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Synthesis and Characterization of a Novel Series of Metallothiocarbohydrazone Polymers and Their Adducts

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ABSTRACT: *A novel linear polymeric pentadentate (O_2N_2S-sites) ligand (H_3L) bearing both soft and hard donors was prepared by the reaction of a bifunctional carbonyl compound, 4,6-diacetylresorcinol, with a bifunctional hydrazide compound, thiocarbohydrazide. Mono- and binuclear Cu^{II} and Ni^{II} complexes/each monomeric unit of the polymeric ligand were obtained depending on the pH of the reaction medium and the metal ion. Adducts with 1,10-phenanthroline (Phen) and 2,2′-bipyridyl (Bpy) were obtained. Anomalous dimeric Co^{II}/Co^{III} complexes of the polymeric ligand were obtained in which two molecules of the linear polymeric ligand trapped two cobalt ions (Co^{II} and Co^{III}) in each monomeric unit. These structures are very interesting in that they contain Co^{II}/Co^{III}, side by side, as high-spin square planar coordinated Co^{II} ions and low-spin (diamagnetic) octahedral coordinated Co^{III} ions. The suggested structures of the complexes have been elucidated on the basis of elemental and thermal analyses, conductance, and magnetic susceptibility measurements as well as spectral studies (electronic, IR, and ESR spectra).* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:100–107, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20239

INTRODUCTION

The design and study of the well-arranged metal-containing macrocycles is one of the major current research areas in modern supramolecular chemistry [1]. Such complexes are of interest not only for their unusual structures and the simple synthetic methods used to prepare them but also for their special functional properties such as luminescence [2], redox activity [3], and magnetism [4]. However, in the absence of a templating agent, the reaction of 4,6-diacetylresorcinol with thiocarbohydrazide afforded a polymeric ligand, poly(thiocarbohydrazone) (H_3L). Herein, we report a novel rigid pentadentate O_2N_2S polymeric ligand (H_3L) bearing both hard and soft donor atoms and its metal complexes with Cu^{II}, Co^{II}, and Ni^{II} ions. This study is a continuation of our interest on thiosemicarbazones and semicarbazones [5–8].

EXPERIMENTAL

The chemicals used were either Aldrich, BDH, or Merck products. Apparatus and physical measurements are same as previously described [6–8].

Preparation of H_3L Ligand

A boiling solution of 4,6-diacetyl resorcinol (0.01 mol) in methanol containing two drops of concentrated HCl was added to the suspension of thiocarbohydrazide (0.02 mol) in methanol with stirring. The reaction mixture was refluxed for

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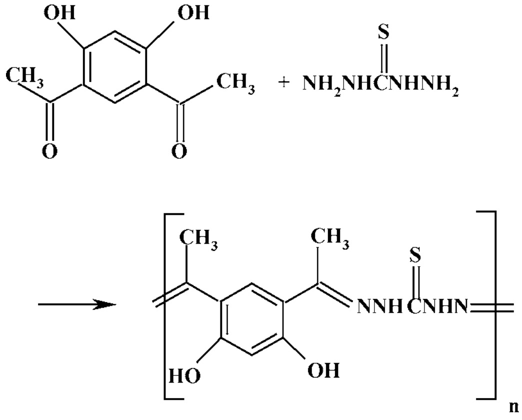
TABLE 1 Analytical and Physical Data of H_3L Ligand and its Metal Complexes

