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Synthesis, Spectral Studies, and Biological Activity of Metal Complexes of Benzofuran Thiosemicarbazides

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ABSTRACT

The complexes of Co(II), Cu(II), Ni(II), Cd(II), Hg(II), Zn(II), UO_2(VI), and Th(IV) with benzofuran thiosemicarbazides have been prepared. All complexes have the general formula MLX_n, where $n = 2$ or 4, X = Cl or NO_3 and L is the ligand prepared by the reaction of benzofuran-2-carboxyhydrazide with *p*-methyl, *p*-methoxy, or *p*-bromophenylisothiocyanate. The complexes were characterized on the basis of elemental analyses, spectral, magnetic moment, and conductance studies. The ligands coordinate to the metal ions through the oxygen of the arbonyl group and the nitrogen of the hydrazine group. We have assigned the probable geometry for all of these complexes based on their physico-chemical data. All

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the metal complexes and ligands were screened for their anti-microbial activity.

Key Words: Metal complexes; Spectral studies; Biological activity; Benzofuran thiosemicarbazides.

INTRODUCTION

Thiosemicarbazide derivatives have been reported to possess antibacterial,[1,2] antiviral,[3] and antifungal[4] activities. As a ligand they provide three potential donor sites *viz.* O, N, and S and form complexes with various transition and non-transition metal ions. The metal complexes with thio-derivatives of the hydrazine have occupied a very important place in the future development and progress of coordination chemistry. In the present study, we report the thiosemicarbazide ligands derived from the reaction between *p*-methylphenylisothiocyanate, *p*-methoxyphenylisothiocyanate or *p*-bromophenylisothiocyanate, and benzofuran-2-carboxyhydrazide with a view that benzofuran thiosemicarbazide derivatives and their metal complexes might exhibit high biological activity compared with benzofurans[5] or thiosemicarbazides alone. The metal ions used are Co(II), Cu(II), Ni(II), Cd(II), Hg(II), Zn(II), UO_2(VI), and Th(IV).

EXPERIMENTAL

All the chemicals used were of analytical grade. The metal, chloride, and nitrogen contents in the complexes were determined by standard methods.[6] The physical methods used were the same as reported earlier.[7] The ligands benzofuro-2-carboxy-[4′-methylphenyl] thiosemicarbazide (BCMePT), benzofuro-2-carboxy-[4′-methoxyphenyl] thiosemicarbazide (BCMeOPT), and benzofuro-2-carboxy-[4′-bromophenyl] thiosemicarbazide (BCBrPT) were synthesized by the following method.

Preparation of Thiosemicarbazide Ligands

The thiosemicarbazide ligands are prepared by the reaction of benzofuran-2-carboxyhydrazide (2.18 g, 5 mmol) in ethyl alcohol (25 mL) and *p*-methylphenylisothiocyanate (1.11 g, 5 mmol) or *p*-methoxyphenylisothiocyanate (1.25 g, 5 mmol) or *p*-bromophenylisothiocyanate (1.69 g, 5 mmol) in ethyl alcohol (10 mL). The reaction mixture was refluxed on a water bath for about 2 hr. The thiosemicarbazide ligands separated out on cooling to room temperature and were filtered, washed with ethyl alcohol, recrystallised from ethyl alcohol, and dried in vacuo over fused $CaCl_2$ (analytical data are shown in Table 1).

Preparation of Metal Complexes

The metal complexes were prepared by reacting the thiosemicarbazide ligand (1.62 g, BCMePT; 1.7 g, BCMeOPT; 1.95 g, BCBrPT, 1 mmol) in ethyl alcohol (50 mL) with the corresponding metal chlorides or nitrates (1 mmol) in ethyl alcohol (15 mL). The reaction mixture was refluxed on a water bath for about 3 hr during which time solid complexes separated. In the case of the Zn(II), Cd(II), and UO_2(VI) complexes the pH of the solution was adjusted to 5–6 by adding 50% (2–3 mL) aqueous alcoholic solution of sodium acetate. The reaction mixture was cooled to room temperature, the solid complexes filtered, washed with alcohol, and water to remove the unreacted metal salts and ligands. The complexes were dried in a vacuum over fused $CaCl_2$.

