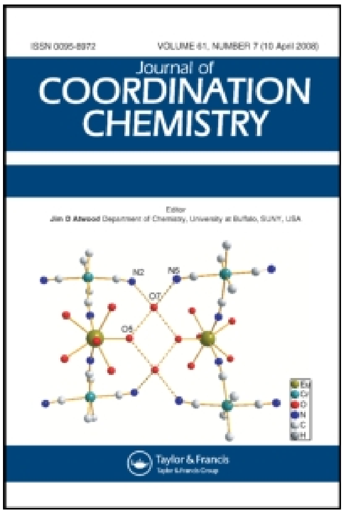

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Synthesis, spectral, thermal and electrochemical characterization of metal(II) complexes with 1-S-methylcarbodithioate-4-substituted thiosemicarbazides

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Synthesis, spectral, thermal and electrochemical characterization of metal(II) complexes with 1-S-methylcarbodithioate-4-substituted thiosemicarbazides

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1-S-Methylcarbodithioate-4-substituted thiosemicarbazides (L^1-L^3) have been prepared and confirmed by spectral data and elemental analysis. Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) complexes with L^1-L^3 have been prepared and characterized by elemental and thermal analyses, molar conductance, magnetic moment, as well as spectral data (IR, ^{1}H NMR, mass and electronic spectra). The molar conductance data reveal that the chelates are non-electrolytes. The IR and ^{1}H NMR spectra showed that L^1-L^3 are deprotonated in the complexes and act as binegative SNNS donors. The electronic spectra of the complexes as well as their magnetic moments provide information about geometries. Thermogravimetric analysis of some complexes suggests different decomposition steps and ending with metal sulfide as final product. The redox properties of the complexes are explored by cyclic voltammetry.

Keywords: S-Methylcarbodithioatethiosemicarbazide complexes; Spectra; Thermal; Electrochemical behavior

1. Introduction

Coordination chemistry of thiosemicarbazides has been studied in the past due to their mixed hard-soft donor character and versatile coordination behavior [1–4]. Thione compounds can act as anticarcinogenic or antitumor reagents [5–9]. In their metal complexes such donor systems are able to generate novel stereochemical, electrochemical and electronic properties [10–19]. Metal complexes of chelating agents derived from hydrazine-S-methyldithiocarboxylate and its acid amide were widely used as nitrogen-sulfur containing ligands [20–26]. In fact, hydrazinethiocarboxylate functioned as a bidentate ligand coordinating *via* one sulfur and the amino nitrogen of hydrazine residue [27]. The coordination chemistry of Schiff bases derived from hydrazine-S-methyldithiocarboxylate and the corresponding acid amide has been the subject of many studies [21, 25–30] and a series of *bis* ligand-Cu(II), Ni(II), Pd(II), and Pt(II) complexes were prepared and characterized [31]. Also, the synthesis and magnetic

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properties of Co, Ni, Cu and Pd complexes of a number of ONS tridentate Schiff bases derived from dithiocarboxylate have been reported [32].

Selective combination of two or more different donating groups into one molecule leads to a series of new ligands. Such composite ligands are 1-S-methylcarbodithioate-4-substituted thiosemicarbazides (L^1-L^3).

In the present work, 1-S-methylcarbodithioate-4-substituted thiosemicarbazides (L^1-L^3) (figure 1) were prepared. Their reactions with Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) salts were investigated and the complexes isolated (table 1) were studied using elemental and thermogravimetric analyses, molar conductance, magnetic measurements and spectral data (IR, ^{1}H NMR, mass and electronic spectra). One aim of the present study is focused on the redox behavior of 1-S-methycarbodithioate-4-phenylthiosemicarbazide-Co(II), Ni(II), Cu(II) or Cd(II) complexes, where the electron-accepting and electron-donating properties of the ligands are reflected in the electrochemical properties.

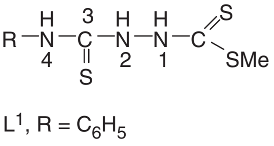
2. Experimental

2.1. *Materials*

The metal salts cobalt(II) chloride, nickel(II) chloride, copper(II) chloride, cadmium(II) chloride and zinc(II) chloride were analytical grade (Aldrich) and the solvents were purified by standard method [33]. Spectroscopic grade DMSO purchased from Aldrich was used for electronic spectral measurements.

2.2. *Preparation of 1-S-methylcarbodithioate-4-substituted thiosemicarbazides (L^1-L^3)*

To a stirred solution of hydrazine S-methyldithiocarboxylate (1.22 g, 10 mmol) in 30 ml dimethylformamide, each of the following isothiocyanates, phenylisothiocyanate (1.35 g, 10 mmol), benzylisothiocyanate (1.49 g, 10 mmol) or allylisothiocyanate (0.99 g, 10 mmol) was added dropwise at room temperature. Stirring was continued for 3 h at room temperature and the mixture set aside overnight, then added to 300 ml ice/water. A white precipitate formed and was recrystallized from ethanol to give L^1 (m.p. 169–171°C), L^2 (m.p. 186–188°C) and L^3 (m.p. 117–119°C). The IR and ^{1}H NMR spectral data of L^1-L^3 are in tables 2 and 3. The mass spectra of L^1, L^2 and L^3 as well as microanalytical data showed the following: L^1: 257 (M^+, 26), 209 (36), 135 (88), 77 (100), 65 (72). Anal. Calcd for $C_9H_{11}N_3S_3$ (%): C, 42.00;



L^1, R = C_6H_5
L^2, R = $C_6H_5CH_2$
L^3, R = CH_2=CH–CH_2

Figure 1. Formulas of ligands.

