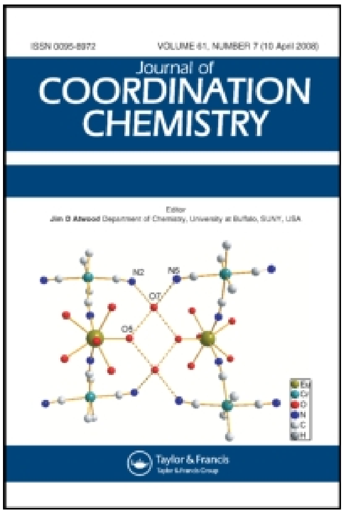

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Synthesis, characterization and antimicrobial studies on metal complexes with a naphthofuran thiosemicarbazide derivatives

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Synthesis, characterization and antimicrobial studies on metal complexes with a naphthofuran thiosemicarbazide derivatives

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Complexes of the type $MLCl_2$, where $M = Co(II)$, Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) and L is a thiosemicarbazide ligand derived from reaction between naphthofuran-2-carboxyhydrazide and *p*-chlorophenylisothiocynate (NCClPT)/*p*-bromophenylisothiocynate (NCBrPT) characterized by elemental analysis, conductance, magnetic susceptibility measurements, UV-Vis, IR, ^{1}H NMR, and ESR. The thiosemicarbazide ligands are bidentate by coordinating through the oxygen of the carbonyl group and the nitrogen of the hydrazide residue. Based on the results, we propose structures for all the metal complexes. Both the ligands and their complexes have been screened for their fungicidal and bactericidal activities.

Keywords: Naphthofuran thiosemicarbazides; Metal complexes; Spectral studies and antimicrobial activities

1. Introduction

Thiosemicarbazides and thiosemicarbazones have gained special attention due to their activity against protozoa [1], influenza [2], small-pox [3], malaria, cancer [4] and tuberculosis. As ligands they provide three potential donor sites viz, O, N and S and form complexes with various metal ions. Owing to the wide range of microbial properties [5, 6] of thiosemicarbazides and thiosemicarbazones and their ability to form chelates with metal ions, in the present study, we report the synthesis and characterization of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) metal complexes with the thiosemicarbazide ligands derived from reaction between naphthofuran-2-carboxyhydrazide and *p*-chlorophenlyisothiocyante/*p*-bromophenlyisothiocyante. All the complexes have been characterized by elemental analysis, conductance, magnetic susceptibility measurements, UV-Vis, IR, ^{1}H NMR, and ESR spectral studies.

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2. Experimental

All the chemicals used were of Analytical Grade. Naphthofuran-2-carboxyhydrazide was prepared by the literature method [7]. The metal and chloride contents are determined as per Vogel's procedure [8]. The nitrogen content was estimated micro-analytically.

2.1. *Preparation of naphthofuran-2-carboxy-[4′-chlorophenyl]thiosemicarbazide[NCClPT] and naphthofuran-2-carboxy-[4′-bromophenyl]thiosemicarbazide [NCBrPT]*

The *p*-chlorophenylisothiocynate/*p*-bromophenylisothiocynate (0.5 mol) in alcohol (10 cm^3) was added to an ethanolic (20 cm^3) solution of naphthofuran-2-carboxyhydrazide (1.7 g, 0.5 mol). The reaction mixture was kept under reflux in a water bath for 3–4 h. The solid thiosemicarbazide ligands start separating out after a few minutes. The reaction mixture was cooled room temperature; the product was collected by filteration and washed with alcohol. The compound was recrystallized from alcohol and dried in vacuum over fused $CaCl_2$ (figure 1).

[Mol. formula – $C_{20}H_{14}O_2N_3SCl$, m.p. = 210°C, yield 80% and $C_{20}H_{14}O_2N_3SBr$, m.p. = 196°C, yield 85%].