RESULTS AND DISCUSSION

All complexes gave satisfactory N, M, and Cl analysis. The formation of the ligands and complexes (Fig. 1) may be represented by the following equations.

$$n\mathrm{CuCl_2 \cdot 2H_2O} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} [\mathrm{CuLCl_2}]_n + \mathrm{2H_2O}$$
$$(\mathrm{L} = \text{BCMePT or BCMeOPT or BCBrPT}) \qquad (1)$$

Table 1. Analytical data of the benzofuran thiosemicarbazide ligands.

Molecular formula	Formula weight	Yield (%)	M.p. (°C)	Anal. %, Found (calcd.) C	H	N
[BCMePT]	325.00	80	225	62.50	4.60	15.80
$C_{17}H_{15}N_3O_2S$				(62.70)	(4.61)	(16.00)
[BCMeOPT]	341.00	85	250	59.65	4.12	15.00
$C_{17}H_{15}N_3O_3S$				(59.82)	(4.39)	(15.24)
[BCBrOPT]	390	85	270	49.50	4.20	10.60
$C_{16}H_{12}BrN_3O_2S$				(49.23)	(3.07)	(10.76)

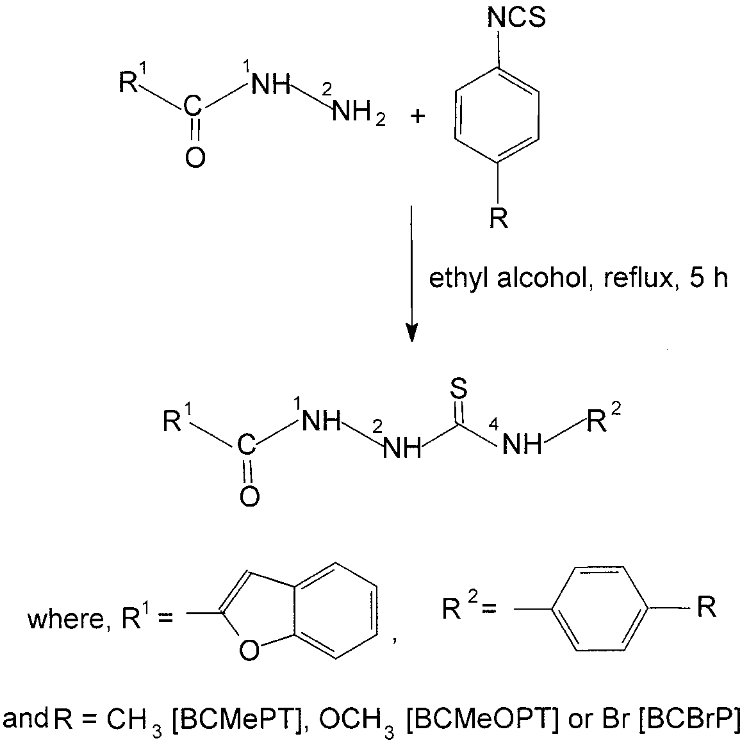


Figure 1. Synthesis and structure of the ligands.

$$n\mathrm{CoCl_2 \cdot 6H_2O} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} [\mathrm{CoLCl_2}]_n + \mathrm{6H_2O}$$
$$(\mathrm{L} = \mathrm{BCMePT\ or\ BCMeOPT}) \qquad (2)$$

$$n\mathrm{CoCl_2 \cdot 6H_2O} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} \{[\mathrm{CoLCl_2}] \cdot \mathrm{H_2O}\}_n + \mathrm{5H_2O}$$
$$(\mathrm{L} = \mathrm{BCBrPT}) \qquad (3)$$

$$n\mathrm{NiCl_2 \cdot 6H_2O} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} [\mathrm{NiLCl_2}]_n + \mathrm{6H_2O}$$
$$(\mathrm{L} = \mathrm{BCBrPT}) \qquad (4)$$

$$n\mathrm{NiCl_2 \cdot 6H_2O} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} \{[\mathrm{NiLCl_2}] \cdot \mathrm{H_2O}\}_n + \mathrm{5H_2O}$$
$$(\mathrm{L} = \mathrm{BCMePT\ or\ BCMeOPT}) \qquad (5)$$

$$n\mathrm{CdCl_2} + n\mathrm{L} \xrightarrow{\text{EtOH, reflux, 2 hr}} [\mathrm{CdLCl_2}]_n$$
$$(\mathrm{L} = \mathrm{BCMePT\ or\ BCMeOPT\ or\ BCBrPT}) \qquad (6)$$