					Elemental Analysis, Found/(Calcd) (%)				
Compound	*Reactants*	*Complexes*	*Color*	*Yield (%)*	*C*	*H*	*N*	*S*	*M*
	H_3L		Yellow	52	50.00 (49.99)	4.30 (4.58)	20.87 (21.20)	12.35 (12.13)	–
1	$H_3L + Cu(NO_3)_2{\cdot}2.5H_2O$	$\{[(HL)Cu(H_2O)]\}_n$	Deep green	65	38.40 (38.42)	3.90 (3.52)	15.85 (16.29)	9.12 (9.32)	18.50 (18.48)
2	$H_3L^3 + Cu(NO_3)_2{\cdot}2.5H_2O + LiOH$	$\{[(L)Cu_2(OH)(H_2O)]H_2O\}_n$	Brown	55	30.13 (29.93)	3.38 (3.20)	12.31 (12.69)	7.41 (7.26)	28.50 (28.79)
3	$H_3L + Cu(OAc)_2{\cdot}H_2O$	$\{[(H_2L)Cu(OAc)]2EtOH\}_n$	Green	72	43.10 (42.71)	4.90 (5.48)	11.28 (11.72)	6.54 (6.71)	13.10 (13.29)
4	$H_3L + Cu(NO_3)_2{\cdot}2.5H_2O + LiOH + Phen$	$\{[(L)Cu_2(OH)(H_2O)_2(Phen)]1/2EtOH\}_n$	Olive-green	35	44.84 (44.72)	3.84 (3.91)	12.79 (913.04)	5.12 (4.94)	19.50 (19.71)
5	$H_3L + Cu(NO_3)_2{\cdot}2.5H_2O + LiOH + Bpy$	$\{[(L)Cu_2(NO_3)(H_2O)_4(Bpy)]\}_n$	Olive-green	33	37.21 (37.17)	3.83 (3.71)	14.71 (14.45)	4.37 (4.72)	18.40 (18.73)
6	$H_3L + Ni(NO_3)_2{\cdot}6H_2O + LiOH$	$\{[(L)Ni_2(OH)(H_2O)_3]1/2EtOH\}_n$	Deep brown	61	30.96 (30.49)	3.98 (4.05)	11.58 (11.85)	6.41 (6.78)	24.60 (24.84)
7	$H_3L + Ni(NO_3)_2{\cdot}6H_2O + LiOH + Phen$	$\{[(L)Ni_2(OH)(H_2O)_4(Phen)]1/2H_2O\}_n$	Brown	40	41.92 (42.05)	3.56 (4.14)	12.45 (12.79)	5.02 (4.88)	17.70 (17.87)
8	$H_3L + Ni(NO_3)_2{\cdot}6H_2O + LiOH + Bpy$	$\{[(L)Ni_2(OH)(H_2O)_4(Bpy)]\}_n$	Brown	43	40.28 (40.42)	4.00 (4.20)	13.80 (13.47)	5.30 (5.14)	18.70 (18.82)
9	$H_3L + Co(NO_3)_2{\cdot}6H_2O$	$\{[(L)(HL)Co_2(H_2O)_2]H_2O\}_n$	Brown	77	37.90 (37.99)	4.00 (3.62)	15.70 (16.11)	9.40 (9.22)	16.70 (16.95)
10	$H_3L + Co(NO_3)_2{\cdot}6H_2O + LiOH$	$\{[(L)Co_2(OH)(H_2O)]1/2EtOH\}_n$	Brown	74	33.02 (32.97)	3.62 (3.46)	12.44 (12.81)	7.61 (7.33)	26.60 (26.96)
11	$H_3L + Co(NO_3)_2{\cdot}6H_2O + Phen$	$\{[(L)(HL)Co_2(Phen)(H_2O)]1/2EtOH\}_n$	Brown	50	48.93 (48.90)	4.50 (4.21)	15.60 (15.41)	6.90 (7.06)	12.80 (12.97)
12	$H_3L + Co(NO_3)_2{\cdot}6H_2O + Bpy$	$\{[(L)(HL)Co_2(Bpy)(H_2O)]1/2H_2O\}_n$	Brown	50	45.65 (45.61)	4.02 (3.83)	16.20 (16.62)	7.80 (8.61)	13.70 (13.99)

4 h, cooled, filtered off, washed with methanol, and crystallized from water/DMF. The preparation was repeated using (0.01 mol) thiocarbohydrazide, where the same product was obtained. The results of elemental analyses, color, and percentage yield are shown in Table 1.



