Synthesis And Characterization A New Ligand Derived From The Dithiocarbamate Compounds For Removing Divalent Hg, Pb, Co, Ni And Zn Ions From Their Aqueous Solutions

Ibrahim A. Abdulqader
Department of Chemistry, College of Science, University of Anbar, Anbar, Iraq, chemist.bmw@gmail.com

Aeed S. Al-Fahdawi
Department of Chemistry, College of Education for Women, University of Anbar, Anbar, Iraq.

Firas fadhel Ali
Department of Chemistry, College of Education for Women, University of Anbar, Anbar, Iraq.

Abstract

This study included the preparation of new dithiocarbamate ligand, namely: potassium ((1,4-phenylenebis(azanediyl)) bis(2-oxoethane-2,1-diyl)) bis (benzylcarbamodithioate), ($C_{26}H_{24}K_2N_4O_2S_4$). The prepared ligand and its complexes of Co(II), Ni(II), Zn(II), Hg(II) and Pb(II) ions were characterized by FTIR, UV-Vis, 1H and 13C-NMR, Mass spectroscopy, magnetic sensitivity measurements, in addition to measurements of molar electrical conductivity and melting point. The measurements indicated that the DTC ligand has successfully coordinated to ions in a bidentate mode and the geometry of all complexes were octahedral around the dithiocarbamate groups. The prepared ligand was used for removing the aforementioned ions from their aqueous solutions, and studying the effect of pH and temperature on the removal efficiency. It was found that the effect of pH on the removal rates was much greater than the effect of temperature, and that the best rates of removal efficiency when using 0.035 g of ligand per 30 ml of solution at a concentration of 100 mg/L were: 99.18% for Hg^{2+} ions at (pH = 8 and 35 °C), 100% for Pb^{2+} ions at (pH=6 and 25 °C), and (pH=7 and 35 °C), 98.82% for Co^{2+} ions at (pH = 8 and 25 °C), 99.93% for Ni^{2+} ions at (pH = 8 and 25 °C), and 85.42% for (Zn^{2+}) ions at (pH = 8 and 25 °C).

Keywords: *Dithiocarbamate; Complexes; Removal; Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} ions.*

INTRODUCTION

It is well known that water is necessary for all living things, therefore, any type of water resource contamination would result in severe environmental problems and increases health risks for people and other living things [1]. Increasingly rapid development over the past century has increased the amount of pollutants in surface and groundwater by discharging wastewater from numerous industrial processes into the ecosystem. Among these pollutants, heavy metals are the most significant and main contaminants to water resources [2]. Heavy metals are permanent contaminants which are well-known for their non-biodegradable behavior, bioaccumulation even at very low levels coupled with prolong biological half-live, making them difficult to be removed from the body of wildlife species, unlike organic pollutants that are capable of undergoing biodegradation to reduce their toxicity [3].

Environment contamination and human exposure to heavy metals such as mercury (Hg), lead (Pb), nickel (Ni), and other heavy metals is a serious problem and has become one of the most important environmental issues throughout the world [4]. The release of wastewater containing heavy metals to the environment without treatment makes a serious global problem. Therefore, the technologies for purifying contaminated water have aroused the interest of researchers in recent years [1]. Removal of heavy metals from contaminated water has been addressed through a number of technologies over the past few years. Among those processes are: adsorption, ion exchange, membrane filtration, distillation, coagulation, flocculation, and chemical precipitation [5, 6]. Chemical precipitation is a widely used method for treating water pollution with heavy metals due to its simple equipment, low cost, as well as its ability for treating a large volume of water with a high metal concentration [7]. Chelating precipitation is one of precipitation method that uses strong chelating agents, such as Dithiocarbamates (DTCs) and its derivatives for removal of heavy metals through the formation of insoluble chelates [8]. DTCs with the formula (R2N-CS2-) can form stable coordination complexes with most elements, especially the transition elements, undergone different oxidation states by strongly and selectively binding to metal ions through the two donor sulphur atoms [9, 10].

Material

Acetonitrile, Benzylamine, Bromoacetyl bromide, Carbon disulphide, Chloroform, Cobalt chloride hexahydrate, Dichloromethane, Dimethyl sulfoxide, Ethanol, Mercury(II) Chloride, Nickel chloride hexahydrate, P-Phenylenediamine, Potassium hydroxide, Lead nitrate, Zinc(II) chloride hexahydrate were used in chemical reactions with no further purification, and they are available commercially.

Physical measurements

Melting points of the prepared compounds were obtained by using an Electro-Thermal Stuart melting point SMP-20. Infrared spectra were recorded as KBr discs using PerkinElmer FT-IR spectrophotometer in the range 4000-450 cm-1. Electrical conductivity measurements (EC) of the complexes were recorded at 25 ºC for solutions of 10-3 M in DMSO using HI2300 Microprocessor Conductivity Meter. Electronic spectra were measured at concentration of 10-3 and 10-5 M in DMSO solutions in the region (200-800) nm using 6405 UV/Vis Spectrophotometer. 1H and 13C-NMR spectra of the ligand and its Zn-complex were recorded by a BRUKER 400MHz Spectrometer. Mass spectra of the ligand was measured by MS Model: 5973 spectrometer. Magnetic moments were measured for complexes of Co and Ni at 25°C with a magnetic susceptibility balance (Sherwood Scientific). Heavy metals in solutions were determined, using atomic absorption spectrophotometer (AA-7000 SHIMADZU).

Synthesis

Synthesis of free ligand (L) and its precursors

The Ligand and its precursors were prepared according to the published method, with some modifications. The overall reactions are presented in scheme 1.

