}} [CuLL^ICl_2] + 2H_2O$ …3

(L = BTMeOPMC and L^I = 1,10- pnthr / 2,2^I- bipy)

$CdCl_2 + L + L^I \xrightarrow{\text{alcohol, reflux, 2 hrs}} [CdLL^I Cl_2]$

…4

(L = BTMeOPMC and L^I = 1,10- pnthr / 2,2^I- bipy)

$MCl_2 + L + L^I \xrightarrow{\text{alcohol, reflux, 2 hrs}} [MLL^I Cl_2]$ …5

(L = BTMeOPMC and L^I = 1,10- pnthr / 2,2^I- bipy)

M = Zn or Hg

Physical Measurements

All the complexes were analyzed for their metal content, following the standard procedures[9]. Sulpher and chloride contents were determined as $BaSO_4$ and $AgCl_2$, respectively. The magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrate. Electronic spectra of the Cu(II), Co(II) and Ni(II) complexes in DMF (10^{-3} M) solution were recorded using a Hitachi 150-20 model spectrophotometer in the range of 200-1100 nm. IR spectra of the ligands and their complexes were recorded in KBr pallets on Perkin Elmer-783 model IR spectrometer in the range of 4000-350 cm^{-1} and Impact 410 Nicolet FT-IR spectrometer in the range of 4000-250 cm^{-1}. The proton magnetic resonance spectra of ligands and few complexes were recorded on a Brucker 300 MHz at IISc Bangalore and Bracker A.C. 300 F at USA, NMR spectrometer using TMS as an internal standard and DMSO-d6 were used as solvents. The electron spin resonance spectra of Cu(II) complexes in polycrystalline state (powder spectra) were recorded on Varian E-4X-band ESR spectrometer using tetracyanoethylene (TCNE) free radical as 'g' marker (g=2.0036) at room temperature. The X-ray spectra were recorded on Phillips PW 3710 diffractometer attached to a digitized computer along with graphical assembly using CuKα radiation source. The X-ray tube was operated at 25KV/20mA. The sample was scanned in the 2θ range from 0-80°C at a scanning speed of 2θ/min.

The antimicrobial activities of the compounds synthesized in the present investigation were screened for their antibacterial and antifungal activities by agar cup plate technique[10]. These bacterial species namely Escherichia coli, Pseudomonas and Bacillus and three fungal species

Aspergillus Niger, Aspergillus fumigatus and Aspergillus flavons procured from the Department of Microbiology, Gulbarga University, Gulbarga were used in the present study. DMF was used as the solvent and it has been well established as an inert solvent with negligible antimicrobial activity. The experiments were conducted in triplicate and the average activity is reported.

Result and Discussion

The metal ions used are Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II) and Mn(II). The complexes are formed insitu by the reaction of aqueous appropriate metal salt solution with alcoholic solution of BFTMeOPMC and alcoholic solution of second ligand i.e., pnthr and bipy, at a pH of ~8.0. All the metal complexes have been characterized on the basis of elemental analysis, molar conductance, magnetic and spectral studies these complexes are given in **table-1** and **table -2**
All the complexes are generally non-hygroscopic, stable solid, insoluble in water with varying solubility in common organic solvents. All the complexes are thermally stable at least up to 175°C indicating a strong metal-ligand bond. When heated, they undergo decomposition at a temperature higher than the melting point of the ligands. The elemental analysis data of the metal complexes shown **table-1and table-2** are consistent with their general formation as mixed ligand complexes of the type $MLL^{l}Cl_2$ where 'L' is BFTMeOPMC and L^{l} is the secondary ligand i.e., pnthr and bipy while M is divalent metal ion.
All the complexes are insoluble in common organic solvents and soluble in DMF, DMSO and Pyridine. The observed molar conductance values for the complexes fall in the range 9.847-24.240 Ohm^{-1} cm^2 $mole^{-1}$. These values are too low to account for any electrolytic behavior of the complexes. Therefore, they may be regarded as non-electrolytic in nature[11].

Magnetic Properties

The magnetic susceptibility measurements on the mixed ligand transition metal complexes of Co(BFTMeOPMC) (pnthr) and (bipy), show magnetic moments 3.98 and 3.94, B.M. respectively, at room temperatures. The observed magnetic moment of Co(BFTMeOPMC) (pnthr) and (bipy), complexes suggest octahedral geometry for these complexes.
The experimentally observed room temperature magnetic moments for the Ni(II) complexes are in the range 3.58 and 3.34 B.M. In almost all its six-coordinate complexes Ni(II) has a octahedral stereochemistry with spin-triplet ground state in high spin configuration.
The magnetic moments are usually in the range 1.94 and 1.89 B.M. and are temperature independent. The moments for planar complexes are normally lower than for the octahedral ones[12]. Distortion in tetrahedron leads to a decrease in the temperature dependence and reduces the room temperature moment to the normal range observed for octahedral complexes.