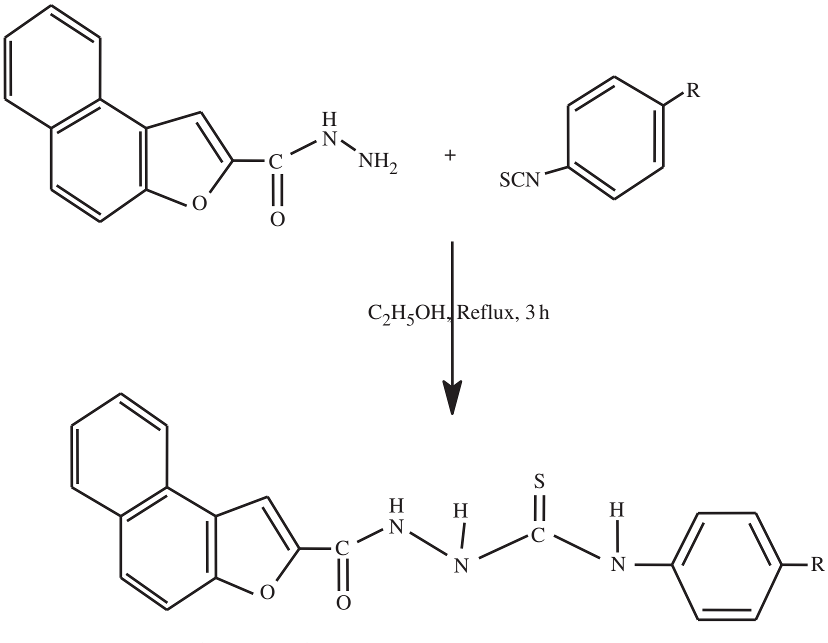


Figure 1. Synthesis of the ligands, naphthofuran-2-carboxy-[4′-chlorophenyl]thiosemicarbazide[NCClPT] and naphthofuran-2-carboxy-[4′-bromophenyl]thiosemicarbazide[NCBrPT].

2.2. *Preparation of complexes*

Metal complexes were prepared by adding an aqueous solution of metal(II) chloride (0.1 mol, 20 cm^3) to the thiosemicarbazide ligands (1.55 g NCClPT; 1.73 g NCBrPT, 0.1 mol) in alcohol (50 cm^3) with vigorous stirring. The complexes were not separated immediately, and the reaction mixture was boiled under reflux on a water bath for about 2 h, during which complexes started separating out. The reaction solution was concentrated and cooled to room temperature. The crystalline light colored complexes were filtered, washed with water and alcohol to remove the unreacted salts and ligands. All the complexes were dried in open air and kept in a vacuum desiccator. The formation of the complexes may be represented by the following equations:

$$\begin{gathered}\mathrm{nCoCl_2 \cdot 6H_2O + nL \xrightarrow{alcohol,\ reflux,\ 2\,h} \{[CoLCl_2] \cdot H_2O\}_n + 5H_2O} \\ \mathrm{(L = NCClPT/NCBrPT)}\end{gathered} \tag{1}$$

$$\begin{gathered}\mathrm{nNiCl2 \cdot 6H_2O + nL \xrightarrow{alcohol,\ reflux,\ 2\,h} \{[NiLCl_2]\}_n + 6H_2O} \\ \mathrm{(L = NCClPT/NCBrPT)}\end{gathered} \tag{2}$$

$$\begin{gathered}\mathrm{nCuCl_2 \cdot 2H_2O + nL \xrightarrow{alcohol,\ reflux,\ 2\,h} \{[CuLCl_2]\}_n + 2H_2O} \\ \mathrm{(L = NCClPT/NCBrPT)}\end{gathered} \tag{3}$$

$$\begin{gathered}\mathrm{nCdCl_2 + nL \xrightarrow{alcohol,\ reflux,\ 2\,h} [CdLCl_2]_n} \\ \mathrm{(L = NCClPT/NCBrPT)}\end{gathered} \tag{4}$$

$$\begin{gathered}\mathrm{MCl_2 + L \xrightarrow{alcohol,\ reflux,\ 2\,h} [MLCl_2]} \\ \mathrm{(L = NCClPT/NCBrPT)} \\ \mathrm{M = Zn\ or\ Hg}\end{gathered} \tag{5}$$

2.3. *Physical measurements*

All the complexes were analyzed for their metal content, following standard procedures [8]. Sulphur and chloride content was determined as $BaSO_4$ and $AgCl_2$, respectively. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant. 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 200–1100 nm. IR spectra of the ligands and their complexes were recorded in KBr pellets on a Perkin-Elmer-783 model IR spectrometer in the range 4000–350 cm^{-1} and an Impact 410 Nicolet FTIR spectrometer in the range 4000–250 cm^{-1}. The proton magnetic resonance spectra of ligands and a 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-d$_6$ and $CDCl_3$ as solvents. The electron spin resonance spectra of Copper(II) complexes in polycrystalline state (powder spectra) were recorded on a Varian E-4X-band ESR spectrometer using tetracyanoethylene (TCNE) free radical as '*g*' marker ($g = 2.0036$) at room temperature.