Synthesis of N,N'-(1,4-phenylene) bis(2-bromoacetamide), [A1]

Potassium hydroxide (1.0356 g, 18.4945 mmol) in H2O (20 mL) was added to a mixture of 1,4-diaminobenzene [Ao] (1g, 9.2472mmol) dissolved in CHCl3 (50 mL) in a round flask at ice bath with stirring. Then to the above mixture, bromoacetyl bromide (3.7333g, 18.4945mmol) dissolved in $CHCl_3$ (50mL) was added dropwise with vigorous stirring. A light purple precipitate was formed after completion of the reaction time (about 15 minutes). The product was filtered off under reduced pressure and then washed with ethanol and water, then dried in an oven at 40 oC and weighed [11].

Synthesis of N,N'-(1,4-phenylene)bis(2-(benzylamino)acetamide), [A2]

In a round flask, (1g, 2.856 mmol) of [A1] was added portionwise to an excess of benzylamine (9.8 g, 91.452 mmol). The mixture was stirred for 30 minutes at room temperature, then (200 mL) of distilled water was added. A light pink precipitate was obtained. The product was filtered, washed with distilled water and ethanol under vacuum, then dried in an oven at 40 ºC and weighed [12].

Synthesis of, potassium ((1,4-phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl))bis (benzylcarbamodithioate), [L]

To (1g, 2.4842 mmol) of [A2] in a round flask, 40 mL of dichloromethane (DCM) and acetonitrile (3:1) was added and mixed with a little heating for dissolving. The solution was allowed to cool down to room temperature, then potassium hydroxide (0.2784 g, 4.9625 mmol) in 5 ml distilled water was added and stirred for 10 minutes. An excess of carbon disulfide (1g, 13.1354 mmol) was drop wisely added to the reaction mixture, then, the flask was sealed and the mixture stirred for 12 h at room temperature. A red precipitation was collected after evaporating the solvents, washed with diethyl ether, then dried in an oven at 40 ºC and weighed [13].

Synthesis of $[Co(L)(H_2O)_2]_2$, $[Ni(L)(H_2O)_2]_2$, $[Zn(L)(H_2O)_2]_2$, $[Hg(L)(H_2O)_2]_2$ and $[Pb(L)(H_2O)_2]_2$ complexes

0.1885 g of cobalt (II) chloride, 0.1883 g of nickel (II) chloride, 0.1079 g of zinc (II) chloride, 0.2151 g of mercury (II) chloride and 0.2624 g of lead nitrate, (0.7922 mmol) were transferred into a 250 ml beaker each. Distilled water (100 ml) was added to each beaker with stirring. To each beaker, (0.5 g, 0.7922 mmol) of ligand dissolved in 100 ml of distilled water was added. The mixture was stirred for about 3 h. The formed precipitate was filtered off, rinsed with distilled water and ethanol, dried at ambient temperature and weighed [14].

Removal of heavy metals by the prepared ligands

Heavy metals ions (Co^{+2},Ni^{+2}, Zn^{+2}, Hg^{+2} and Pb^{+2}) were removed from their aqueous solutions by the prepared ligand through the following steps:

1. Solutions of above ions were prepared with a concentration of (120 mg / L) and adjusted to pH=7.
2. Solutions of L was prepared with a concentration of (0.035 g / 5 ml) by dissolving 0.21 g of ligand in 5 ml of ethanol and diluted to 30 ml with distilled water.
3. To 25 ml of each metal ion solution, 5 ml of (L) solution was added in a plastic container of 50 ml volume and closed tightly. The total concentration of metal ion solution would be (100 mg / L).
4. The containers were moved to a shaker in a thermostatic cabinet, the temperature was adjusted at (15 °C), and the shaker at (250 r/min) for 2 h.

5. After the time of reaction have been finished, the samples were filtered with Micro-Glass fiber papers and the concentration of ions was measured.

6. The steps (1-5) were repeated at 25 and 35 °C with pH of 7.

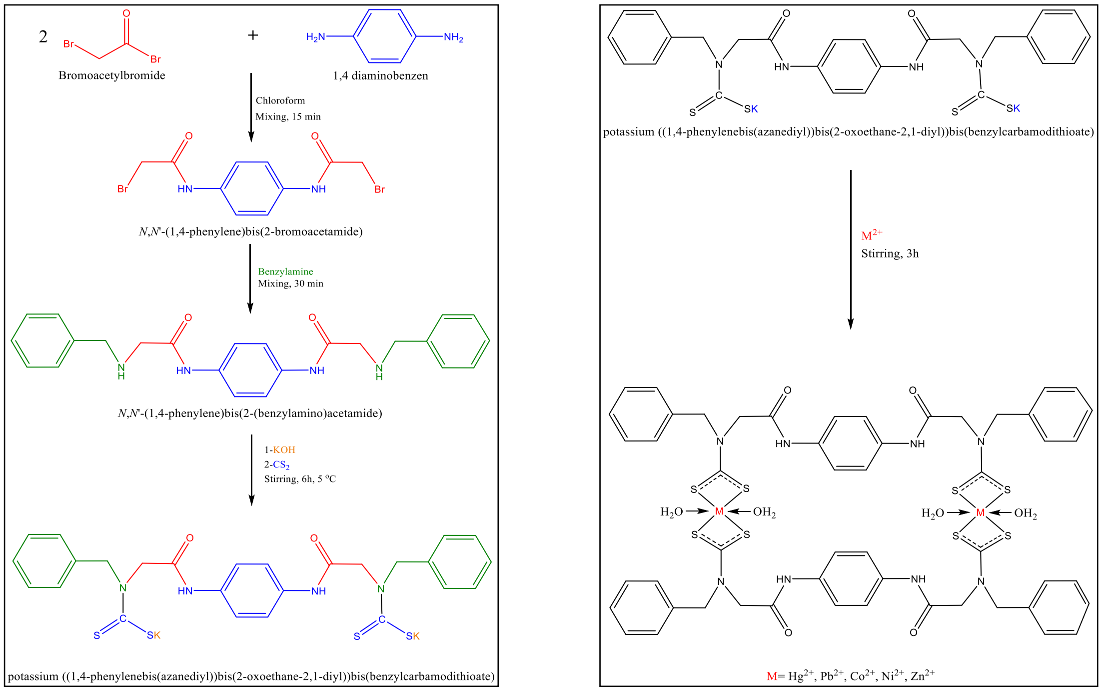
7. The steps (1-5) were repeated at 25 °C with pH of 6 and 8.