$$\begin{aligned}&MCl_2 + L \xrightarrow{\text{EtOH, reflux, 2 hr}} [MLCl_2]\\&\quad (L = \text{BCMePT or BCMeOPT or BCBrPT and}\\&\quad M = \text{Zn(II) or Hg(II)})\end{aligned} \tag{7}$$

$$\begin{aligned}&nM(NO_3)_x \cdot 6H_2O + nL \xrightarrow{\text{EtOH, reflux, 2 hr}} [ML(NO_3)_x]_n + 6H_2O\\&\quad (L = \text{BCMePT or BCMeOPT or BCBrPT;}\\&\quad M = UO_2(\text{VI}), x = 2 \text{ and } n = 2;\ M = \text{Th(IV)}, x = 4)\end{aligned} \tag{8}$$

The analytical data (Table 2) indicate 1 : 1 metal : ligand ratio for all complexes. All the complexes are stable towards air and light and are soluble in DMF, DMSO, and pyridine and insoluble in common organic solvents. The molar conductance values of the complexes in DMF (10^{-3} M) solution fall in the range of 8.25–18.80 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$. These values are too low to account for any electrolytic behaviors of the complexes[8] (Table 2).

Electronic Spectra

In the electronic spectrum of the Co(II) complexes in DMF (10^{-3} M) solution, the two bands observed in the regions 17,860–18,180 and 20,000–20,830 cm^{-1} are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively, in an octahedral environment.[9] The high-energy band observed around 30,000 cm^{-1} is assigned to metal–ligand charge transfer bands. The octahedral geometry is further supported by the values of the ligand field parameters Dq, B', β, $\beta\%$, and LFSE (Table 3). The reduction in the values of the Racah parameter B' from the free ion value (971) and the $\beta\%$ values testify to the presence of strong metal–ligand covalent bonding in the complexes. The magnetic moment values of the Co(II) complexes lie in the range of 4.69–5.09 B.M. and these values are indicative of octahedral structures for these complexes.[10]

The light-green Ni(II) complexes show two bands the regions 13,510–14,080 and 25,320–26,040 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively, in an octahedral geometry in view of earlier reports.[11] However, the ν_1 band could not be observed due to the limited spectral range of the instrument and, hence, these values were calculated using band-fitting procedures.[12] The values of the Racah parameter B' is less than the free ion (1040) value indicating considerable covalent character of the metal–ligand bond. The transition ratio ν_2/ν_1 is in the range 1.61–1.82 as expected for octahedral Ni(II) complexes.

Table 2. Analytical, molar conductance, and magnetic susceptibility data of the thiosemicarbazide complexes.

				Anal. %, Found (calcd.)					
Ligand/complex	Formula weight	Yield (%)	M.p (°C)	M	N	Cl	S	Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$)	μ_{eff} (B.M.)
$[Co(BCMePT)Cl_2]_n$	454.93	70	279	12.91	9.21	15.61	7.01	17.95	5.00
$C_{17}H_{15}Cl_2CoN_3O_2S$				(12.95)	(9.23)	(15.60)	(7.03)		
$\{[Ni(BCMePT)Cl_2]\cdot H_2O\}_n$	472.69	75	290 d	12.40	8.85	15.41	6.35	16.85	2.98
$C_{17}H_{17}Cl_2N_3NiO_3S$				(12.41)	(8.88)	(15.02)	(6.76)		
$[Cu(BCMePT)Cl_2]_n$	459.50	80	>300	13.79	9.62	15.92	6.45	10.65	1.89
$C_{17}H_{15}Cl_2CuN_3O_2S$				(13.81)	(9.14)	(15.45)	(6.96)		
$[Zn(BCMePT)Cl_2]$	459.37	80	250 d	14.12	9.10	15.24	6.55	15.85	—
$C_{17}H_{15}Cl_2N_3O_2SZn$				(13.79)	(9.14)	(15.45)	(6.93)		
$[Cd(BCMePT)Cl_2]_n$	508.41	75	280	22.65	8.04	13.45	5.95	14.54	—
$C_{17}H_{15}CdCl_2N_3O_2S$				(22.11)	(8.26)	(13.96)	(6.29)		
$[Hg(BCMePT)Cl_2]$	596.59	75	275	33.30	7.55	11.45	5.85	17.00	—
$C_{17}H_{15}Cl_2HgN_3O_2S$				(33.62)	(7.04)	(11.90)	(5.36)		
$[UO_2(BCMePT)(NO_3)_2]$	719.00	80	290 d	33.55	9.51	—	4.80	16.45	—
$C_{17}H_{15}N_5O_{10}SU$				(33.10)	(9.73)		(4.45)		
$[Th(BCMePT)(NO_3)_4]$	805.00	75	250	28.65	12.57	—	3.65	10.65	—
$C_{17}H_{15}N_7O_{14}STh$				(28.81)	(12.17)		(3.97)		
$[Co(BCMeOPT)Cl_2]_n$	470.93	78	285 d	12.02	8.55	14.50	6.52	15.40	4.69
$C_{17}H_{15}Cl_2CoN_3O_2S$				(12.51)	(8.92)	(15.07)	(6.79)		
$\{[Ni(BCMeOPT)Cl_2]\cdot H_2O\}_n$	488.69	80	>300	12.42	8.90	15.01	6.76	13.65	3.20
$C_{17}H_{17}Cl_2NiN_3O_4S$				(12.00)	(8.59)	(14.52)	(6.55)		
$[Cu([BCMeOPT)Cl_2]_n$	475.50	80	290 d	13.85	8.25	14.54	6.85	16.95	2.01
$C_{17}H_{15}Cl_2CuN_3O_2S$				(13.35)	(8.83)	(14.93)	(6.72)		