The antimicrobial activities of the compounds synthesized in the present investigation were screened for their antibacterial and antifungal activities by agar cup plate technique [9]. These bacterial species namely *Escherichia coli*, *Pseudomonas* and *Bacillus* and three fungal species *Aspergillus Niger*, *A. fumigatus* and *A. flavons* procured from the Department of Microbiology, Gulbarga University, Gulbarga were used in the present study. DMF, well established as an inert solvent with negligible antimicrobial activity, was used as the solvent. The experiments were conducted in triplicate and the average activity is reported.

3. Results and discussion

Analytical data for the complexes indicate 1 : 1 stoichiometry for all the complexes (table 1). All the complexes possess high melting points and are stable towards air and are partially or insoluble in common organic solvents and soluble in DMF, DMSO and Pyridine. The molar conductance of the complexes falls in the range of 8.95–20.29 $\Omega^{-1}\,cm^2\,mol^{-1}$ in DMF (10^{-3} M) solution. The values are too low to account for any electrolytic behaviors of the complexes [10].

The observed magnetic moment values for Co[NCClPT] and Co[NCBrPT] complexes are 4.93 and 5.15 B.M. respectively, have been used as a criterion to determine the type of geometry around the metal ions, these values suggests an octahedral geometry for Co(II) complexes [11]. The magnetic moment values for Ni(II) complexes 2.94 and 3.20 B.M. for NCClPT and NCBrPT ligands, respectively, suggests the hexa-coordinate Ni(II) ions [12]. The effective magnetic value for Cu[NCClPT] and Cu[NCBrPT] complexes, 2.05 and 2.12 B.M. respectively suggest distorted octahedral geometry.

3.1. *Electronic spectra*

The electronic spectra of the Co(II) complexes show two bands at 16,120 and 20,740 cm^{-1} and 16,450 and 21,320 cm^{-1} for NCClPT and NCBrPT, respectively, assigned to $^4T_{1g}(F) \rightarrow {}^3A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$ transitions in an octahedral environment [13, 14]. The ν_1 could not be observed due to the limited range of the instrument, however, ν_1 could be calculated using band-fitting procedures [15]. The octahedral geometry [16] is further supported by the values of ligand field parameters, D_q, B', β, β% and LFSE. All these values are given in table 2. The reduction in Racah parameter value from the free ion value (971) suggests covalent character of the M–L bond.

The hexa-coordinated light green colored Ni[NCClPT] and Ni[NCBrPT] complexes exhibit two bands at 16,100 and 27,780 cm^{-1} and 14,620 and 25,640 cm^{-1} respectively assignable to $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively, in view of their octahedral geometry [13]. This is further supported by ligand field parameters like D_q, B', β, β%, ratio $(\nu_2)/(\nu_1)$ and LFSE values.

The Cu(II) complexes show a broad asymmetric band in the region 17,020–13,130 cm^{-1}. The broadness of the band may be due to dynamic Jahn-Teller distortion [17]. These observations suggest distorted octahedral structures.

Table 1. Analytical, molar conductance and magnetic susceptibility data of the metal(II) complexes.