Electronic Absorption Spectra

The electronic absorption spectra of Cu(II), Co(II) and Ni(II) complexes were recorded in DMF (10^{-3}M) in the range 1100-200nm.

All the mixed ligand metal complexes in solution show intra ligand transitions in the ultra-violet region. The $MLL^{I}.Cl_2$ (L^{I} = pnthr and bipy,) complexes show π–π* transitions bands in this metal complexes shows slightly higher energy in the region 20833–26666 cm^{-1}.

The present Cu(II) complexes under investigation exhibit a single broad asymmetric band in the region 12735–17064 cm^{-1} and 13071-17730 cm^{-1}, the symmetry being on 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 John-Teller distortion[13]. The results are given in **table-3.**

The present Co(II) complexes exhibit two absorption bands in the region 15922–21041 cm^{-1} and 16393-20833cm^{-1} in DMF (10^{-3}M) solutions. These bands can be assigned to the $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$ transitions, respectively, in an octahedral geometry[14]. The ligand field parameter value of Dq, B^{I}, β, β% and ν_2/ν_1 ratio are presented in the **table-3**. These values agree well with other reported values for octahedral Co(II) complexes.

The electronic spectra of the Ni(II) complexes exhibited two bands in the regions 16129-2666 and 16528–25974 cm^{-1} in DMF solution. These transition $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)(\nu_3)$ respectively. These bands are characteristic of octahedral geometry[15]. However ν_1 band can be calculated using band fitting procedure and found to be range 9970–10700 cm^{-1}. The spectral band positions in DMF solution are present in the **table-3.**

ESR Spectra of Cu[BFTMeOPMC/ pnthr] and Cu[BFTMeOPMC / bipy] mixed ligand

The complexes under present investigation possess a characteristics spectrum having one assymmetric band with two 'g' values (g_{II} and $g_{\perp}$). The $g_{\perp}$ values is obtained from the ratio of microwave frequency (ν) to the magnetic field 'H' at the zero crossing of H, g_{II} is obtained from the ratio of microwave frequency to the magnetic field at the peak position.

The spectrum of mixed ligand complexes shown at room temperature is isotropic with g_{iso} and A_{iso} values 2.116 and $124x10^{-4}cm^{-1}$ respectively. The value of g_{iso}, the lande's splitting factor, is calculated and is found to be 2.116, while the value of nuclear hyperfine splitting constant A_{iso} is found to be $124x10^{-4}cm^{-1}$. This is suggestive of dissimilar field strength[19] and is probably also inductive of the mixed Cu–N and Cu–O bonding as infrared from the I.R studies of the complex. The spectrum permits the calculation of various ESR parameters which are presented in **table-4.**

IR spectra of complexes with BFTMeOPMC and pnthr / bipy mixed ligand

The IR spectra of the BFTMeOPMC and secondary ligand pnthr / bipy complexes are exhibit a broad band at 3286, 3256 cm^{-1} / 3296, 3256 cm^{-1} due to ν(NH) of hydrazine moiety. This band shifts to higher frequency side in all the complexes thereby indicating non-involvement of NH in bonding with metal ion.

The ν(C=O) stretching vibrations in all complexes are observed in the region 1650–1672 cm^{-1} / 1662–1679 cm^{-1}. The shift of ν(C=O) stretch from 1695 cm^{-1} to 1650–1679 cm^{-1} in spectra of

complexes indicating the coordination of ligand moiety to the metal ion through carbonyl oxygen[16,17] in all the complexes.

The ν(C=N) stretch of ligand due to -HC=N– azomethine group is observed at 1626 cm^{-1}/ 1626 cm^{-1}. In the complexes these bands appears in the region 1590–1557cm^{-1}. The shift toward lower wave number side suggests coordination through azomethine nitrogen.