Table 1. Microanalytical data, physical properties, molar conductance, electronic spectra and magnetic moments of the prepared complexes.

					Found (Calcd%)							
Complex (Empirical formula)	M. Wt.	Color	M.P. (°C)	Yield (%)	C	H	N	S	Cl	Λm ($Ohm^{-1} cm^{-1} mol^{-1}$ L)	λ_{ax}(nm)	μ_{eff} (BM)
$Co_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ $(C_9H_{13}Cl_2Co_2N_3S_3O_2)$	480.19	Blue	291	71	22.74 (22.51)	2.61 (2.73)	8.58 (8.75)	19.83 (20.03)	14.95 (14.77)	14.80	624	4.80
$Co_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ $(C_{10}H_{15}Cl_2Co_2N_3S_3O_2)$	494.22	Blue	311	64	24.52 (24.30)	2.84 (3.06)	8.36 (8.50)	19.74 (19.46)	14.58 (14.35)	10.95	615	4.68
$Co_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$ $(C_6H_{13}C_{12}Co_2N_3S_3O_2)$	444.16	Pale blue	278	67	15.98 (16.23)	3.14 (2.95)	9.65 (9.46)	21.89 (21.66)	16.21 (15.96)	8.78	600	4.40
$Cu_2[L^1\text{-}2H] \cdot 4H_2O$ $(C_9H_{17}Cu_2N_3S_3O_4)$	454.54	Yellow	310	59	23.92 (23.78)	3.57 (3.77)	9.04 (9.24)	21.33 (21.16)	–	9.32	432	–
$Cu_2[L^2\text{-}2H] \cdot 4H_2O$ $(C_{10}H_{19}Cu_2N_3S_3O_4)$	468.57	Yellow	327	55	25.87 (25.63)	3.86 (4.09)	9.24 (8.97)	20.28 (20.53)	–	12.85	422	–
$Cu_2[L^3\text{-}2H] \cdot 4H_2O$ $(C_6H17Cu_2N_3S_3O_4)$	418.51	Yellow	286	57	17.45 (17.22)	4.28 (4.09)	10.32 (10.04)	23.25 (22.99)	–	13.65	416	–
$Ni_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ $(C_9H_{13}Cl_2N_3Ni_2S_3O_2)$	479.71	Green	302	74	22.76 (22.53)	2.89 (2.73)	8.52 (8.76)	19.82 (20.05)	14.51 (14.78)	15.63	565	–
$Ni_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ $(C_{10}H_{15}Cl_2N_3Ni_2S_3O_2)$	493.74	Pale green	320	79	24.12 (24.33)	2.85 (3.06)	8.73 (8.51)	19.71 (19.48)	14.19 (14.36)	10.93	554	–
$Ni_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$ $(C_6H_{13}Cl_2N_3Ni_2S_3O_2)$	443.68	Green	271	68	16.51 (16.24)	3.24 (2.95)	9.25 (9.47)	21.84 (21.68)	16.23 (15.98)	16.25	528	-
$Cd_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ $(C_9H_{13}Cd_2Cl_2N_3S_3O_2)$	587.15	Pale yellow	329	77	18.19 (18.41)	2.38 (2.23)	6.88 (7.16)	16.15 (16.38)	11.82 (12.08)	13.75	308, 348	–
$Cd_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ $(C_{10}H_{15}Cd_2Cl_2N_3S_3O_2)$	601.17	Pale yellow	337	74	20.26 (19.98)	2.77 (2.51)	7.28 (6.99)	16.27 (16.00)	11.96 (11.79)	14.90	305, 335	–
$Cd_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$ $(C_6H_{13}Cd_2Cl_2N_3S_3O_2)$	551.11	Pale yellow	304	75	12.88 (13.08)	2.19 (2.38)	7.83 (7.62)	17.67 (17.46)	13.12 (12.87)	17.30	300, 323	–
$Zn_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ $(C_9H_{13}Cl_2N_3S_3O_2Zn_2)$	493.10	White	282	65	22.21 (21.92)	2.43 (2.66)	8.77 (8.52)	19.23 (19.51)	14.54 (14.38)	11.35	258, 310, 350	–
$Zn_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ $(C_{10}H_{15}Cl_2N_3S_3O_2Zn_2)$	507.13	White	295	71	23.43 (23.68)	3.16 (2.98)	8.05 (8.29)	19.24 (18.97)	14.21 (13.98)	13.91	252, 307, 338	–
$Zn_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$ $(C_6H_{13}Cl_2N_3S_3O_2Zn_2)$	457.07	White	263	62	15.95 (15.77)	3.06 (2.87)	8.82 (9.19)	21.31 (21.05)	15.29 (15.51)	14.80	250, 305, 325	–

Table 2. Significant IR spectral data (cm^{-1}) of L^1–L^3 and their metal(II) complexes.