[Zn([BCMeOPT)Cl$_2$]	475.38	75	290	13.02	8.50	14.45	6.95	8.95	—
$C_{17}H_{15}Cl_2N_3O_2SZn$				(13.33)	(8.83)	(14.93)	(6.73)		
[Cd([BCMeOPT)Cl$_2$]$_n$	524.41	75	280 d	20.15	8.50	13.01	5.80	16.78	—
$C_{17}H_{15}CdCl_2N_3O_2S$				(20.43)	(8.01)	(13.53)	(6.10)		
[Hg([BCMeOPT)Cl$_2$]	612.59	80	255 d	32.32	6.95	11.16	5.65	17.97	—
$C_{17}H_{15}Cl_2HgN_3O_2S$				(32.74)	(6.85)	(11.59)	(5.22)		
[UO$_2$([BCMeOPT)(NO$_3$)$_2$]	735.00	85	280	32.00	9.10	—	4.75	18.80	—
$C_{17}H_{15}N_5O_{11}SU$				(32.38)	(9.52)		(4.35)		
[Th([BCMeOPT)(NO$_3$)$_4$]	821.00	80	300 d	28.78	11.41	—	3.54	10.87	—
$C_{17}H_{15}N_7O_{15}STh$				(28.22)	(11.93)		(3.89)		
{[Co(BCBrPT)Cl$_2$] · H$_2$O}$_n$	537.93	80	>300	10.45	8.15	13.65	5.42	17.95	5.09
$C_{16}H_{14}BrCl_2CoN_3O_3S$				(10.95)	(7.80)	(13.20)	(5.94)		
[Ni(BCBrPT)Cl$_2$]$_n$	519.69	75	>300	10.89	7.80	13.22	5.91	17.00	3.21
$C_{16}H_{12}BrCl_2N_3NiO_2S$				(11.29)	(8.08)	(13.66)	(6.15)		
[Cu(BCBrPT)Cl$_2$]$_n$	524.50	80	288 d	12.52	7.88	13.12	5.85	10.75	1.90
$C_{16}H_{12}BrCl_2CuN_3O_2S$				(12.10)	(8.00)	(13.54)	(6.10)		
[Zn(BCBrPT)Cl$_2$]	524.39	80	260	13.31	8.58	14.44	6.51	15.80	—
$C_{16}H_{12}BrCl_2N_3O_2SZn$				(12.08)	(8.00)	(13.53)	(6.10)		
[Cd(BCBrPT)Cl$_2$]$_n$	573.41	78	260	19.49	7.68	12.02	5.15	14.54	—
$C_{16}H_{12}BrCdCl_2N_3O_2S$				(19.60)	(7.32)	(12.38)	(5.58)		
[Hg(BCBrPT)Cl$_2$]	661.59	70	290	30.45	6.00	9.95	4.45	8.25	—
$C_{16}H_{12}BrCl_2HgN_3O_2S$				(30.32)	(6.34)	(10.73)	(4.83)		
[UO$_2$(BCBrPT)(NO$_3$)$_2$]	783.90	75	>300	30.10	8.58	—	4.40	10.65	—
$C_{16}H_{12}BrN_5O_{10}SU$				(30.36)	(8.92)		(4.08)		
[Th(BCBrPT)(NO$_3$)$_4$]	869.90	78	285 d	26.25	11.00	—	3.21	18.00	—
$C_{16}H_{12}BrN_7O_{16}STh$				(26.66)	(11.26)		(3.67)		