Results and Discussion

Synthesis of ligand and bimetallic DTC-based macrocyclic complexes

Synthesis ligand was based on the reaction of N-H group of secondary amine with CS2 in the presence of KOH, using dichloromethane and acetonitrile (3:1) as a solvent. The complexes were obtained by reacting the ligand with metal (II) salt in a 1:1 mole ratio at room temperature. The ligand was soluble in water, so, water was used as a medium in synthesis of the complexes. The general formula [M(L)(H2O)2]2 is stated for DTC macrocyclic complexes (where M = Co(II), Ni(II), Zn(II) Hg(II), and Pb(II) ; L = ligand). The scheme (1) shows synthetic route of ligand and its complexes. The dinuclear DTC based macrocyclic complexes are solid, soluble in DMSO and not soluble in water. Table (1) explains some physical properties of the ligand and its complexes.

Scheme (1): Synthetic route of free ligand and its complexes.



Electrical conductivity measurements and magnetic susceptibility

The electrical conductivity measurements (EC) have been used for the determination of the electrolytic or non-electrolytic nature of the prepared complexes. The molar conductance data for the prepared complexes at concentration of 10-3 M in DMSO are shown in Table 1. The electrical molar conductivity of complexes solutions in DMSO indicate the non-electrolytic nature of these complexes [15]. The magnetic moment measurements showed values of meff in 4.25 and 2.76 B.M. for Co and Ni complexes identical with the values of high spin and they are agreement with octahedral geometry around Co (II) and Ni(II) ions [16].

Table 1: some physical properties of the ligand and its complexes.

Compound	Empirical formula	M.wt (g/mol)	Yield (g)	Yield %	M.p. (ºC)	EC S cm^{-1} mol^{-1}	Colour
(A$_o$)	$C_6H_4(NH_2)_2$	108.14	-	-	145-147	-	White to violet
(A1)	$C_{10}H_{10}Br_2N_2O_2$	350.01	2.8600	88.35	245 *	-	Light purple
(A2)	$C_{24}H_{26}N_4O_2$	402.50	1.1123	96.73	172-176	-	Light beige
L	$C_{26}H_{24}K_2N_4O_2S_4$	630.94	1.1966	76.34	181-184	-	Maroon
[Co(L)(H$_2$O)$_2$]$_2$	$C_{52}H_{56}Co_2N_8O_8S_8$	1295.43	0.3001	58.47	175-179	2.9	Olive
[Ni(L)(H$_2$O)$_2$]$_2$	$C_{52}H_{56}N_8Ni_2O_8S_8$	1294.95	0.3054	59.52	180-183	2.6	caramel
[Zn(L)(H$_2$O)$_2$]$_2$	$C_{52}H_{56}N_8O_8S_8Zn_2$	1308.3	0.3702	71.43	248 *	2.0	peach
[Hg(L)(H$_2$O)$_2$]$_2$	$C_{52}H_{56}Hg_2N_8O_8S_8$	1578.75	0.5606	89.62	168-172	9.2	Maroon
[Pb(L)(H$_2$O)$_2$]$_2$	$C_{52}H_{56}N_8O_8b_2S_8$	1591.97	0.5850	92.75	185-188	4.9	Maroon

M.p. = Melting point, (*) = Decomposed

FTIR spectral data for the ligand, its precursors and complexes

The FTIR spectrum of compound [A1] showed a stretching band at (3274) cm-1 that assigned to (N-H) of amide moiety, and evanescence of stretching bands around (3304) and (3200) cm-1 related to (-NH2) group of primary amine which appeared in [Ao] spectrum. Absorption band at (1664) cm-1 in the spectrum of the compound [A1] is belong to (C=O) of the amide group [17]. In addition, two new stretching bands at (2875) and (2953) cm-1 appeared in [A1] spectrum belong to (-CH2-) group. These spectra indicate the formation of the [A1]. The spectrum of compound [A2] showed new bands at (3334) cm-1 for (N-H) stretching, and at (2857, 2840, 2796, 1454, 1426, 1359) cm-1 for aliphatic (-CH2-) stretching and bending. Also, there is an increasing in absorbance density at (1235) cm-1, and appearance of new absorption band at (1226) cm-1 for (C-N). At (832) cm-1 there was an increase in absorption density attributed to (C-H) out of plane deformation of aromatic ring. On the other hand, the absorption bands of (C-Br) at (646) and (1184) cm-1 have disappeared from the spectrum of compound [A1]. That confirms [A2] formation [18].The FTIR spectrum of ligand showed a broad absorption band at (3288) cm-1 assigned to (N-H) of amide group, and disappearance of (N-H) stretching and bending bands of secondary amine at (3334) and (1581) cm-1 respectively which was appeared in [A2] spectrum. The spectrum also showed absorption bands at (1000) and (1187) cm-1 attributed to (CS2) , and at (1381) cm-1 belong to (N-CS2) [12, 19]. These spectra confirm the formation of ligand. The FTIR spectra of the complexes were similar but had a very slight shift in wavenumbers of some bands. They showed absorption bands at (1478),(1463) and (1431) cm-1 corresponding to (N-CS2). The shifting in (C-N) band indicates that it has the property of partial double bond due to the delocalization of electron pair of nitrogen atom which transfer to metal, where its value lies between the absorption values of (C=N) and (C-N) bands. The characteristic bands of (C-S) at (669) and (1000) cm-1 in the spectrum of ligand has been appeared as a very week bands in all spectra of the complexes, while the (C=S) band at (1187) cm-1 shifted to (1218)-(1229). The appearance of single ν(CS2) band of complexes, and the blue shift in absorption of (N-CS2) indicates the bidentate chelate coordination mode of (CS2) moiety with the metals [16, 20, 21].