Compound	ν(OH)	ν(NH)	ν(S–C=N)	ν(NCSSMe)	ν(M–N)	ν(M–O)1
L^1	–	3310, 3195	–	1060, 960, 755	–	–
$Co_2CI_2[L^1\text{-}2H] \cdot 2H_2O$	3485	3270	1530	1090, 980, 790	470	510
$Cu_2[L^1\text{-}2H] \cdot 4H_2O$	3480	3285	1525	1095, 980, 760	465	530
$Ni_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$	3475	3265	1520	1105, 970, 785	450	505
$Cd_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$	3490	3275	1525	1080, 975, 765	462	595
$Zn_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$	3480	3280	1520	1100, 970, 775	490	535
L^2	–	3325, 3160	–	1075, 945, 770	–	–
$Co_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$	3480	3260	1525	1065, 975, 780	474	515
$Cu_2[L^2\text{-}2H] \cdot 4H_2O$	3485	3280	1530	1100, 970, 765	470	525
$Ni_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$	3470	3270	1525	1095, 985, 770	445	510
$Cd_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$	3480	3265	1530	1100, 970, 790	465	605
$Zn_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$	3475	3255	1520	1090, 980, 765	485	530
L^3	–	3315, 3140	–	1055, 965, 760	–	–
$Co_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$	3490	3250	1535	1070, 985, 780	480	510
$Cu_2[L^3\text{-}2H] \cdot 4H_2O$	3475	3265	1525	1085, 980, 765	465	530
$Ni_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$	3475	3275	1530	1080, 975, 755	450	515
$Cd_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$	3470	3270	1515	1070, 980, 765	470	600
$Zn_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$	3485	3265	1525	1085, 970, 775	490	525

Table 3. ^1H NMR spectra of L^1-L^3 and some corresponding metal(II) chelates in DMSO-d_6.

	δ (ppm)					
Compound	SMe	^{1}NH	^{2}NH	^{4}NH	H_2O	R
L^1	2.66	10.51	10.30	9.94	–	R=Ph; $\delta = 6.96$–7.56 (m,5H,Ar-H)
$Cd_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ ($C_9H_{13}Cd_2Cl_2N_3S_3O_2$)	2.70	–	–	10.03	3.40	R=Ph; $\delta = 7.00$–7.46 (m, 5H, Ar–H)
L^2	2.68	10.48	10.26	8.43	–	R=$PhCH_2$; $\delta = 4.63$ (s,2H,CH_2), 6.94–7.46 (m,5H,Ar–H)
$Cu_2[L^2\text{-}2H] \cdot 4H_2O$ ($C_{10}H_{19}Cu_2N_3S_3O_4$)	2.69	–	–	8.89	3.46	R=$PhCH_2$; $\delta = 4.60$ (s, 2H, CH_2), 7.00–7.51 (m,5H,Ar-H)
L^3	2.65	10.45	10.27	7.56	–	R=CH_2=$CHCH_2$; $\delta = 4.05$ (m,2H, allyl-CH_2N), 5.17–5.21 (m, 2H,allyl–CH_2=), 5.88–5.93 (m, 1H,allyl–CH=)
$Ni_2Cl_2[L^3\text{-}2H] \cdot 2H_2O$ ($C_6H_{13}Cl_2N_3Ni_2S_3O_2$)	2.69	–	–	7.83	3.44	R=CH_2=$CHCH_2$; $\delta = 4.08$ (m,2H,allyl–CH_2N), 5.19–5.22 (m,2H,allyl–CH_2=), 5.89–5.96 (m,1H,allyl–CH=)

H, 4.31; N, 16.32; S, 37.37. Found: C, 41.86; H, 4.42; N, 16.17; S, 37.57. L^2: 271 (M^+, 19), 223 (29), 149 (73), 91 (100), 77 (82), 65 (62). Anal. Calcd for $C_{10}H_{13}N_3S_3$ (%): C, 44.25; H, 4.83; N, 15.48; S, 35.44. Found: C, 44.46; H, 5.05; N, 15.25; S, 35.21. L^3: 221 (M^+, 31), 173 (27), 99 (96), 41 (100). Anal. Calcd for $C_6H_{11}N_3S_3$ (%): C, 32.55; H, 5.00; N, 18.98; S, 43.46. Found: C, 32.41; H, 4.82; N, 19.26; S, 43.22.

2.3. *Synthesis of the metal complexes*

The complexes were prepared by reacting 1:1 ratios of ligands L^1-L^3 (5 mmol; $L^1 = 1.285$ g, $L^2 = 1.355$ g, $L^3 = 1.105$ g) and 5 mmol of each of the following metal salts: $CuCl_2 \cdot 2H_2O$ (0.852 g), $CoCl_2 \cdot 6H_2O$ (1.190 g), $NiCl_2 \cdot 6H_2O$ (1.189 g), $CdCl_2 \cdot H_2O$ (1.007 g) and $ZnCl_2$ (0.682 g) in 50 mL of absolute ethanol. The reaction mixtures were heated under reflux for a time (3 h for L^1 complexes, 3.5 h for L^2 complexes and 5 h for L^3 complexes). The precipitate thus formed was filtered off, washed several times with hot water, hot ethanol, and diethyl ether and then dried *in vacuo* over P_4O_{10}. All the metal complexes are stable to air and moisture.