Note: d, decomposition temperature.

Table 3. Electronic spectral data and ligand field parameters of the Ni(II), Cu(II), and Co(II) complexes with BCMePT, BCMeOPT, and BCBrPT thiosemicarbazide ligands.

	Transitions (cm^{-1})								
Complex	ν_1^a	ν_2^b	ν_3^b	Dq (cm^{-1})	B' (cm^{-1})	β'	$\beta\%$	ν_2/ν_1	LFSE kcal.
[Co(BCMePT)Cl$_2$]$_n$	8,512	18,180 (150)	20,000 (440)	996	842	0.99	13.20	2.14	16.57
{[Ni(BCMePT)Cl$_2$] · H$_2$O}$_n$	8,310	13,890 (98)	25,320 (340)	831	952	0.92	8.46	1.67	28.49
[Cu(BCMePT)Cl$_2$]$_n$	14,930–13,790 (275)			1,316	—	—	—	—	22.56
[Co(BCMeOPT)Cl$_2$]$_n$	8,430	18,020 (145)	20,200 (425)	954	862	0.89	11.22	2.14	16.44
{[Ni(BCMeOPT)Cl$_2$] · H$_2$O}$_n$	8,010	13,510 (95)	25,640 (350)	801	1,008	0.97	30.76	1.68	27.46
[Cu (BCMeOPT)Cl$_2$]$_n$	15,620–12,990 (290)			1,370	—	—	—	—	23.48
{[Co(BCBrPT)Cl$_2$] · H$_2$O}$_n$	8,338	17,860 (140)	20,830 (350)	952	911	0.94	6.11	2.14	16.32
[Ni(BCBrPT)Cl$_2$]$_n$	8,395	14,080 (100)	26,040 (370)	839	995	0.96	4.27	1.67	28.76
[Cu(BCBrPT)Cl$_2$]$_n$	16,260–15,380 (310)			1,550	—	—	—	—	26.58

[a] Calculated values.

[b] Extinction coefficient values are given in parentheses (in units of L/mol/cm).

The magnetic moment values of the Ni(II) complexes are in the range of 2.98–3.21 B.M., and are evidence for an octahedral structure.[13] The bands around 29,000 cm^{-1} are assigned to charge transfer bands.

The Cu(II) complexes exhibit a broad asymmetric band envelop in the region of 16,260–12,990 cm^{-1} attributable to the $^2E_g \rightarrow {}^2T_g$ transition in a distorted octahedral environment. The broadness of the band may be due to dynamic Jahn-Teller distortion. The magnetic values of 1.89–2.01 B.M. further support the octahedral structures for the Cu(II) complexes.[7]

Infrared Spectra

All the ligands show three absorption bands in the regions of 3442–3431, 3227–3370, and 3158–3180 cm^{-1} which are assigned to ^{4}NH, ^{2}NH, and ^{1}NH stretching vibrations, respectively.[14,15] The bands due to ^{4}NH and ^{1}NH stretching vibrations are observed almost at the same position or shifted to the higher wave number side by about 5–10 cm^{-1} in some complexes, thereby indicating no coordination through these groups with metal ions. The shift to the lower wave number side observed for the ^{2}NH stretching vibrations in the spectra of all complexes by about 15–40 cm^{-1} indicates the coordination of the ligand through the nitrogen atom of the ^{2}NH group.

No bands were observed above 3500 cm^{-1} and around 2600 cm^{-1} due to OH and SH stretching vibrations in the free ligands which suggests that all of the ligands exists in the thioketo form. The Ni(II) complexes of BCMePT and BCMeOPT and the Co(II) complex of BCBrPT contain a water molecule of hydration and this is confirmed by their weight loss when these complex on drying in an oven at around 110 °C lose a water molecule suggesting the presence of a lattice-held water molecule and not a coordinated one. According to Nikolaev *et al.*[16] water eliminated below 150 °C can be considered as lattice-held water molecules.