Figure 1: FTIR spectra of [Ao] and [A1].

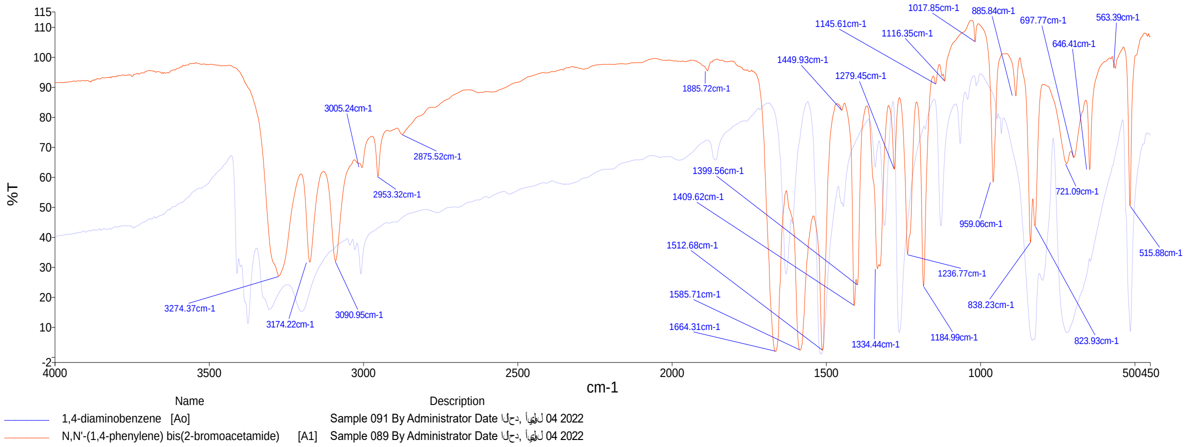


Figure 2: FTIR spectra of [A1] and [A2].

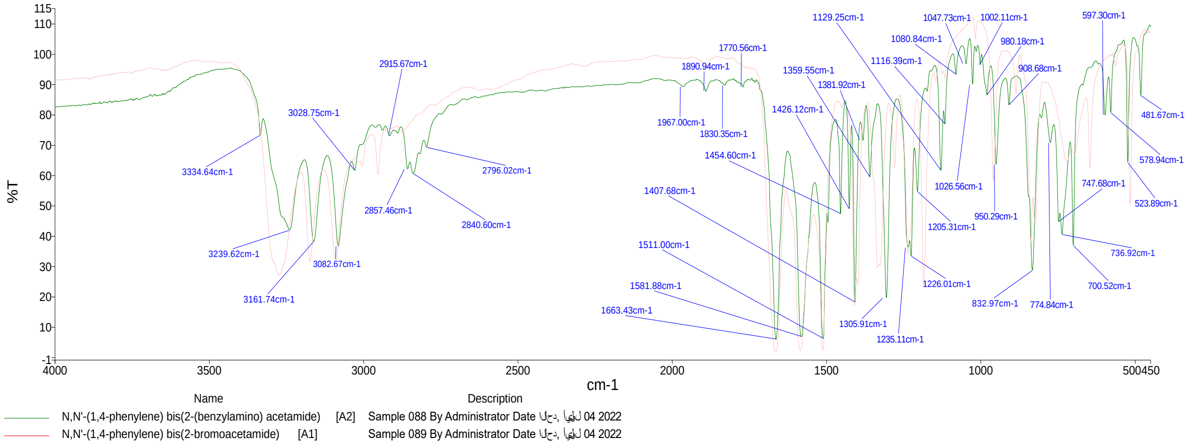


Figure 3: FTIR spectra of [A2] and the ligand

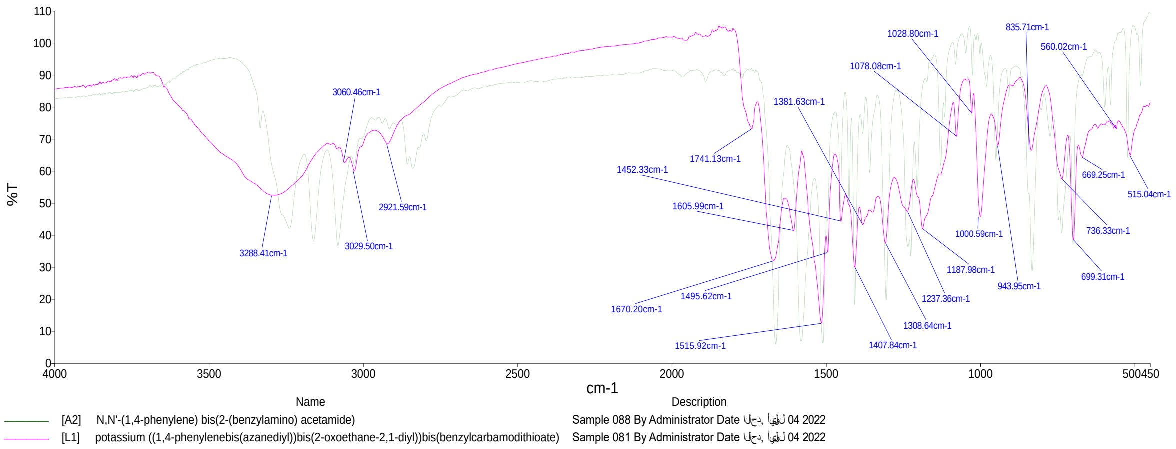


Figure 4: FTIR spectra of ligand and [Co(L)(H2O)2]2.