2.4. *Chemical and physical measurements*

The infrared spectra of the ligands and their isolated complexes, as KBr discs, were recorded on a FTIR 1650 (Perkin Elmer) spectrophotometer in the 4000–200 cm^{-1} range. The UV/VIS spectra of the complexes were recorded for freshly prepared solutions of the complexes in DMSO at 25°C by a Unicam Scanning UV/VIS spectrophotometer Model UVA 1000 E between 200–1000 nm.^{1} H NMR spectra in DMSO-d_6 for the ligands and their complexes were recorded on a Varian Gemini spectrometer (200 MHz) at Cairo University. Mass spectra of the ligands and Co(II)-L^1 complex were recorded on a Varian MAT 311 instrument. Molar conductances of DMSO solutions of the synthesized complexes were measured at 25°C using a model 31 YSI conductivity bridge with conductivity cell constant = 0.10 M. Magnetic moment values were evaluated at room temperature (25°C) using a Johnson Matthey magnetic susceptibility balance. Thermogravimetric curves (TGA and DTG) were recorded using a Dupont 9000 thermal analyzer at a heating rate 10°C/min in air over the temperature range 10–600°C. The C, H, N, S and Cl contents of the complexes were determined by the Microanalytical unit at Cairo University, Egypt. Co(II), Cu(I), Ni(II), Cd(II) and Zn(II) analyses were determined complexometrically by known standard methods [34]. The electrochemical studies were carried out at room temperature in a three-electrode cell using nitrogen purged DMSO solution containing 0.1M TBAP and 10^{-3} M complex. A Pt wire was used as a counter electrode, another Pt wire was used as working electrode and Ag/AgCl reference electrode. Potential range was from −2.5 to 2.5 V and scan rate 100 mV/s. The cyclic voltammetry curves were run on a potentiostat (AMEL model 2049), which was PC-controlled.

3. Results and discussion

The isolated complexes are stable in air, insoluble in water and common organic solvents, but soluble in DMSO. The formulas of the complexes are listed in table 1 together with their physical properties, elemental analyses, magnetic measurements, molar conductance and electronic spectra.

3.1. *IR spectral studies*

The IR spectra of L^1-L^3 do not exhibit the υ (S-H) band at ca $2560\,cm^{-1}$, thus are probably of the thione form in the solid state. Their solution ^1H NMR spectra exhibit no peak attributed to the S-H proton. However, in the reaction with M(II) salts, tautomerization to the thiol form is enhanced with formation of metal complexes.

The existence of numerous coordination sites gives variable bonding modes. Careful comparison of IR bands of the bivalent metal complexes with those of the organic ligands reveals bonding of the ligand with two metal ions in different coordination sites.

The most important infrared bands of the ligand and its bivalent metal complexes together with their assignments are in table 2. The spectra proved that ^1NH, ^2NH, CSS^- and C=S groups are coordination centers. Figure 1 shows the numbering used for the assignments of IR and ^1H NMR spectra. The N–H stretching of ^4NH at 3325–$3310\,cm^{-1}$ shifted to lower frequencies (3285–$3250\,cm^{-1}$) in complexes, due to strong hydrogen bonding with water molecules present in the complexes. The ^1NH and ^2NH bands present in the parent ligand at 3195–$3140\,cm^{-1}$ disappear from the spectra of the complexes, indicating deprotonation of the ligand upon coordination. Removal of the proton on the nitrogen adjacent to the dithiocarboxylate [26–28, 32] or thioamide [17–19, 35] groups was reported. The disappearance of the υ(C=S) band of the free ligands in the spectra of complexes supports deprotonation followed by coordination *via* the mercaptide sulfur.

As a result of thioenolization, the thioamide group (NH–CS, 1600–$1590\,cm^1$), followed by metal complex formation, gives thioureide (S–C=N) bands at 1535–$1515\,cm^{-1}$. This band is observed at lower frequency due to coordination [36]. The two bands at 1075–1055 and 965–$645\,cm^{-1}$ in the spectra of the parent ligand can tentatively be assigned to the asym. and sym. stretching modes of the CSS^- group. In the complexes, these bands shift to higher frequencies (table 2).

The coordinating water in M(II) (L^1-L^3) complexes is characterized by υ (OH) vibrations at 3490–3470; the 600–$505\,cm^{-1}$ band, assigned to υ (M–O), is a strong evidence for participation of water in coordination [37, 38]. Coordination of azimethine nitrogen is also consistent with the presence of a new band at 490–$445\,cm^{-1}$ assignable to the υ(M–N) [38, 39].

The IR spectral data cited in table 2 suggest that in Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) chelates of L^1-L^3, the ligand is a quadridentate dibasic (S–NN–S) donor chelated to the central metal ion *via* thioureidyl nitrogen and the deprotonated thiol sulfur.

3.2. *^1H NMR spectral studies*

The ^1H NMR spectra of L^1-L^3 and their corresponding diamagnetic metal(II) chelates also provide evidence for the structure of these chelates. The ^1H NMR spectra of 1-S-methylcarbodithioate-4-substituted thiosemicarbazide L^1-L^3, table 3, show downfield signals due to ^1NH, ^2NH and ^4NH at $\delta = 10.51$–10.45, 10.30–10.26 and 9.94–7.56 ppm. Also, the ^1H NMR spectra of L^1-L^3 show the $-SCH_3$ signal at 2.68–2.65 ppm which is constant and independent of the rest of the molecule. The δ-values for the NH attached to R groups in L^1-L^3 are dependent on the nature of R (around 9.94 for $R = C_6H_5$, 8.43 for $R = C_6H_5CH_2$ and 7.56 for R = allyl). In the ^1H NMR spectra of the complexes, the signals due to SCH_3 did not undergo significant chemical shift because they are not involved in coordinating the metal cation. The absence of ^{1}NH and ^{2}NH in the ^{1}H NMR spectra of the complexes substantiates that the ligands coordinate in their thiol form in all the complexes. In the ^{1}H NMR spectra of the complexes, the deshielding observed for the ^{4}NH nuclei may be related to increase in the C–N double bond character (table 3).