The medium to strong intensity bands observed in the region 1657–1680 cm^{-1} in the free ligands are assigned to C=O stretching vibrations.[17] These bands shift to the lower wave number side by about 20–50 cm^{-1} in the complexes suggesting the coordination of the oxygen atom of the carbonyl group. The coordination of the nitrogen of the hydrazine group is further supported by the shift of the (N–N) stretching vibrations in the complexes to higher wave numbers by about 5–10 cm^{-1}, which were observed in the 1010–1030 cm^{-1} region in the free ligands.[18]

The thioketo C=S stretching absorption bands observed in the region of 730–800 cm^{-1} show no shift on complexation compared with the free ligand, thus, the sulfur atom does not take part in bonding with metal ions. The thioamide bands observed in the regions 1545–1520, 1350–1340, 1080–1040, and 720–800 cm^{-1} are due to the amide I, II, III, and IV bands, respectively.[19] The band IV having a major contribution from the C=S stretching vibration shows no change in its position in the complexes suggesting the non-participation of the sulfur atom in coordination.

The assignments of bands in the far-infrared region have been controversial over the years, yet studies are useful as direct information about the metal–ligand coordination bond are obtained. The non-ligand bands observed in the regions 575–495 and 480–420 cm^{-1} are assigned to ν(M–N) and ν(M–O) stretching vibrations, respectively, in all of the complexes.[20] In the case of polymeric complexes where both terminal and bridging metal halogen linkages are present, the terminal M–Cl stretch occurs at the higher wave number side than the bridging M–Cl stretching vibrations[21] In view of this, we have assigned broad and weak-intensity, non-ligand bands observed in, the regions 380–360 and 290–320 cm^{-1} to ν(M–Cl) terminal and ν(M–Cl) bridging vibrations, respectively, for the Co(II), Cu(II), Ni(II), and Cd(II) complexes in view of their chloride bridged polymeric structures. The bands in the region 320–360 cm^{-1} are assigned to ν(M–Cl) vibrations of the Zn(II) and Hg(II) complexes (Fig. 2).

In the UO_2(VI) and Th(IV) complexes the additional bands observed at 1030 and 1040 cm^{-1} are assigned to ν_3 vibrations of the coordinated NO_3 group.[22] The characteristic bands observed at 910 and 930 cm^{-1}, respectively, indicate the linear character of the UO_2 group.

Biological Activity

All the thiosemicarbazide ligands, complexes, and metal salts were tested for their antimicrobial activity against the bacteria *E. coli*, *Pseudomonas*, *B. subtilus*, and *Wild bacillus* by the cup–plate zone inhibition technique,[23] at concentrations of 10 mg/mL in DMF solution. The standard used was gentamycine sulfate 40 μg/mL and the solvent control was also used to determine the activity of the solvent. The Ni(II), Cd(II), and Hg(II) complexes of BCMePT are more active against all the bacteria compared with the metal salts and ligands, whereas the UO_2(VI) and Th(IV) complexes are more active against *Wild bacillus* only. In the case of BCMeOPT, the Hg(II) and UO_2(VI) complexes are moderately active towards *Wild bacillus.* The Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes of BCBrPT are moderately active against *Wild bacillus* and the Ni(II) and Hg(II) complexes are moderately active against *Pseudomonas* and *E. coli* bacteria, respectively. All the ligands and the other metal complexes are inactive against all the bacteria tested. The Ni(II), Cd(II), and Hg(II) complexes of BCMePT are almost as