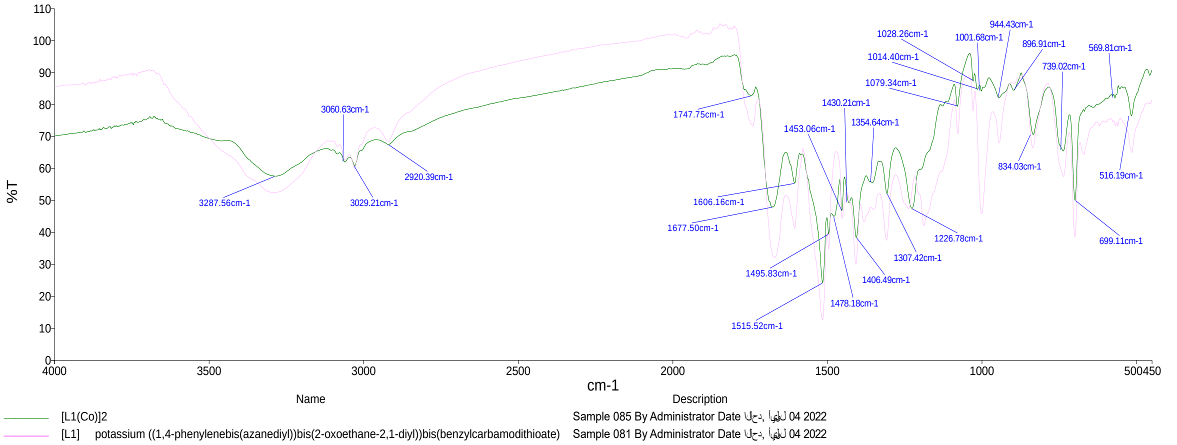


Figure 5: FTIR spectra of ligand and [Ni(L)(H2O)2]2.

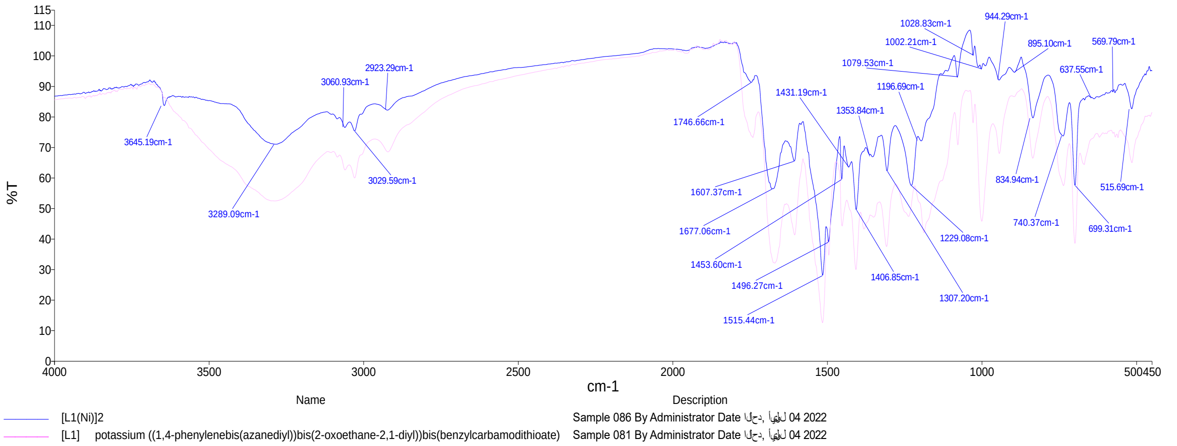


Figure 6: FTIR spectra of ligand and [Zn(L)(H2O)2].

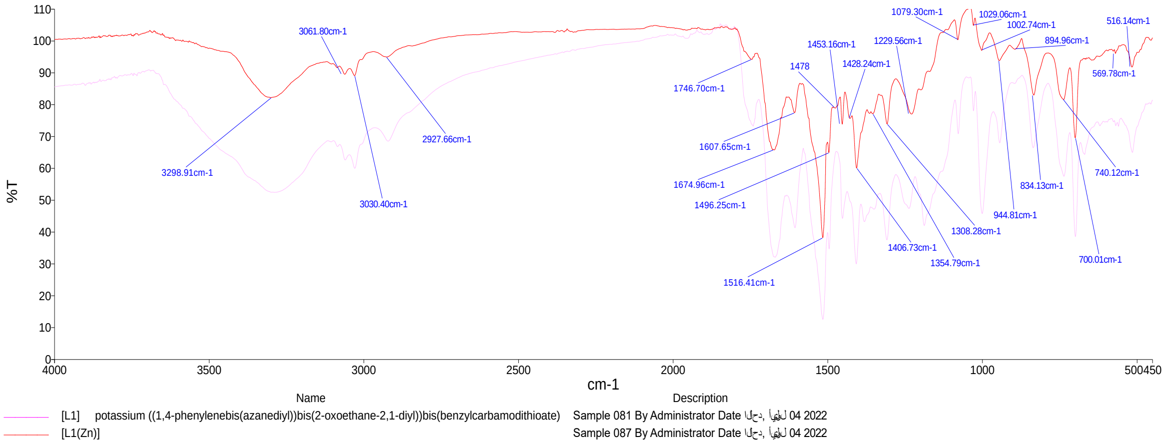


Figure 7: FTIR spectra of ligand and [Hg(L)(H2O)2]2.