The ^{1}H NMR spectrum of $Cd_2Cl_2[L^1{-}2H] \cdot 2H_2O$ (figure 2) shows the absence of ^{1}NH and ^{2}NH signals, whereas ^{4}NH and SCH_3 as well as phenyl protons are present. The singlet at $\delta = 3.40$ is attributable to H_2O molecules (table 3). Thus, these results are in agreement with the suggested structure.

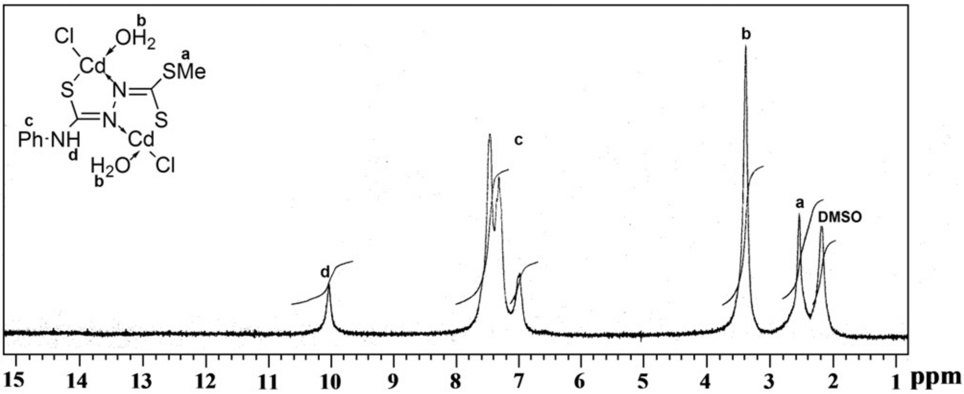
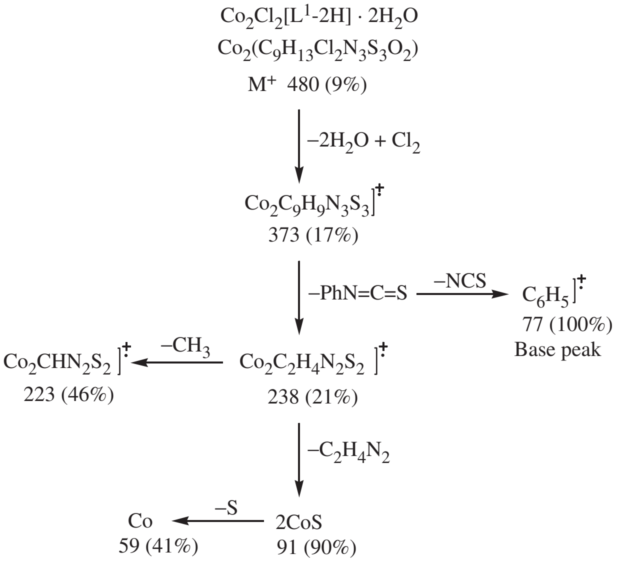


Figure 2. ^{1}H NMR spectrum of $Cd_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$.



Scheme 1. Proposed degradation of $Co_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ by mass spectra.

3.3. *Mass spectroscopy*

The mass spectrum of $Co_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ shows the molecular ion peak of the complex with abundance 9% at m/e = 480. The base peak (100% abundance) with m/e = 77 represents $C_6H_5.^+$ while the final fragment Co appears at 59 with abundance (41%). Further, the following common features of the fragmentation patterns lend support to the assigned structures: Loss of $(2H_2O + Cl_2)$ from the molecular ion giving intense $(M^+ - 107)$ ions, followed by loss of PhN=C=S giving rise to m/z = 238 $(Co_2C_2H_4N_2S_2)^+$. The fragment at 91 (CoS) formed by release of $(C_2H_4N_2)$. Suggested degradation steps of the $Co_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ complex are shown in scheme 1.

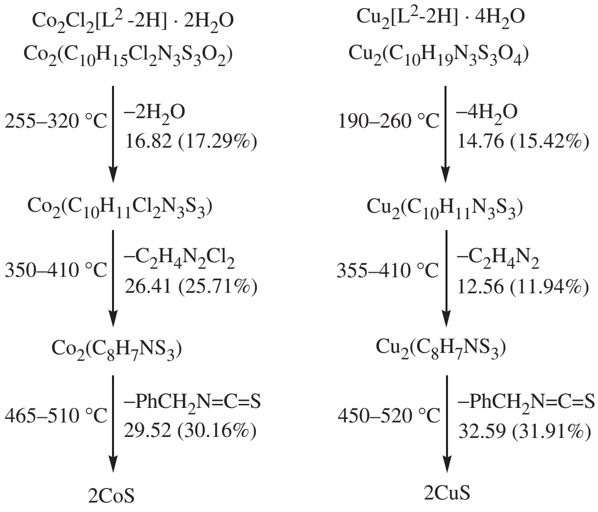
3.4. *Molar conductance*

The molar conductance data (8.78–17.30 $Ohm^{-1}\,cm^{-1}\,mol^{-1}$ L) of the complexes discussed herein indicate that Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) complexes are non-electrolytes (table 1), suggesting that the chloride anions are covalently bonded to the metal ions.