$(C_{11}H_{12}N_4O_2S)_n$

H_3L

Preparation of the Metal Complexes

The following detailed preparations are given as examples and the other complexes were obtained similarly.

Preparation of the $\{[(H_2L)Cu(OAc)]{\cdot}2EtOH\}_n$ Complex. An ethanolic solution (40 mL) of $Cu(OAc)_2{\cdot}H_2O$ (0.775 g; 3.78 mmol) was added gradually to the suspension of the ligand (H_3L) in ethanol (40 mL) (0.5 g; 1.89 mmol). The mixture was refluxed for 5 h and a green complex was precipitated. The precipitate was filtered off, washed with ethanol and then diethyl ether, and finally air-dried. Yield, 0.652 g (72%).

Preparation of the $[(HL)Cu(H_2O)]_n$ Complex. An ethanolic solution (40 mL) of $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.88 g; 3.78 mmol) was added gradually to the suspension of the ligand (H_3L) in ethanol (40 mL) (0.5 g; 1.89 mmol). The mixture was refluxed for 5 h and a green complex was precipitated. The precipitate was filtered off, washed with ethanol and then diethyl ether, and finally air-dried. Yield, 0.422 g (65%).

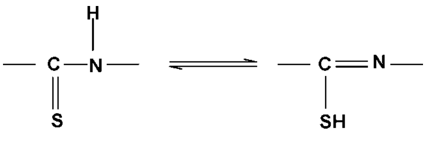
Preparation of Mixed Ligand Complexes (Adducts)

An ethanolic solution (40 mL) of $Cu(NO_3)_2{\cdot}2.5H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, or $Co(NO_3)_2{\cdot}6H_2O$ was added gradually to the suspension of the ligand (H_3L) in ethanol (40 mL) in the 2:1 molar ratio ($M{:}H_3L$). The mixture was refluxed for 1/2 h, and then an ethanolic solution of 1,10-phenanthroline (Phen) or 2,2′-bipyridyl (Bpy) was added to the previous solution to verify the molar ratio 2:1:2 (metal ion:ligand:base). The solution was refluxed continuously for 5 h when the solid complexes were precipitated. The precipitates were filtered off, washed with ethanol and then diethyl ether, and finally air-dried. Some complexes were prepared in the presence of LiOH (Table 1) as follows: 2 mmol of $LiOH{\cdot}H_2O$ was dissolved in a least amount of bidistilled water (~5 mL). This solution was added dropwise to the suspension of the ligand (1 mmol) with stirring, then an ethanolic solutions of metal ion (2 mmol) was added gradually, and finally the reaction mixture was refluxed for 5 h as described previously.

RESULTS AND DISCUSSION

Ligand

The structure of the ligand has been elucidated by elemental analysis, UV-Vis, IR, and ^1H NMR spectra. The results of elemental analyses (Table 1) are consistent with both the empirical formula ($C_{11}H_{12}O_2N_4S$) of the H_3L ligand and the proposed stoichiometries of its solid complexes. The IR spectrum of the polymeric H_3L ligand (Table 2) shows bands at 3323, 2924, and 1639 cm^{-1}, which are attributed to $\nu(NH)$, $\nu(OH{\cdots}N)$ and $\nu(C{=}N)$, respectively. The four bands at 1513, 1371, 1022, and 816 cm^{-1} may be assigned to thioimide-I, -II, -III, and -IV vibrations, respectively. The four thioimide bands are due to strong coupling between C=S and C—N stretching modes [9,10]. In particular, band I has contributions from $\delta(NH) + \delta(CH) + \nu(CN)$, band II has contributions from $\nu(CN) + \delta(NH) + \delta(CH) + \nu(CS)$, band III has contributions from $\nu(CN) + \nu(CS)$, and band IV has contributions from $\nu(CS)$. The four thioimide bands as well as an IR band around 2600 cm^{-1} due to $\nu(SH)$ indicate the thione nature of the ligand as evidenced from the ^1H NMR spectrum. The ligand has the following tautomeric structures:



The electronic spectrum of the ligand in DMF showed bands at 225, 249, 272, 284, and 340 nm (Table 3). The higher energy bands in the region 225–272 nm are assigned to π–π^* transitions of the azomethine linkage and the aromatic benzene ring.