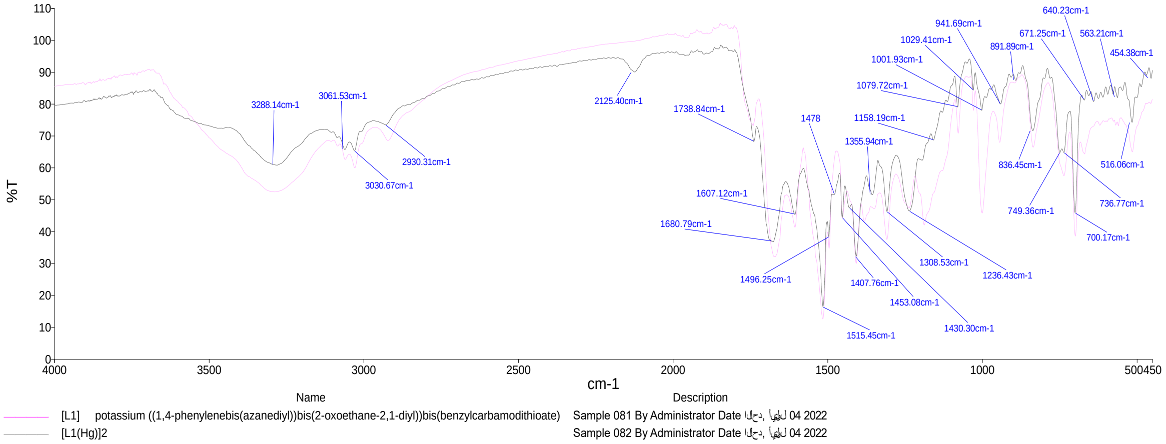


Figure 8: FTIR spectra of ligand and [Pb(L)(H2O)2].

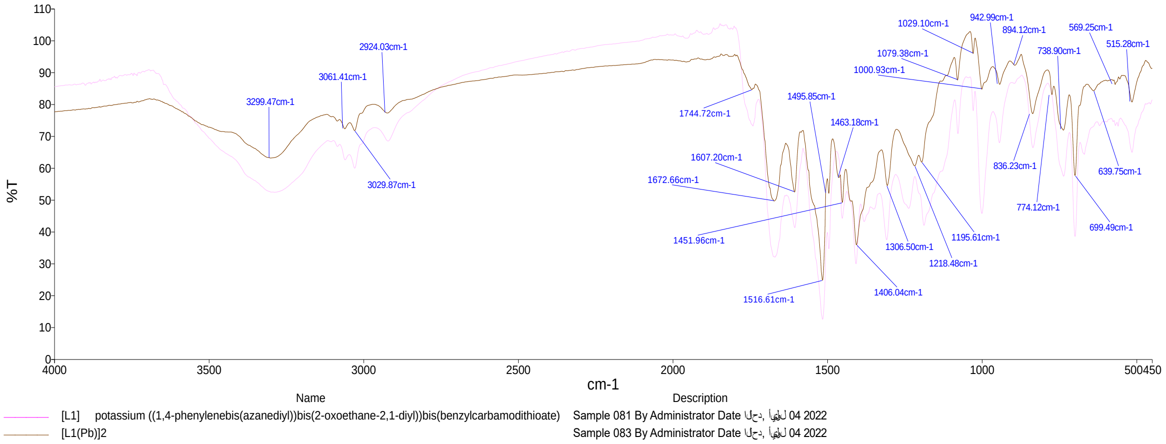


Table 2: FTIR spectral data (wave number) cm-1 for the ligand, its precursors and complexes

Compound	υ (O-H)	υ (N-H)	υ(C=O)	υ (C=C)	$υ_{Ar}$ (C-H)	$υ_{Aliph}$ (C-H)	υ (C-N)	υ (N-CS_2)	υ (CS_2)
A_o	-	3304 3200	-	1516	3044 3028 3008	-	-	-	-
A1	-	3274	1664	1512	3005	2953 2875	1235	-	-
A2	-	3334 3239 1581	1663	1511	3116 3082 3028	2857 2840 2796	1235	-	-
L	-	3288	1670	1515	3029 3060	2921	1237	1381	1187 1000
$[Co(L)(H_2O)_2]_2$	3400-3150	3287	1677	1515	3060 3029	2920	1226	1430	1171 1001
$[Ni(L)(H_2O)_2]_2$	3400-3150	3289	1677	1515	3060 3029	2923	1229	1431	1172 1002
$[Zn(L)(H_2O)_2]_2$	3400-3150	3298	1674	1516	3061 3030	2927	1229	1428	1170 1002
$[Hg(L)(H_2O)_2]_2$	3400-3150	3288	1680	1515	3061 3030	2930	1236	1430	1117 1001
$[Pb(L)(H_2O)_2]_2$	3400-3150	3299	1672	1516	3061 3029	2924	1218	1463	1171 1000

UV-Vis spectral data of ligand, its precursors and complexes

The UV-Vis spectra of ligand, its precursors and complexes in DMSO solutions revealed high intense absorption peaks for all compounds around (257-274) nm and (272-335) nm assigned to π → π* and n → π* electronic transitions, respectively [19]. The spectra of ligand and all its complexes showed charge transitions (CT) around (377-399) nm [22]. The complexes of Co and Ni exhibited (d-d) transitions (4T1g(F)→4T1g(P), 3A2g(F)→ 3T1g(F)) and (3A2g(F)→3T1g(P), 3A2g(F)→ 3T1g(F)) in the visible region at (503), (635), (503) and (635) nm for d7 and d8 systems of Co(II) and Ni(II) respectively. These transitions belong to octahedral structures around the metal ions [15]. The other complexes did not show any (d-d) transitions because they had (d) saturated systems [23]. The spectral data of ligand, its precursors and complexes are illustrated in table 3.