3.5. *Thermal analysis*

Thermogravimetric (TGA and DTG) analyses (10–600°C) for some complexes distinguish between the coordinated and hydrated water and give insight into thermal stability of the complexes.

The TG thermogram of $Co_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ (figure 3) as a representative example, has three degradation steps, overlapping creating a slight difference between the calculated and found weight losses. The first step (255–320°C) indicates the removal of two coordinated water molecules by 16.82% found (17.29 Calcd) weight%. The second



Scheme 2. Proposed thermal decomposition patterns of $Co_2Cl_2[L^2\text{-}2H] \cdot 2H_2O$ and $Cu_2[L^2\text{-}2H] \cdot 4H_2O$.

step occurs in the temperature range 350–410°C with a weight loss of 26.41%. This value is very close to that calculated (25.71%) for formation of $Co_2(C_8H_7NS_3)$ as an intermediate with evolution of $C_2H_4N_2Cl_2$. The third step occurs in the temperature range 465–510°C corresponding to loss of $PhCH_2N{=}C{=}S$. The thermogram shows progressive decomposition up to 550°C after which a constant weight was observed and 2CoS (37.32 found and 36.84% Calcd) was the final residue. Table 4 shows the temperature range, weight loss and fragments.

$Cu_2[L^2\text{-}2H]\cdot 4H_2O$ was thermally decomposed in three successive decomposition steps. The first mass loss of 14.76% within the temperature range 190–260°C may be attributed to the liberation of four coordinated water molecules (calculated mass

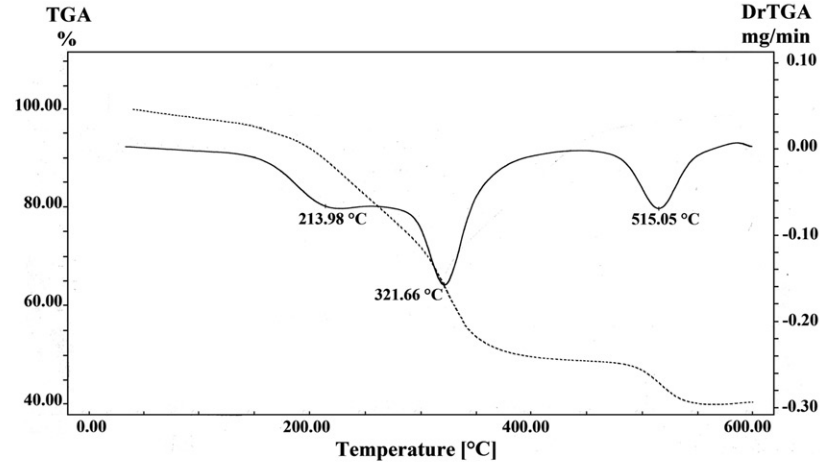


Figure 3. TG and DTG curves of $Co_2Cl_2[L^2\text{-}2H]\cdot 2H_2O$.

Table 4. Decomposition steps with the temperature range and weight loss for some complexes.

Complex (Empirical formula)	Temp. range (°C)	Weight loss Found (Calcd%)	Fragment
$Co_2Cl_2[L^2\text{-}2H]\cdot 2H_2O$	255–320	16.82 (17.29)	$2H_2O$
$(C_{10}H_{15}Cl_2Co_2N_3S_3O_2)$	350–410	26.41 (25.71)	$C_2H_4N_2Cl_2$
	465–510	29.52 (30.16)	$PhCH_2N{=}C{=}S$
	–	37.32 (36.84)	2CoS
$Cu_2[L^2\text{-}2H]\cdot 4H_2O$	190–260	14.76 (15.42)	$4H_2O$
$(C_{10}H_{19}Cu_2N_3S_3O4)$	240–420	12.56 (11.99)	$C_2H_4N_2$
	450–500	32.59 (31.91)	$PhCH_2N{=}C{=}S$
	–	39.97 (40.69)	2CuS
$Ni2Cl_2[L^1\text{-}2H]\cdot 2H_2O$	238–305	8.11 (7.53)	$2H_2O$
$(C_9H_{13}Cl_2N_3Ni2S_3O_2)$			
	386–495	54.18 (54.81)	$C_2H_4N_2Cl_2 + PhN{=}C{=}S$
	–	38.21 (37.66)	2NiS
$Cd_2Cl_2[L^3\text{-}2H]\cdot 2H_2O$	248–290	6.21 (6.55)	$2H_2O$
$(C_6H_{13}Cd_2Cl_2N_3S_3O_2)$	325–390	23.76 (23.09)	$C_2H_4N_2Cl_2$
	425–476	17.55(18.00)	$CH_2{=}CHCH_2N{=}C{=}S$
	–	51.82 (52.36)	2CdS
$Zn_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$	220–282	7.87 (7.32)	$2H_2O$
$(C_9H_{13}Cl_2N_3S_3O_2Zn_2)$	395–482	53.74 (53.25)	$C_2H_4N_2Cl_2 + PhN{=}C{=}S$
	–	39.02 (39.43)	2ZnS

loss 15.42%). The second step occurs within the temperature range 340–420°C with an estimated mass loss of 12.56% (calculated mass loss 11.99%) from removal of ($C_2H_4N_2$). The third step is attributed to the removal of PhCH$_2$N=C=S (found 32.59%, Calcd 31.91%). The higher residual weight percent (table 4) indicates a higher thermal stability of $Cu_2[L^2\text{-}2H]\cdot 4H_2O$ complex, perhaps from the presence of two five-membered rings.