TABLE 2 IR Spectral Data of the Metal Complexes

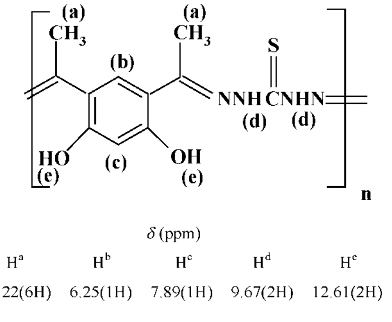
	IR Spectral Bands (cm^{-1})								
Complex	νH_2O	νNH	$\nu C{=}N$ *Free*	$\nu C{=}N$ *Coord*	$\nu C{=}S$	$\nu C{-}N + \delta NH$	δNH	$\nu C{-}S$	*Other Bands*
1	3422	3323	1634	1581	–	1374	1024	832	–
2	3401	3298	1634	1583	–	1369	1023	831	–
3	3393	3207	–	1583	1500	1373	1026	–	1610, $\nu C{=}O$; 1380, $\nu C{-}O$
4	3420	3210	1631	1599	–	1370	1022	846	1534,$\nu C{=}N$ (Phen)
5	3400	3324	1635	1594	–	1372	1023	862	1522, $\nu C{=}N$ (Bpy), 1441(ν_5),1373 (ν_1)(NO_3^-)
6	3381	3218	1632	1587	–	1368	1023	858	–
7	3397	3194	1631	1589	–	1373	1024	847	1538, $\nu C{=}N$ (Phen)
8	3390	3200	1631	1584	–	1366	1024	861	1536, $\nu C{=}N$ (Bpy)
9	3390	3143	1635	–	–	1370	1026	842	–
10	3382	3170	1633	1600	–	1371	1023	848	–
11	3424	3212	1632	–	–	1373	1022	844	1538, $\nu C{=}N$ (Phen)
12	3417	3324	1635	–	–	1369	1024	850	1535, $\nu C{=}N$ (Bpy)

TABLE 3 Electronic Spectra, Magnetic Moments, and Molar Conductivity Data of the Metal Complexes

Complex	*Electronic Spectral Bands (nm)*	$\mu^a_{eff.}$ *(BM)*	$\mu^b_{complex}$ *(BM) Found/Calcd*	*Conductance*[c] ($\Omega^{-1} cm^2\ mol^{-1}$)
1	424, 443, 465	1.60	–	25.0
2	(530)[d]	1.60	2.10/2.45	Insol.
3	425, 440, 474	1.55	–	5.0
4	420, 448, 465	1.66	2.10/2.45	28.0
5	425, 447	1.70	2.15/2.45	24.0
6	425, 556	2.30	2.30/4.0	16.0
7	430, 543	2.15	2.90/4.0	10.0
8	424, 540	2.30	3.10/4.0	8.0
9	425, 453	2.07	–	38.0
10	(415, 610)[d]	3.23	4.60/5.48	Insol.
11	425, 439	1.76	–	10.0
12	425, 447	1.72	–	19.0

[a] μ_{eff} is the magnetic moment of one cationic species in the complex.
[b] $\mu_{complex}$ is the total magnetic moment of all the cations in the complex.
[c] Solutions in DMF (10^{-3}M).
[d] Nujol mull.

The medium energy band at 284 nm may be assigned to n–π^* transitions of the C=N and C=S groups. Finally, the lower energy band at 340 nm is attributed to charge transfer (CT) transitions within the molecule. The ^{1}H NMR spectral data (δ ppm) of the ligand relative to TMS (0 ppm) in DMSO-d_6 lend further support to the suggested structure of the ligand (Scheme 1). All peaks were recorded as singlets and are exchangeable with D_2O except methyl and aromatic protons. These data together with the data derived from the elemental analysis, IR, and electronic spectra confirmed the structure of the H_3L ligand.