Table 3: Electronic spectral data for ligand, its precursors and complexes in DMSO solutions at 1*10-4 and 1*10-3 M

Compounds	Wavelength (nm)	Wave number (cm^{-1})	Assignment	Suggested geometry
A_O	263 330	38023 30303	π → π* n→π*	-
A1	257 285	38911 35088	π → π* n→π*	-
A2	258	38760	π → π*	-

	272	36765	n→π*	
L^1	269	37175	π → π*	-
	301	33223	n→π*	
	377	26525	C.T	
	450	22222	L.F	
$[Co(L)(H_2O)_2]_2$	274	36496	π → π*	Octahedral
	320	31250	n→π*	
	385	25974	C.T	
	503	19881	$^4T_1g^{(F)}\rightarrow{}^4T_1g^{(P)}$	
	635	15748	$^4T_1g^{(F)}\rightarrow{}^4A_2g^{(F)}$	
$[Ni(L)(H_2O)_2]_2$	268	37313	π → π*	Octahedral
	326	30675	n→π*	
	386	25907	C.T	
	440	22727	$^3A_2g^{(F)}\rightarrow{}^3T_1g^{(P)}$	
	501	19960	$^3A_2g^{(F)}\rightarrow{}^3T_1g^{(F)}$	
$[Zn(L)(H_2O)_2]_2$	268	37313	π → π*	Octahedral
	325	30769	n→π*	
	399	25063	C.T	
	500	20000	L.F	
$[Hg(L)(H_2O)_2]_2$	270	37037	π → π*	Octahedral
	327	30581	n→π*	
	398	25126	C.T	
	485	20619	L.F	
$[Pb(L)(H_2O)_2]_2$	270	37037	π → π*	Octahedral
	335	29851	n→π*	
	399	25063	C.T	
	475	21053	L.F	

1H-NMR, 13C-NMR and Mass spectra of the free ligand

The 1H-NMR spectrum of the ligand in DMSO-d6 solution, Figure 9, showed a doublet signal at chemical shifts (δ= 9.98 and 10.04) ppm belong to protons of the two symmetric secondary amine groups (N a, a` -H) in the ligand. The singlet signal at chemical shift (δ= 7.55) ppm refers to the protons (C11, 11` , 12, 12` -H) of aromatic ring. The multiplet signals of chemical shifts at the range between (7.2-7.53) ppm are assigned to (C1, 1`, 2, 2`, 3, 3`, 4,4`, 5,5` -H) of the two homologous aromatic ring. The doublet signals at chemical shifts (δ= 3.41, 3.44) and (δ= 3.89, 3.86) ppm corresponding to (C7, 7` -H) and (C8, 8` -H) respectively, which belong to protons of the symmetric methylene groups. Signals at (δ =2.54 and 3.25) ppm are due to the deuterated dimethyl sulfoxide [18, 24]. The signal at (δ= 4.76) ppm refers to water molecule as moisture [25]. The 13C-NMR spectrum of L1, Figure (3.60), showed a signal at chemical shift (δ= 212.10) ppm attributed to (C13, 13`) for CS2 groups, while it showed a chemical shift (δ= 168.72) ppm belong to (C9, 9`) of carbonyl groups. The chemical shifts (δ= 139.04, 134.65, 128.54, 127.77, 127.05 and 120.10) ppm are related to carbon atoms of benzene rings, (C6, 6`), (C10, 10`), (C2, 2`, 4, 4`), (C1,1`, 5, 5`), (C3, 3`) and (C11, 11`, 12, 12`), respectively.

The signals at (δ= 56.35 and 52.42) ppm are attributed to carbon atoms of methylene groups, (C8, 8`) and (C7, 7`), respectively. The chemical shifts between (40.62-39.36) ppm are corresponding to DMSO [24,26]. The electrospray ES (+) mass spectra of ligand showed successive fragments belong to structure of the ligand. The parent ion peak of ligand is observed at m/z = 631.1 which corresponds to (M)+ (%) for $C_{26}H_{24}K_2N_4O_2S_4$; requires = 630.01. Other peaks related to ligand skeleton can be seen in Figure 11.

Figure 9: 1H-NMR spectrum of ligand in DMSO-d6 solution.