In the case of mixed ligand complexes[18] have reported ν(N–N) stretch of hydrazine residue in the region 1010–1040 cm^{-1} and this band shift to higher wave number side indicating involvement of one of the nitrogen of hydrazine residue in bonding. The weak to medium intensity bands in the region 567–518 and 520–471 cm^{-1} in the spectra of the metal complexes may be assigned to the ν(M–O) and ν(M–N) stretching vibration. It may be noted that these bands are not present in the spectra of the ligand. The stretching vibrations respectively, in free ligands and its metal(II) complexes are given in **table-5** and **table-6.**

^{1}H -NMR of BFTMeOPMC and pnthr / bipy mixed ligand

The ^{1}H-NMR spectra of the mixed ligand complexes are recorded in DMSO–d_6 solution. The tentative assignments of the observed signals are summarized in **table-7**. The spectra of the metal complexes show in general lot of noise at the base line and in most cases the signals are very broad and often not completely resolved. The ligand BFTMeOPMC, shows amide proton [CONH] at δ 11.53 (s, 1H) as a singlet. The azomethine proton has appeared at δ 8.45 (s, 1H) as a singlet, seven aromatic protons have resonated in the region δ 6.89–7.92 (m, 7H) as a multiplate. A singlet at δ 3.66–3.90 (s, 9H) is due to the nine methoxy proton present on the phenyl ring.

Thermogravimetric of Zn[BFTMeOPMC/ pnthr] and Cd[BFTMeOPMC / bipy]mixed ligand

Thermogravimetric studies of the mixed ligand complexes of the non-transition metal ions Zn(II) of pnthr and Cd(II) of bipy have been carried out and resulting thermograms.

The Thermogravimetric analysis of the complexes shows that they are thermally stable to varying degree. As the thermograms indicate the complexes show a gradual and in significant loss in weight this observation suggests the absence of any lattice or crystal water in the complexes.

The thermal decomposition of Zn(II) of pnthr and Cd(II) of bipy complexes takes place in several stages. The decomposition of organic moiety undergoes first thermal degradation in the range 253–524°C.

The thermogram of Zn[BFTMeOPMC / pnthr] complex showed an inflexation in the curve at 294°C the total weight loss of 15.66% corresponding to the expulsion of loss $–OCH_3$, $–OCH_3$ and $–OCH_3$ groups, its theoretical weight loss calculated at this temperature was found to be 15.62%. The experimental and theoretical values are in good agreement. Thereafter the compound started decomposing at 342°C is indicated by thermogram showed a loss of 17.99% due to removal of $–C_6H_2$ and –CH the theoretical weight loss calculated at this temperature was

17.32% well matching with experimental values. The decomposition of compound underwent further degradation and thermogram shows a weight loss of 7.94% at 436°C due to loss of –N, –NH which is corresponding to the theoretical weight loss of 7.05% are agreement with these values. Finally zinc metal oxides remain constants.

The mixed ligand of Cd[BFTMeOPMC / bipy] complex showed a first inflexation point in the temperature 253°C with the total weight loss of 27.03% corresponding to $–OCH_3$, $–OCH_3$, $–OCH_3$ $–C_6H_2$. Its theoretical weight loss calculated at this temperature was found to be 26.88%. The experimental and theoretical weight losses are in good agreement. In second inflection point at 524°C, with the weight loss of 9.42% which amounts to loss of –NH, –N –CH in TGA curve. The elimination is evidenced by the theoretical weight loss are 9.26% of this second step decomposition. The third inflection point result with decomposition over the temperature 796°C at this temperature the bipyridyl moiety is decomposed. The observed weight loss of 36.90% is in agreement with theoretical weight loss of 33.77%, leaving behind is metal oxide only.

Variable Temperature ESR - Spectra

The temperature dependence ESR spectra of Cu[BFTMeOPMC/ pnthr] complex in solid state reproducing in the temperature 100-580K. The spectrum shows a single peak's over the entire temperature range of 100-580 K. The 'g' values have been calculated for each ESR signals at particular temperature and tabulated in **table-8,** at low temperature 100-300 K, the ESR signals appears sharp and the broad ESR signals are observed in the temperature 448-573 K a broad ESR signals may be due to 'g' values remains constant and the ESR signals remains basically unchanged[20,21]

Antimicrobial Activity Studies

The antimicrobial activity results show that the compounds exhibit antimicrobial properties and it is important to note that the metal complexes exhibit more inhibitory effects than the parent ligand; the values are given in **table-9.** The increase in the antibacterial and antifungal activity of the metal complexes is due to the presence of metal ions in the compounds. The increased activity of the metal chelates can be explained on the bases of chelation theory [22]. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that, in a complex, the positive charge of the metal is partially shared with donor atoms present in the ligand and there may be π–electron delocalization over the whole chelating [23]. The complexes exhibited enhanced activities, which is due to the synergistic effect that increases the lipophilicity of the complexes. Chelation decreases the polarity of the metal ion which further leads to the enhancement of lipophilicity of the complex. Since the microorganism cell is surrounded by lipid membrane which favors the passage of lipid soluble materials, increased lipophilicities allows the penetration of the complex into, and through sites of the microorganisms. There are other factors which also increase the activity, which are solubility, conductivity and bond length between the metal and ligand.