SCHEME 1 ^{1}H NMR spectral data of the H_3L ligand.

Metal Complexes

All the complexes are stable at room temperature, nonhygroscopic, and insoluble in water, alcohols, and most organic solvents. Their colors range from olive green to dark brown. The melting points of both the ligand and its complexes are above 300°C. Characterization and structure elucidation of the solid metal complexes have been deduced by elemental and thermal (TG-DSC) analyses, spectral data (UV-Vis, IR, and ESR spectra) as well as conductivity and magnetic susceptibility measurements.

The reaction of the ligand with the transition metal ions can proceed via the phenolic oxygen and azomethine nitrogen in addition to either thione or thiol sulfurs.

IR Spectra of the Metal Complexes

The IR spectra of all the complexes have nearly the same general features. On examining the IR spectra of the metal complexes in comparison to that of the free ligand (Table 2), one can conclude the following: (i) All the complexes exhibit broad bands around 3400 cm^{-1} attributed to ν(OH) of the coordinated/solvated water or ethanol molecules and/or the noncoordinated phenolic groups. (ii) The ν(OH$\cdots$N) band located at 2924 cm^{-1} in the free ligand disapeared in the spectra of all the binuclear complexes, suggesting the participation of the phenolic group in the chelation after deprotonation and hence leading to a covalent linkage. (iii) The strong band at 1639 cm^{-1} assigned to ν(C=N) in the free ligand was splitted into two bands at 1631–1635 cm^{-1} and 1581–1600 cm^{-1} due to the free and coordinated C=N groups, respectively, in most complexes (Table 2). (iv) The disappearance of ν(C=S) band at 1513 cm^{-1} as well as the appearance of ν(C—S) band at 831–862 cm^{-1} (Table 2) upon complexation provides a strong evidence that the thiol sulfur participates in the chelation after deprotonation. (v) In case of the mixed ligand complexes (**4, 5, 7, 8, 11**, and **12**), the new bands at 1522–1538 cm^{-1}, which is attributed to the coordinated C=N group, indicate nitrogen coordination of the heterocyclic aromatic base (1,10-phenanthroline or 2,2′-bipyridyl) [11]. (vi) The appearance of two new bands around 1440 cm^{-1} (ν_5) and 1370 cm^{-1} (ν_1) in complex **5** confirmed the monodentate nature of the coordinated NO_3^- group [12]. As expected for the C_{2v} symmetry, these two NO stretching bands are assigned to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$, respectively. Also, the separation of these two bands, $\Delta\nu = \nu_5 - \nu_1 = \sim 70$ cm^{-1}, is comparable to the cited values reported for the unidentate character of the NO_3^- group [12]. (vii) For complex **3**, the bands located at 1610 and 1380 cm^{-1} (absent in the spectra of the free ligands) are due to ν(C=O) and ν(C—O) of the acetate group, respectively. These two bands indicate the coordinated nature of the acetate ion as a unidentate ligand [12]. (viii) Of the several bands observed in the far IR spectra, the non-ligand bands, ν(M—O), ν(M—N), and ν(M–S), were observed tentatively at 570–500, 450–415, and 350–300 cm^{-1}, respectively.

Conductivity Measurements

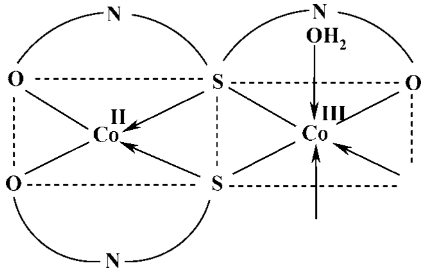
Molar conductances of 1×10^{-3} mol dm^{-3} solutions of the metal chelates in DMF were measured at room temperature and the results are listed in Table 3. The values lie in the range 5–38 ohm^{-1} cm^2 mol^{-1}, which indicate the nonelectrolytic nature of all the complexes.