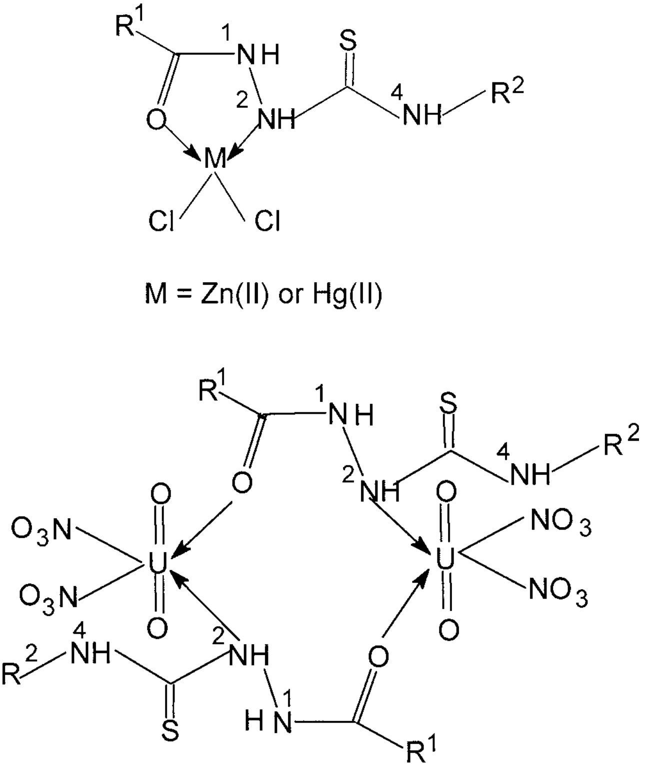
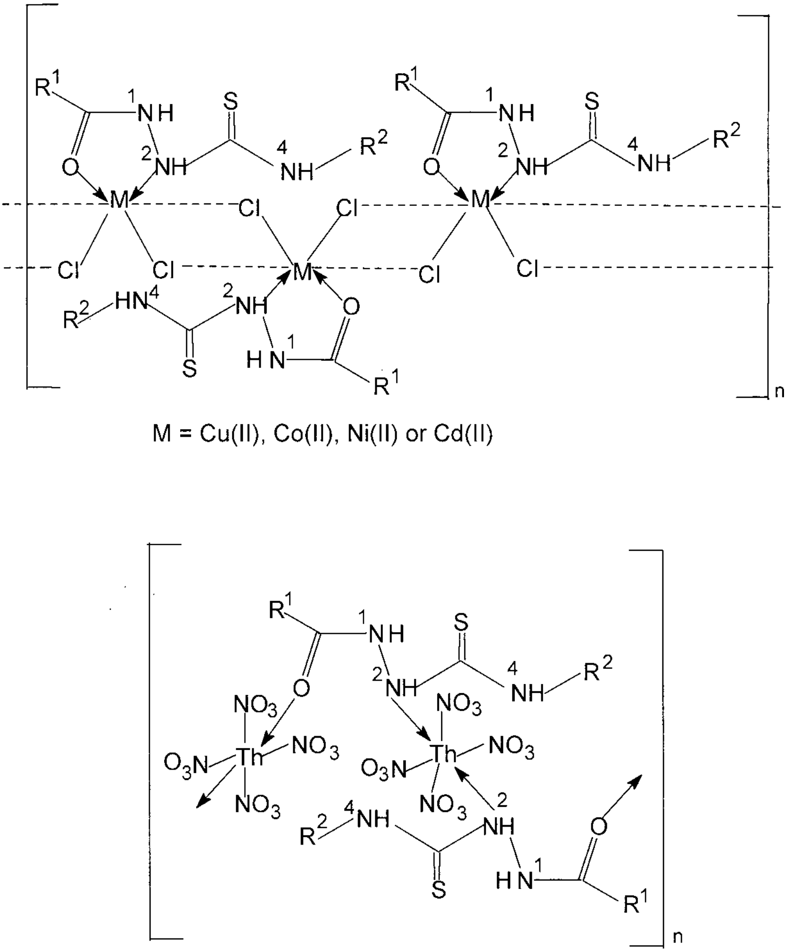


Figure 2. Suggested structures of the complexes.

active as the standard gentamycine sulfate. These preliminary results show that the activity of the ligands has been enhanced when it is applied in the form of metal complexes.

CONCLUSION

On the basis of elemental analyses, magnetic moments, conductance data, IR, and electronic spectral studies and the high melting points and insolubility in common organic solvents, we tentatively propose chloride bridged polymeric octahedral structures for the Co(II), Cu(II), Ni(II), and Cd(II) complexes whereas monomeric tetrahedral structures are suggested for Zn(II) and Hg(II) complexes. A diameric octahedral structure is suggested for the



Scheme 1.

UO_2(VI) complexes and ligand bridged polymeric six coordination is assigned to the Th(IV) complexes.

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