Antibacterial and antifungal screening data clearly to the following conclusion.

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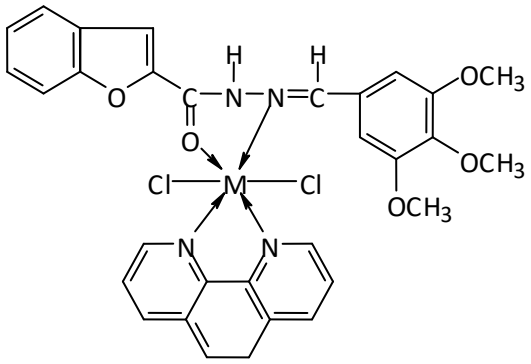
I. The complexes are slightly more toxic than their parent ligand against tested microorganisms under identical experimental conditions.

II. The antimicrobial activity results indicate that the activity of Cu(II) and Zn(II) complexes show better activity than that of Co(II), Ni(II), Cd(II) and Hg(II) complexes.

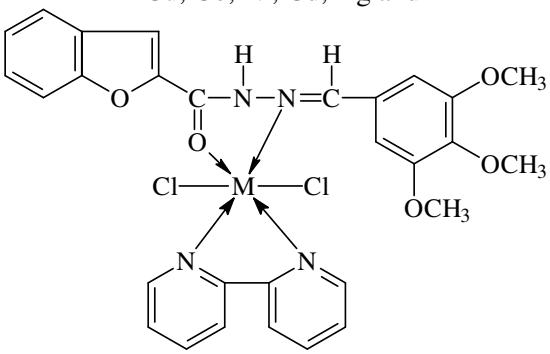
III. The antimicrobial activity results clearly show that the inhibition of fungal growth increases with increasing the concentration of the complexes.

Conclusion

On the Basis of the above observations of Elemental Analysis, Magnetic Moments, Conductance Data, Electronic, IR, NMR, Mass and ESR spectral data and their insolubility in common organic solvents and high melting points, we assigned the following tentative structures for all the complexes of BFTMeOPMC and pnthr / bipy mixed ligand.



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



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

Table-1

Physical, Analytical data, Magnetic Susceptibility and Molar Conductance data of [BFTMeOPMC /pnthr] ligand and its complexes

Compound	Empirical formula/	Mol. Wt	M. P	Yield	Elemental analysis (%) Found / (Calculated)	μ_{eff} B.M	Molar conducta

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	Molecular formula		^{0}C	%	M	C	H	N	Cl		nce Λohm^{-1} cm^2 mole^{-1}
[BFTMeOPMC/ pnthr]	[Co($C_{31}H_{24}N_4O_5$)Cl_2]	660.93	>350	65	8.654 (8.916)	56.598 (56.284)	3.356 (3.631)	10.234 (10.591)	10.584 (10.893)	3.98	18.230
	[Ni($C_{31}H_{24}N_4O_5$)Cl_2]	660.71	>350	70	8.542 (8.885)	56.587 (56.303)	3.415 (3.632)	10.369 (10.594)	10.518 (10.879)	3.58	16.150
	[Cu($C_{31}H_{24}N_4O_5$)Cl_2]	663.50	300	75	9.210 (9.541)	55.454 (55.897)	3.458 (3.606)	10.354 (10.369)	10.621 (10.818)	1.94	9.847
	[Zn($C_{31}H_{24}N_4O_5$)Cl_2]	666.38	295	70	9.645 (9.842)	55.797 (55.829)	3.542 (3.601)	10.647 (10.504)	10.521 (10.654)	--	13.847
	[Cd($C_{31}H_{24}N_4O_5$)Cl_2]	713.41	325	60	15.548 (15.756)	52.358 (52.143)	3.542 (3.364)	9.987 (9.817)	9.816 (9.952)	--	19.452
	[Hg($C_{31}H_{24}N_4O_5$)Cl_2]	800.93	>350	80	25.144 (25.044)	46.617 (46.407)	3.014 (2.994)	8.701 (8.732)	8.724 (8.857)	--	24.240