UV-Visible, ESR, and Magnetic Moment Measurements

The visible spectra of the metal complexes (Table 3) were carried out as DMF solutions and/or Nujol mulls as some metal complexes were sparingly soluble in most common solvents. The bands of the free ligand were slightly shifted to blue or red regions of the spectrum in all the complexes and new bands were observed in the visible region due to d–d transitions (Table 3).

*Cobalt Complexes (**9–12**)*

The reaction of $Co(NO_3)_2 \cdot 6H_2O$ with the polymeric H_3L ligand in the absence and presence of Phen or Bpy afforded brown dimeric complexes (**9, 11**, and **12**) having magnetic moments, μ_{eff}, in the range 1.72–2.07 BM (Table 3). These lower values of magnetic moments suggest the presence of one unpaired electron as expected for a square planar geometry around Co^{II} ions. Also, the results of both elemental and thermal analyses suggest that both otcahedral (low spin) and square planar geometries exist together. In addition, the visible spectra of the dimeric cobalt complexes (**9, 11**, and **12**) showed two bands at 425 and 439–453 nm. The higher energy band at 425 nm in all the complexes is due to ligand-to-metal CT transitions while the bands at 439–453 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$, ν_2 transition for Co^{III} in low-spin octahedral geometry. The following considerations would be taken into account: (i) Octahedral low-spin Co^{II} complexes are nonexistent [13]. (ii) Octahedral high-spin Co^{III} complexes are unknown except $[CoF_6]^{3-}$ complex [13]. (iii) In the presence of strong field ligands, Co^{II} is easily oxidized to Co^{III} even by oxygen in air-giving low-spin diamagnetic octahedral Co^{III} complexes and hence a large CFSE. (iv) Such mixed states (+2, +3) were reported for ruthenium complexes [14] and in our previous study on cobalt thiosemicarbazones [8]. On the basis of the above, the cobalt complexes (monomeric unit) of the polymeric H_3L ligand have the following general structure:



The formation of such macrocycles, which is known as the macrocyclic effect [15], provides more structural stabilization and hence higher stability of the formed cobalt complexes. The replacement of two water molecules in complex **9** by one molecule of Phen or Bpy in complexes **11** and **12** was reflected in their magnetic moments and visible spectra (Table 3). Arguments supporting these anomalous Co^{II}/Co^{III} structures begin with the observation that a pronounced decrease in their μ_{eff} values was observed. Further evidences were found in their visible and IR spectra as well as elemental and thermal analyses. In general, the dimeric S-bonded cobalt complexes of the poly(thiocarbohydrazone) are similar and have the same general features, that is, they contain side by side Co^{II}/Co^{III} ions in which Co^{II} ion has a square planar configuration (high spin), while Co^{III} ion has an octahedral configuration (diamagnetic). In contrast, the reaction of $Co(NO_3)_2{\cdot}6H_2O$ with the polymeric H_3L ligand in the presence of LiOH afforded a binuclear complex/each monomeric unit (**10**) in which the Co^{II} ion has a tetrahedral configuration as evidenced from its magnetic moment ($\mu_{eff} = 3.23$ BM) and its visible spectrum [13]. The visible spectrum (Table 3) showed an intense broad band at 610 nm assignable to the main ν_3 transition, ${}^4A_2(F) \rightarrow {}^4T_1(P)$, which is characteristic of tetrahedral Co^{II} complexes. The higher energy band observed at 415 nm is due to ligand-to-metal CT transition.