				% Found (Calcd)					
Ligands	Complexes	Yield %	Mol. wt.	M	N	Cl	S	Λ_M (Ω^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
NCClPT [$C_{20}H_{14}O_2N_3SCl$]	[$Co(C_{20}H_{14}O_2N_3SCl)Cl_2\cdot H_2O]_n$	60	542.93	10.60 (10.85)	7.98 (7.73)	13.50 (13.07)	6.05 (5.89)	16.65	4.93
	[$Ni(C_{20}H_{14}O_2N_3SCl)Cl_2]_n$	62	524.71	11.15 (11.18)	7.99 (8.00)	13.52 (13.53)	6.07 (6.09)	15.00	2.94
	[$Cu(C_{20}H_{14}O_2N_3SCl)Cl_2]_n$	70	529.50	11.96 (11.99)	7.90 (7.93)	13.37 (13.40)	6.02 (6.04)	10.85	2.05
	[$Zn(C_{20}H_{14}O_2N_3SCl)Cl_2$]	70	531.38	12.29 (12.30)	7.87 (7.90)	13.38 (13.36)	6.01 (6.02)	9.90	–
	[$Cd(C_{20}H_{14}O_2N_3SCl)Cl_2]_n$	70	578.41	19.44 (19.43)	7.25 (7.26)	12.26 (12.27)	5.54 (5.53)	14.90	–
	[$Hg(C_{20}H_{14}O_2N_3SCl)Cl_2$]	65	667.09	30.04 (30.06)	6.30 (6.29)	10.62 (10.64)	4.76 (4.79)	17.85	–
NCBrPT [$C_{20}H_{14}O_2N_3SBr$]	[$Co(C_{20}H_{14}O_2N_3SBr)Cl_2\cdot H_2O]_n$	65	587.93	10.30 (10.02)	7.34 (7.14)	12.42 (12.07)	5.59 (5.44)	10.55	5.15
	[$Ni(C_{20}H_{14}O_2N_3SBr)Cl_2]_n$	70	569.71	10.28 (10.30)	7.36 (7.37)	12.44 (12.46)	5.58 (5.61)	8.95	3.20
	[$Cu(C_{20}H_{14}O_2N_3SBr)Cl_2]_n$	70	574.50	11.04 (11.05)	7.30 (7.31)	12.33 (12.35)	5.56 (5.57)	18.50	2.12
	[$Zn(C_{20}H_{14}O_2N_3SBr)Cl_2$]	72	576.38	11.35 (11.34)	7.28 (7.28)	12.30 (12.31)	5.56 (5.55)	20.29	–
	[$Cd(C_{20}H_{14}O_2N_3SBr)Cl_2]_n$	68	623.41	18.01 (18.03)	6.71 (6.73)	11.39 (11.38)	5.11 (5.13)	13.65	–
	[$Hg(C_{20}H_{14}O_2N_3SBr)Cl_2$]	60	711.49	28.16 (28.19)	5.87 (5.90)	9.95 (9.97)	4.47 (4.49)	9.90	–

Table 2. Electronic spectral data and ligand field parameters of the Co(II), Ni(II) and Cu(II) complexes in DMF (10^{-3} M) solution.

Ligands	Complexes	Transitions in cm^{-1}			D_q (cm^{-1})	B' (cm^{-1})	β	β %	ν_2/ν_1	LFSE (kcal $mole^{-1}$)
		ν_1^*	ν_2	ν_3						
NCClPT	$CoLCl_2$	7500	16120	20740	862	958	0.9866	1.3388	2.1493	14.7771
NCBrPT	$CoLCl_2$	7850	16450	21320	860	949	0.9773	2.2657	2.0955	14.7428
NCClPT	$NiLCl_2$	9780	16100	27780	978	969	0.9317	6.8269	1.6462	33.5314
NCBrPT	$NiLCl_2$	8830	14620	25640	883	918	0.8826	11.7307	1.6557	30.2742
NCClPT	$CuLCl_2$		16450–13760		1447	–	–	–	–	24.8057
NCBrPT	$CuLCl_2$		17020–13130		1510	–	–	–	–	25.8857

* Calculated values.

3.2. *NMR spectra*

The ^{1}H NMR spectrum of NCClPT and NCBrPT ligands and their Zn(II), Cd(II) and Hg(II) complexes in DMSO-d_6 or $CDCl_3$ solvents were recorded. The signals due to CO^{1}NH, ^{2}NH and ^{4}NH protons of ligands appear at δ (10.50, 10.49); (9.96, 9.94) and (9.82, 9.80) ppm respectively in NCClPT and NCBrPT ligands. The signals due to ^{2}NH proton are shifted down field in the spectra of Zn(II), Cd(II) and Hg(II) complexes and the signals due to ^{1}NH proton shows a small down field shift thereby indicating coordination of ligands through the oxygen of CONH and nitrogen of ^{2}NH groups.

3.3. *Infrared spectra*

The thiosemicarbazide ligands exhibit three bands in the regions 3437–3287, 3285–3152 and 3040–3060 cm^{-1} assigned to ν(^{4}NH), ν(^{2}NH) and ν(^{1}NH) respectively, [18, 19]. In the spectra of the complexes the bands due to ν(^{4}NH) shift to higher wavenumber by about 10–20 cm^{-1} or it remains unaltered indicating non-involvement of nitrogen of (^{4}NH) group in coordination with metal ions. The band due to ν(^{2}NH) shifts to lower wavenumber by about 20–30 cm^{-1} in all the complexes and becomes weak in the complexes suggesting coordination of the (^{2}NH) group. The bands observed in the region 3040–3060 cm^{-1} are practically unaltered or shift slightly to higher wavenumber indicating no coordination.