Table-2

Physical, Analytical data, Magnetic Susceptibility and Molar Conductance data of [BFTMeOPMC / bipy] ligand and its complexes

Compound	Empirical formula/ Molecular formula	Mol. Wt.	M.P ^{0}C	Yield %	Elemental analysis (%) Found / (Calculated)					μ_{eff} B.M	Molar conductance Λ ohm^{-1} cm^2 mole^{-1}
					M	C	H	N	Cl		

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[BFTMeOPMC / bipy]	$[Co(C_{29}H_{25}N_4O_5)Cl_2]$	638.93	>350	72	9.548 (9.208)	54.630 (54.380)	3.487 (3.759)	8.624 (8.421)	10.523 (10.728)	3.94	16.392
	$[Ni(C_{29}H_{25}N_4O_5)Cl_2]$	639.71	310	70	9.365 (9.177)	54.602 (54.399)	3.678 (3.908)	8.753 (8.841)	11.587 (11.255)	3.34	17.612
	$[Cu(C_{29}H_{25}N_4O_5)Cl_2]$	644.50	340	70	9.587 (9.852)	53.624 (53.995)	3.624 (3.878)	8.423 (8.688)	11.171 (11.364)	1.89	18.301
	$[Zn(C_{29}H_{25}N_4O_5)Cl_2]$	645.38	289	60	10.248 (10.130)	53.856 (53.921)	3.541 (3.873)	8.457 (8.677)	11.001 (11.126)	--	20.018
	$[Cd(C_{29}H_{25}N_4O_5)Cl_2]$	692.41	300	65	16.478 (16.234)	50.478 (50.259)	3.254 (3.610)	8.247 (8.087)	10.021 (10.254)	--	17.402
	$[Hg(C_{29}H_{25}N_4O_5)Cl_2]$	780.59	>350	80	25.621 (25.700)	49.247 (49.586)	3.658 (3.203)	7.342 (7.174)	9.242 (9.096)	--	19.321

Table-3

Electronic Spectral data and Ligand field parameter of the Co(II), Ni(II) and Cu(II)Complexes with [BFTMeOPMC / pnthr and bipy] Mixed ligand Complexes in DMF (10^{-3}M) solution.

Ligand	Complexes [Molecular formula]	Transition in cm^{-1}			Dq cm^{-1}	B^1 cm^{-1}	β	β%	ν_2/ν_1	L.F.S.E kcal
		ν_1*	ν_2	ν_3						

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BFphthr BFbipy	$[Co(C_{31}H_{24}N_4O_5)Cl_2]$	07552 15922 21041	0847 0858	938 920	1.0247	02.471 05.253	1.336 1.270	14.52 14.70
BFphthr BFbipy	$[Co(C_{29}H_{25}N_4O_5)Cl_2]$	07815 16393 20833	0997 1010	859 677	0.9474 0.8259	17.403 34.903	1.653 1.571	34.18 36.68
BFphthr BFbipy	$[Ni(C_{31}H_{24}N_4O_5)Cl_2]$	09970 16129 26666	1490 1540	-- --	-- 0.6514	-- --	-- --	25.54 26.40
	$[Ni(C_{29}H_{25}N_4O_5)Cl_2]$	10700 16528 25974						
	$[Cu(C_{31}H_{24}N_4O_5)Cl_2]$	12735 – 17064			--			
	$[Cu(C_{29}H_{25}N_4O_5)Cl_2]$	13071 – 17730			--			

* Calculated values

Table-4

ESR Spectral Parameters of Cu(II) complexes with [BFTMeOPMC /pnthr and bipy] Mixed ligand

Complexes	**g_{II}**	**$g_{\perp}$**	**g_{av}**	**g_{iso}**	**A_{II} $1*10^{-4}$ cm^{-1}**	**$A_{\perp}$ $1*10^{-4}$ cm^{-1}**	**A_{av}**	**G**
[BFTMeOPMC/ pnthr] [BFTMeOPMC / bipy]	2.2569 2.2122	2.0643 2.0567	2.1304 2.1098	2.1945 2.1616	198.93 181.66	12.390 10.243	0.007436 0.006738	4.1064 4.0028

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Bonding Coefficient Parameter for the Cu(II), Complexes with [BFTMeOPMC /pnthr and bipy] Mixed ligand