*Ni^{II} Complexes (**6–8**)*

The reaction of $Ni(NO_3)_2{\cdot}6H_2O$ with the poly-H_3L ligand in the absence and presence of Phen or Bpy afforded paramagnetic binuclear complexes/each monomeric units (**6–8**). Their visible spectra in DMF showed strong peaks in the region of 424–430 nm assignable to ν_3 transition, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, and shoulders in the region of 540–556 nm (Table 3) assignable to ν_2 transition, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, which are characteristic of octahedral Ni^{II} complexes. In octahedral Ni^{II} complexes, the lowest energy band could not be located as it might be shifted almost to the near IR region. The magnetic moment of complex **6** (2.30 BM) is lower than that expected for octahedral geometry (4.0 BM) and suggests that both high-spin octahedral and diamagnetic square planar geometries exist together similar to those reported by Glick [16]. On the other hand, the magnetic moments of complexes **7** and **8** are 2.90 and 3.10 BM, respectively. These values are lower than the expected value (4.0 BM in absence of an external exchange interaction), indicating a strong antiferromagnetic exchange interaction between the adjacent Ni^{II} ions.

*Cu^{II} Complexes (**1–5**)*

The reaction of Cu^{II} nitrate or acetate with the poly-H_3L ligand afforded mononuclear complexes/each monomeric unit (**1** and **3**) while its interaction with Cu^{II} nitrate in the presence of LiOH or Phen or Bpy afforded binuclear complexes/each monomeric unit (**2, 4**, and **5**). The magnetic moments of Cu^{II} complexes of H_3L (Table 3) lie in the range 1.55–1.70 BM/Cu^{II} ion, indicating the presence of one unpaired electron (d^9). On the basis of the fact that the electronic spectra are very diagnostic of the stereochemistry, the electronic absorption spectra showed bands having λ_{max} at 420–448 and 465–530 nm, respectively (Table 3), indicating tetragonally elongated octahedral as well as square planar geometries around Cu^{II} ions. The ESR spectra of complex **1**, $\{[(HL)Cu(H_2O)]\}_n$, showed a signal having $g_{eff} = 1.835$, indicating a square planar geometry around Cu^{II} ion.

Thermal Analysis (TG-DSC)

TG-DSC studies were carried out on the ligand and its complexes at a heating rate of 10°C/min in nitrogen atmosphere (30 mL/min) over the temperature range 20–800°C. The results show good agreement with the theoretical formulae as suggested from elemental analyses. The polymeric ligand, H_3L, was found to be stable up to 220°C as indicated from its thermogram. However, the greater stability of the ligand as compared to its chelates suggests a powerful intramolecular H-bonding in the polymeric ligand [17,18]. The thermograms of the chelates can be subdivided into three or two main regions depending on the nature of the chelate. (i) The first region extends up to 158°C corresponding to the weight loss of the hydrated water molecules and/or solvated ethanol molecules during one exothermic process. (ii) The second region extends up to 287°C corresponding to the weight loss of the coordinated water molecules to verify the transformations, octahedral complex to square planar complex, in most systems during one endothermic process. (iii) Above 287°C, the complexes begin to decompose slowly at first, then increasing rapidly up to 800°C, with the formation of the corresponding metal oxides Co_3O_4, NiO, and Cu_2O. The metal content was found to be concordant with the results of elemental analyses. However, these general features depend largely on the nature of each complex. In case of some mixed ligand complexes **11** and **12**, the thermal degradation pattern may be represented as follows:

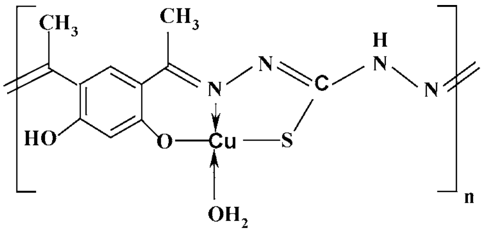
$$[(HL)(L)Co_2(Base)(H_2O)]n\ \text{solvent} \xrightarrow[-n\ \text{solvent}]{\text{up to } 155^\circ C}$$

$$[(HL)(L)Co_2(Base)(H_2O)]\ Co_3O_4 \xleftarrow{\text{up to } 800^\circ C}$$

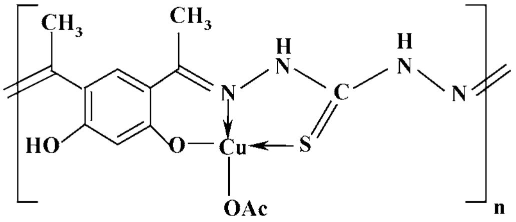
$$[(HL)(L)Co_2] \xleftarrow[-H_2O,\ -\text{Base}]{\text{up to } 360^\circ C}$$