Correlations between the different decomposition steps of Ni(II), Cd(II) and Zn(II) complexes with the corresponding weight losses are given in table 4. represents the degradation steps for $Co_2Cl_2[L^2\text{-}2H]\cdot 2H_2O$ and $Cu_2[L^2\text{-}2H]\cdot 4H_2O$.

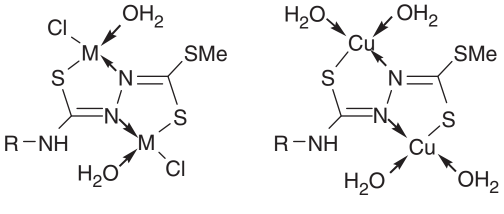
3.6. *Electronic spectra and magnetic moment data*

The magnetic moments and significant electronic absorption bands of Co(II), Cu(I), Ni(II), Cd(II) and Zn(II) complexes (figure 4), recorded in DMSO solution (table 1), play an important role in determining the structures of the metal chelates.

The ligands have bands at 245–305 and 323–350 nm due to π–π^* and n–π^* transitions, respectively. Changes in their energies are recorded in the complex spectra (table 1).

The isolated Co(II) chelates are paramagnetic with magnetic moments within the range reported for tetrahedral Co(II) chelates (4.40–4.80 BM) showing three unpaired electrons according to the CFT or LFT. Their electronic spectra, examined in DMSO solutions (table 1), show an absorption centered at 600–624 nm due to $^4A_2 \rightarrow {}^4T_1(p)$ transition (ν_3 band) characteristic of tetrahedral Co(II).

The copper chelates are diamagnetic; the yellow color shows the metal to be present as Cu(I). The electronic spectra of Cu(I) complexes are characterized by a broad absorption band from 416–432 nm. A tetrahedral structure has been suggested for complexes containing thiosemicarbazide derivatives of Cu(I) [40]. Their DMSO solution electronic spectra do not show any bands characteristic of d-d transitions, confirming complete reduction to Cu(I). The reducing behavior of the thioamido group towards halogeno Cu(II) to give Cu(I) complexes is well known [40–42]. The reduction of Cu(II) to Cu(I) is not surprising for soft sulfur bases, which stabilize Cu(I) as a typical (class b metal) soft acid [43].



R = C_6H_5, $C_6H_5CH_2$ and CH_2=CH–CH_2
M = Co(II), Ni(II), Cd(II) and Zn(II)

Figure 4. Proposed structure of 1-S-methylcarbodithioate-4-substituted thiosemicarbazides-M(II) complexes.

Reduction of Cu(II) salts with aldehydic Schiff bases derived from thiosemicarbazide and hydrazine-S-methyldithiocarboxylate was previously reported and a tentative reduction mechanism proposed [44].

Room temperature magnetic measurements of Ni(II) chelates reveal that the chelates are diamagnetic. The spectra of Ni(II) chelates with ligands of the type L^1-L^3 are consistent with a square-planar structure. The bands located at 528–565 nm in the spectra of Ni(II) chelates can be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$ transitions [45]. The CT-band in the spectra of Ni(II) chelates ($\lambda_{max} = 352$–440) are probably due to a sulfur to metal $S \rightarrow M(II)$ charge transfer transition [46].

The electronic spectra of the diamagnetic Cd(II) and Zn(II) chelates (table 1) are quite similar to the spectra of the anionic form of the corresponding parent ligands and the absorption bands in their spectra are due to L-L* transitions. The spectra lack any bands which can be related to charge transfer (CT). Most likely the Cd(II) and Zn(II) chelates with L^1-L^3 ligands possess tetrahedral structures.

3.7. *Cyclic voltammetry*

The cyclic voltammetric behavior of 1-S-methylcarbodithioate-4-phenylthiosemicarbazide (L^1) and its complexes $Co_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$, $Cu_2[L^1\text{-}2H] \cdot 4H_2O$, $Ni_2Cl_2[L^1\text{-}2H]2H_2O$ and $Cd_2Cl_2[L^1\text{-}2H].2H_2O$ were investigated in CH_3CN/Et_4NClO_4 solutions (in the potential range −2.5 to 2.5 V) at a scan rate of 100 mV s^{-1}. Representative data are shown in figure 5 (as an example). The cyclic voltammogram for L^1 showed four anodic peaks (−0.40, 0.70, 1.08, 2.24 V) with two cathodic peaks (−0.77, −1.23 V). By comparing the cyclic voltammogram for L^1 and its metal (Co, Ni, Cu or Cd) complexes, most of the L^1 redox peaks disappear indicating that most of the ligand sites participate in complex formation. Cyclic voltammograms of the metal complexes depend on the type of the metal.