Complexes	A_{iso} 1*10^{-4} cm^{-1}	K_{II}	$K_{\perp}$	K	β^2	α	K_o^2
[BFTMeOPMC/ pnthr]	136.750	0.6997	0.6905	0.5078	4.7113	0.2313	0.5034
[BFTMeOPMC / bipy]	124.522	0.6435	0.6552	0.4533	1.7916	0.2311	0.4349

Table-5

Infrared Spectra of the [BFTMeOPMC /pnthr] Mixed ligand and its Complexes

Lignad / Complexes	ν_{NH} sym strech	$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-N}	ν_{M-O}	ν_{M-N}	$\nu_{(M-Cl)}$	$\nu_{C=N}$ (ring)
BFTMeOPMC	3256	1695	1626	1010	--	--	--	--
pnthr	--	--	--	--	--	--	--	1645
Cu	3275	1672	1557	1016	544	470	330	1598
Co	3280	1668	1576	1012	526	482	312	1610
Ni	3270	1650	1562	1020	518	471	320	1595
Zn	3282	1670	1570	1031	547	427	326	1612
Cd	3286	1667	1576	1012	567	458	321	1605
Hg	3256	1668	1574	1040	538	419	318	1617

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Table-6

Infrared Spectra of the [BFTMeOPMC / bipy] Mixed ligand and its Complexes

Ligand/ Complexes	ν_{NH} sym strech	$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-N}	ν_{M-O}	ν_{M-N}	$\nu_{(M-Cl)}$	$\nu_{C=N}$ (ring)
BFTMeOPMC	3256	1695	1626	1010	--	--	--	--
bipy	--	--	--	--	--	--	--	1590
Cu	3265	1667	1588	1012	520	418	320	1562
Co	3270	1678	1590	1026	498	384	316	1560
Ni	3262	1679	1581	1040	471	360	318	1572
Zn	3298	1678	1577	1040	526	410	326	1548
Cd	3296	1677	1565	1026	505	414	328	1554
Hg	3256	1662	1570	1036	520	418	326	1559

Table-7

^{1} H-NMR Spectra of the [BFTMeOPMC / pnthr] and [BFTMeOPMC / bipy] Mixed ligand Complexes

Sr. No.	Compound/ Ligand	Solvent	Observed shift in δ	Assignment
1.	Zn[BFTMeOPMC / pnthr]	DMSO-d_6	11.98	NH(CONH)
			8.85	N=CH
			6.52–8.92	Aromatic protons
			3.51–3.91	Methoxy proton on phenyl ring
	Hg[BFTMeOPMC / pnthr]	DMSO-d_6	11.89	NH(CONH)
			8.76	N=CH
			6.92–8.68	Aromatic protons
			3.68–3.92	Methoxy proton on phenyl ring

2.	Cd[BFTMeOPMC / bipy]	DMSO-d_6	11.83	NH(CONH)
			8.83	N=CH
			6.98–8.23	Aromatic protons
			3.65–3.97	Methoxy proton on phenyl ring
	Zn[BFTMeOPMC / bipy]	DMSO-d_6	11.74	NH(CONH)
			8.78	N=CH
			6.85–8.55	Aromatic protons
			3.64–3.89	Methoxy proton on phenyl ring

Table-8

Variable temperature ESR spectral data for Cu(II) complex of the mixed ligand [BFTMeOPMC /pnthr]

Temperature °C	'g' value
-145 °C	2.0860
-105 °C	2.0914
-65 °C	2.0963
-25 °C	2.1042
15 °C	2.1126
55 °C	2.1038
95 °C	2.1015
135 °C	2.0935
175 °C	2.0975
215 °C	2.0956
255 °C	2.1004
295 °C	2.1030

Table-9

Antibacterial and Antifungal activity results of mixed ligands and its metal complexes

Ligands/ Complexes	Zone of inhibition (m.m)			
	Bacterial		Fungal	
	E. Coli	S. Aurious	A. Niger	A. Fumigatus
BFTMeOPMC	12	14	11	10
Cu[BFTMeOPMC /pnthr]	18	18	12	18

Co[BFTMeOPMC /pnthr]	12	11	15	11
Zn[BFTMeOPMC /pnthr]	20	18	15	19
Cd[BFTMeOPMC /pnthr]	16	15	12	16
Hg[BFTMeOPMC /pnthr]	16	14	10	15
Cu[BFTMeOPMC /bipy]	13	17	12	10
Co[BFTMeOPMC /bipy]	12	11	13	11
Zn[BFTMeOPMC /bipy]	18	18	16	17
Cd[BFTMeOPMC /bipy]	12	12	14	17
Hg[BFTMeOPMC /bipy]	14	11	13	12

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