The weak bands observed in the regions 2775–2840 cm^{-1} are assigned to stretching vibrations of intra-molecular hydrogen bonding between CO and ^{2}NH group [20]. The absence of any band above 3500 cm^{-1} due to ν(OH) stretch and 2650–2450 cm^{-1} due to ν(SH) stretch suggests that the ligand exists in the thioketo form.

The strong bands observed [21] at 1669 and 1658 cm^{-1} in free ligands are assigned to ν(CO) stretching vibrations. These bands shift to lower wavenumber by about 30–50 cm^{-1} in all the metal complexes, suggesting the coordination of oxygen. The positive shift of ν(N–N) observed at 1020 cm^{-1} and 1035 cm^{-1} in free ligands by 10–15 cm^{-1} in the complexes shows coordination of one nitrogen of the hydrazinic moiety [22].

The thioketo ν(C=S) band observed at 745–730 cm^{-1} shows no shift in the metal complexes compared with the free ligands, indicating sulphur does not coordinate. The thio-amide [23] bands observed in the regions 1530–1510, 1350–1330, 1080–1060 and 750–710 cm^{-1} due to amide I, II, III and IV, respectively, remain

Table 3. ESR data of Cu(II) complexes.

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} \times 10^{-4}$ (cm^{-1})	$g_{\parallel}/A_{\parallel}$	α^2	G
Cu[NCClPT]	2.2680	2.1270	2.1750	190.588	119	0.8506	2.110
Cu[NCBrPT]	2.2479	2.1601	2.1893	188.899	119	0.8400	1.5610

unaltered in the complexes suggesting the non-involvement of (C=S) group in bonding with metal ions.

In the far infrared spectra of the complexes the bands observed in the region 554–512 cm^{-1} can be assigned to ν(M–N) stretching vibrations and bands in the region 469–423 cm^{-1} to ν(M–O) stretching vibrations in all the complexes [24].

In the case of polymeric complexes ν(M–Cl) terminal and ν(M–Cl) bridging are assigned in the region 366–345 cm^{-1} and 304–285 cm^{-1}, respectively [25]. In Hg(II) and Zn(II) complexes ν(M–Cl) stretch is assigned in the region 354–309 cm^{-1} in view of their monomeric/dimeric structures.

3.4. *ESR spectra*

The ESR spectrum of Cu(II) complexes of [NCClPT] and [NCBrPT] in polycrystalline state have been scanned at room temperature (table 3). These Cu(II) complexes show medium broad signals with of $g_{\parallel} = 2.2680$ and 2.2479 and $g_{\perp} = 2.1270$ and 2.1601, respectively. The g_{av} values of the complexes have been calculated and the obtained g_{av} values for the Cu(II) complexes are 2.1750 and 2.1893 for NCClPT and NCBrPT ligands, respectively. The 'g' values indicate that the free electron is predominantly in $d_{x^2-y^2}$ orbital of Cu(II). The 'G' values are less than 4 indicating antiferromagnetic coupling between metal ions.

Cu[NCClPT] and Cu[NCBrPT] show spectra having asymmetric bands with two 'g' values, $g_{\parallel} > g_{\perp}$. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0036) observed for these complexes indicate that, the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital with the possibility of some mixing of d_{z^2}, because of low symmetry [26].

The value of α^2, which is the residential time of an unpaired electron on a Cu(II) ion, and the value of $g_{\parallel}$ (<2.3) confirm the covalent nature of the complexes [27, 28].