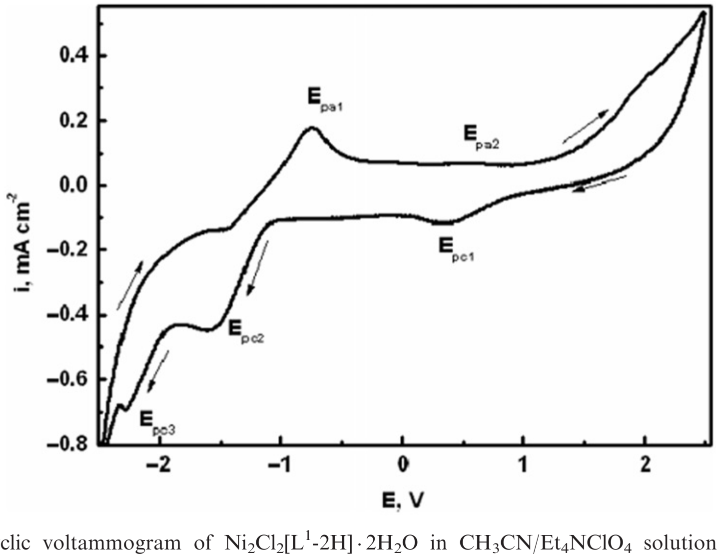


Figure 5. Cyclic voltammogram of $Ni_2Cl_2[L^1\text{-}2H] \cdot 2H_2O$ in CH_3CN/Et_4NClO_4 solutions at scan rate 100 mV s^{-1} *vs.* Ag/AgCl reference electrode.

The cyclic voltammograms for $Co_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$, $Ni_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$ or $Cd_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$ complexes showed three well-defined cathodic peaks [(0.07, −0.52, −1.53 V for Co complex), (0.39, −1.60, −2.29 V for Ni complex) and (0.07, −1.64, −1.85 V for Cd complex)] coupled with two anodic peaks [(−0.58, 0.69 V for Co complex), (−0.79, 0.56 for Ni complex) and (0.29, 1.10 V for Cd complex)]. The first anodic process is assigned to an irreversible M^+/M^{2+} couple with $\Delta E_p > 100\,mV$. The second is assigned to the irreversible electrode couple M^{2+}/M^{3+} by comparison with analogous complexes [17, 47]. The three cathodic peaks can be attributed to the electrode couples M^{3+}/M^{2+}, M^{2+}/M^+ and M^+/M^0 (M = Co, Ni or Cd), respectively.

In $Cu_2[L^1\text{-}2H]\cdot 4H_2O$, only one anodic peak (0.62 V) and two cathodic peaks (0.05, −1.64 V) are observed. The anodic peak represents Cu^+/Cu^{2+}. At the reverse scan, the observed two cathodic peaks can be assigned to one electron reduction processes Cu^{2+}/Cu^+ and Cu^+/Cu^0. On comparison with analogous copper complexes [35, 48, 49], the observed electrode couples are irreversible ($\Delta E_p > 100\,mV$) and are safely assigned to one electron oxidation process. In all investigated complexes the results indicate: (i) the dependence of the cathodic current peak (i_{pc}) of the electrode couples on the square root of the sweep rate ($\surd\nu$) suggesting a diffusion controlled electrochemical process [50], (ii) the cathodic potential peak (E_{pc}) shifted towards more negative values as ν increases indicating irreversible nature, and (iii) the irreversibility was also confirmed from the linear dependence of the cathodic peak potential with log ν [51]. From the above discussion, the electrochemical behavior of $Cu_2[L^1\text{-}2H]\cdot 4H_2O$ (figure 6) is different than ($Co_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$, $Ni_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$ or $Cd_2Cl_2[L^1\text{-}2H]\cdot 2H_2O$). This result may be explained by the difference in its composition and structure related to other complexes [35]. The cyclic voltammograms at scan rates $100\,mV\,s^{-1}$ were repeated in the range −2.5 to 2.5 V for 10 cycles. The results infer that the amount of charge consumed during oxidation and reduction are

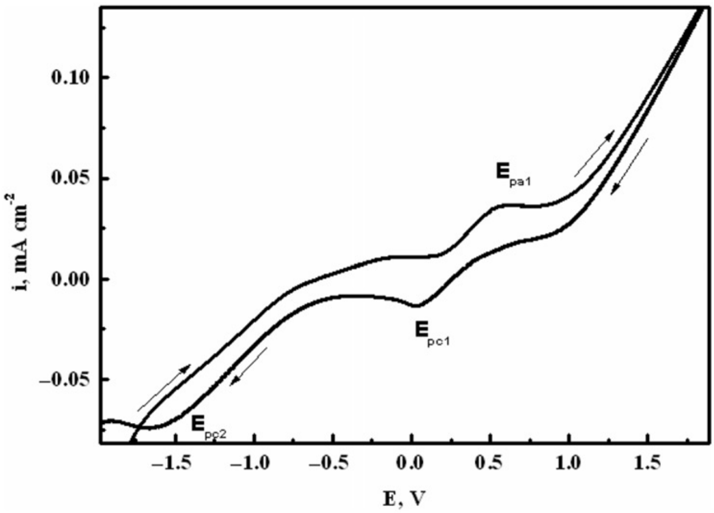


Figure 6. Cyclic voltammogram of $Cu_2Cl_2[L^1\text{-}2H]\cdot 4H_2O$ in CH_3CN/Et_4NClO_4 solutions at scan rate $100\,mV\,s^{-1}$ *vs.* Ag/AgCl reference electrode.

constant with increasing cycle number, i.e. complete reduction of the complexes occurs in the first cycle. The electrochemical behavior of these complexes is in agreement with the results obtained from other techniques used in this article.

The metal complexes are insoluble in ethanol, methanol and various solvents, but soluble in DMSO. All attempts to prepare single crystals of the compounds failed. The analytical and spectroscopic data enable us to predict structures as shown in figure 4.

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