CONCLUSION

The reaction of the poly(thiocarbohydrazone) H_3L ligand with the transition metal ions can proceed according to two pathways attaining either the thione structure (complex **3**) or the thiol structure (the other complexes) (Schemes 2 and 3). The polymeric Cu^{II} and Ni^{II} complexes (**1** and **6**) as well as the dimeric complex Co^{II}/Co^{III} of the polymeric ligand (**9**) showed a higher reactivity towards both Phen and Bpy (Schemes 4 and 5). The ligand showed a variety

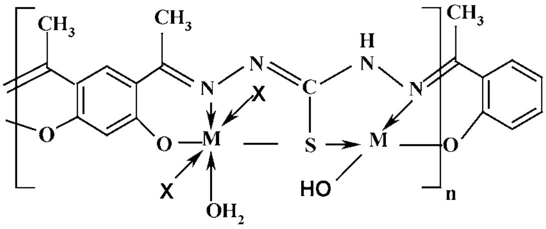


Complex 1



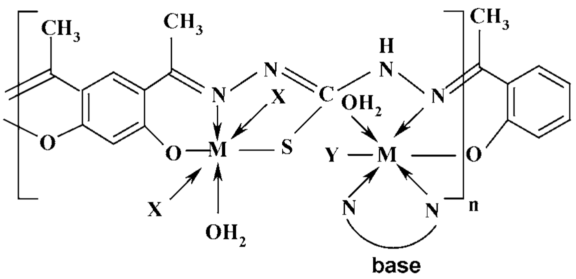
Complex 3

SCHEME 2 Cu^{II} complexes.



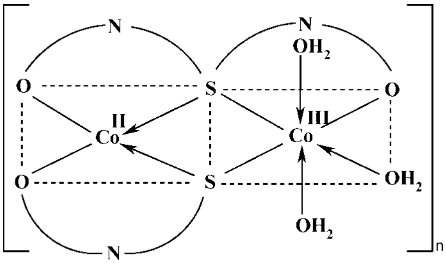
M^{II}	X	Complex
Cu	----	**2**
Co	----	**10**
Ni	H_2O	**6**

SCHEME 3 M^{II} complexes.

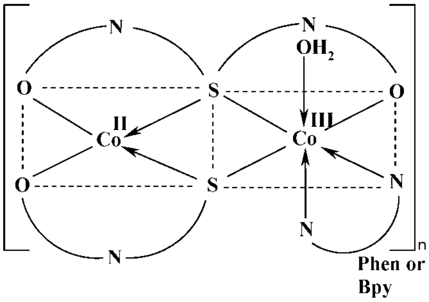


M^{II}	X	Y	Base	Complex
Cu	----	OH^-	Phen	**4**
Cu	OH_2	NO_3^-	Bpy	**5**
Ni	OH_2	OH^-	Phen	**7**
Ni	OH_2	OH^-	Bpy	**8**

SCHEME 4 Cu^{II} and Ni^{II} adducts.



Complex 9



Complexes 11 (Phen) and 12 (Bpy)

SCHEME 5 Dimeric Co^{II}/Co^{III} adducts.

of bonding modes, for example, trianionic pentadentate (O_2N_2S) with S-bridging (complexes **2, 6**, and **10**) and without S-bridging (complexes **4, 5, 7**, and **8**) as well as a dianionic or monoanionic tridentate (ONS) (complexes **1** and **3**).

On the basis of the above results, the proposed structures of the polymeric complexes can be formulated as shown in Schemes 2–5.

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