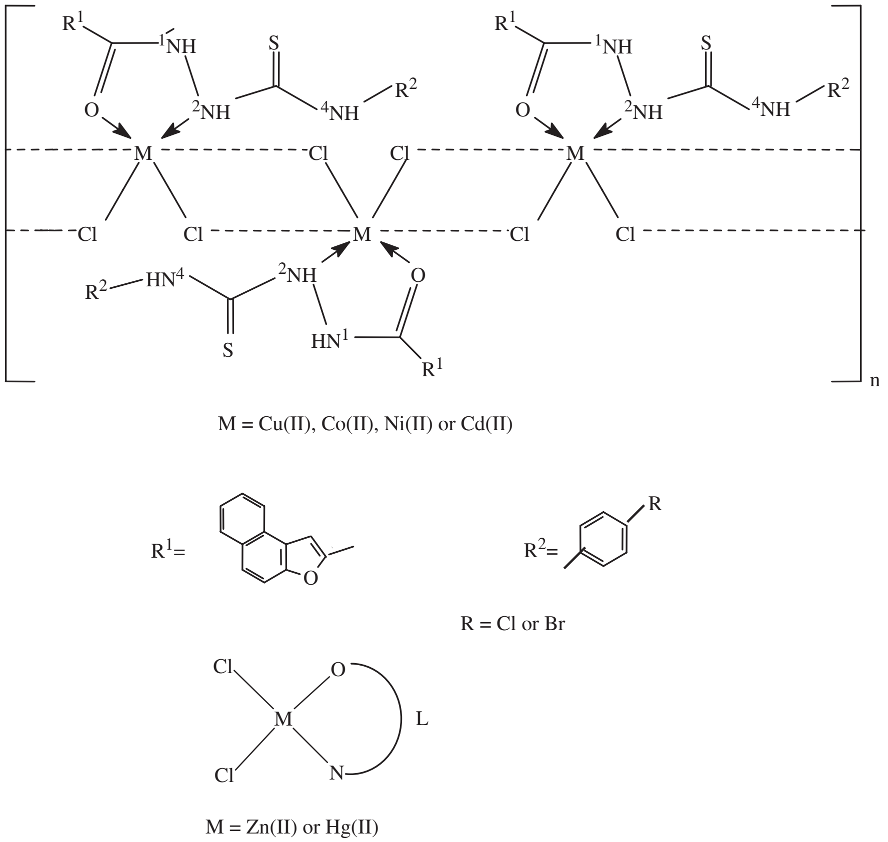
3.5. *Biological activity*

The results of the antibacterial and antifungal studies of NCClPT and NCBrPT and their metal complexes are presented in table 4. The ligands exhibit better antibacterial activity then their metal complexes. The results indicate low to moderate activity against the three bacterial species and antifungal species (table 4).

The ligands exhibited a slightly higher activity against the gram (–ve) bacteria than the gram (+ve) bacteria, whereas the metal complexes exhibited varying degrees of activity. The Cd complexes of both ligands exhibited higher activity then the other metal complexes. However, compared to the antibacterial activity of the standard antibiotic *streptomycin*, the activity exhibited by the ligands and their metal complexes were less.

Table 4. Antibacterial and antifungal activity of the ligands and their metal complexes.

	Zone of inhibition (mm)					
	Bacteria			Fungi		
Complexes/Compounds	*E. coli*	*Pseudomonas*	*Bacillus subtilis*	*A. niger*	*A. falvus*	*A. fumigatus*
NCClPT	19	20	18	14	15	16
Cu[NCClPT]	13	15	14	14	13	16
Co[NCClPT]	11	13	12	11	10	14
Ni[NCClPT]	12	14	11	10	12	13
Zn[NCClPT]	16	16	13	14	15	16
Cd[NCClPT]	18	19	17	16	17	19
NCBrPT	18	19	16	13	17	14
Cu[NCBrPT]	12	13	11	12	14	15
Co[NCBrPT]	10	11	10	11	12	12
Ni[NCBrPT]	11	12	09	10	13	10
Zn[NCBrPT]	13	14	14	12	15	16
Cd[NCBrPT]	16	17	15	15	17	18
Streptomycin	22	23	20	–	–	–
Nystatin	–	–	–	21	19	20



M = Cu(II), Co(II), Ni(II) or Cd(II)

R = Cl or Br

M = Zn(II) or Hg(II)

Figure 2. Suggested structures of the complexes.

Similar observations were made with respect to the antifungal activity of the NCClPT and NCBrPT and their metal complexes. The ligands have better antifungal activity then their metal complexes except the Cd complex of NCClPT. The ligand and metal complexes of NCClPT were more active against *A. fumigatus* then against the other two fungi tested. NCBrPT and its metal complexes exhibited least activity against *A. niger* and moderate activity against the other two fungi. However, compared to the standard antifungal against *Nystatin*, the ligands and metal complexes were not more effective.

4. Conclusion

The ligands [NCClPT] and [NCBrPT] are neutral bidentate coordinating through the amide-O and ^{2}NH nitrogen of the thiosemicarbazide. All the complexes isolated in the solid state possess 1 : 1 (M : L) stoichiometry.

On the basis of elemental analysis, electronic spectra, magnetic susceptibility, IR, NMR and ESR spectral data, we suggest the geometries shown in figure 2.

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