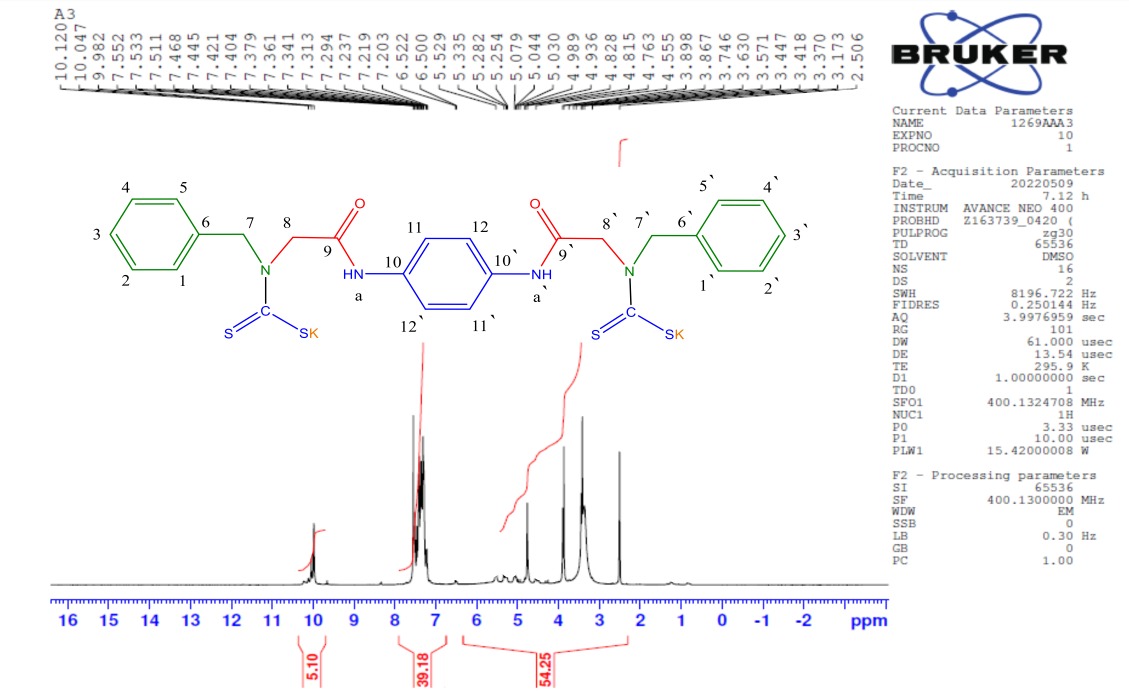


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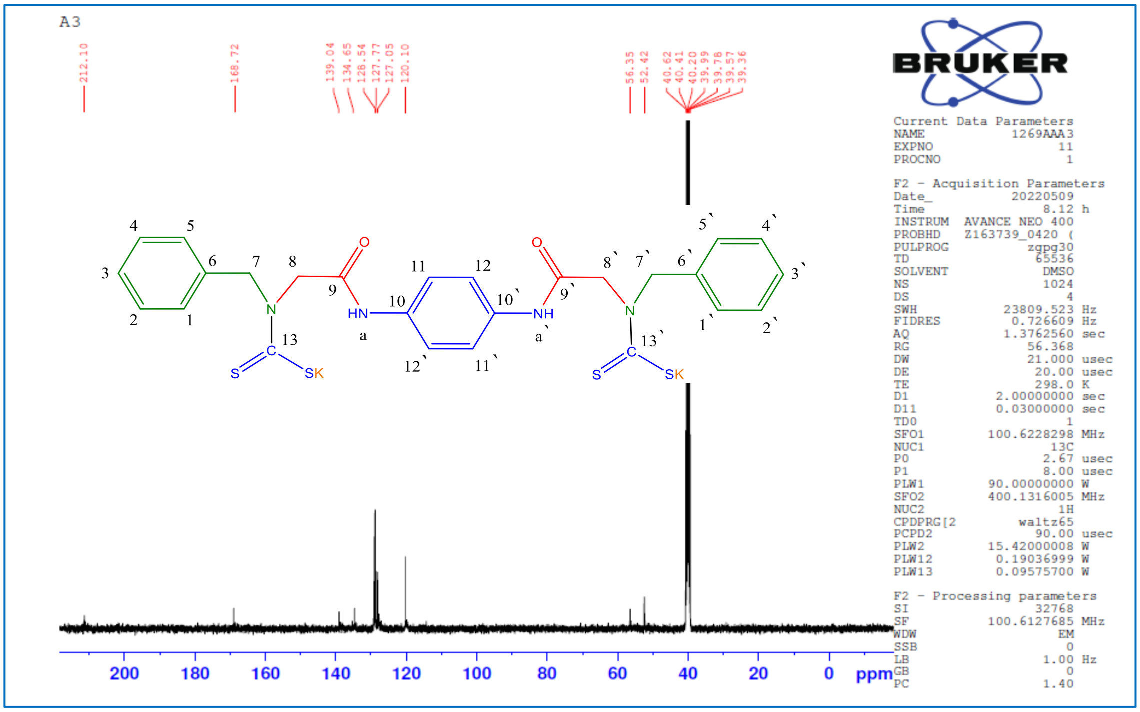
Figure 10: 13C-NMR spectrum of ligand in DMSO-d6 solution.



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TE                    298.0 K
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D11              0.03000000 sec
TD0                       1
SFO1            100.6228298 MHz
NUC1                    13C
P0                     2.67 usec
P1                     8.00 usec
PLW1            90.00000000 W
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz65
PCPD2                 90.00 usec
PLW2            15.42000008 W
PLW12            0.19036999 W
PLW13            0.09575700 W

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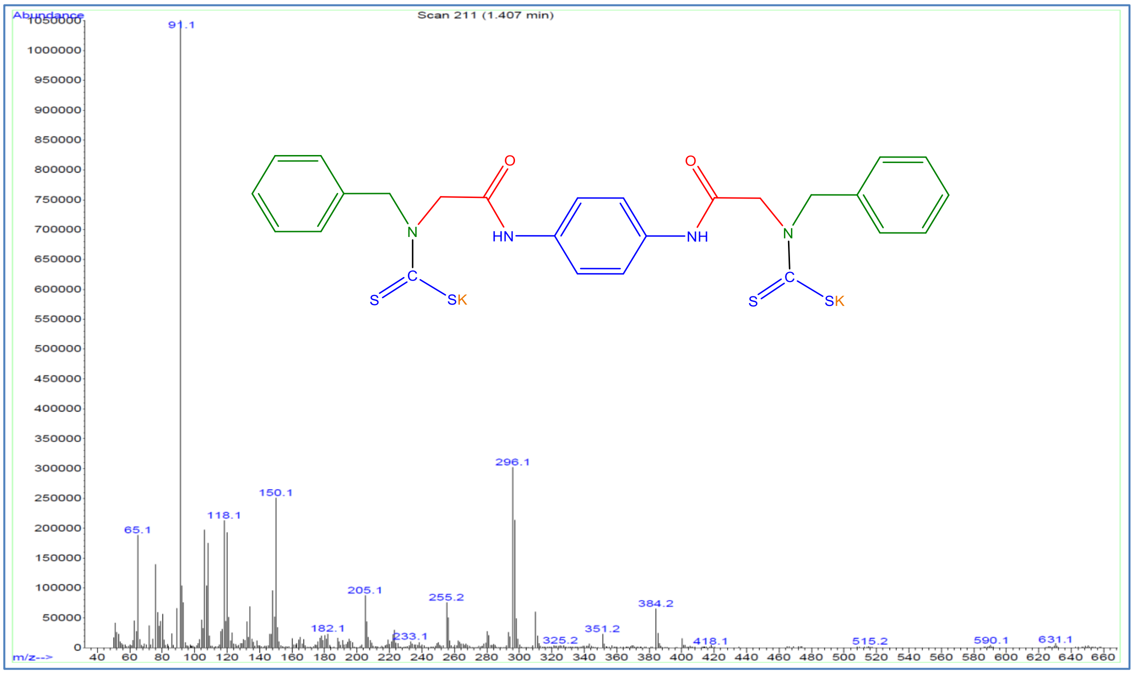
Figure 11: ES(+) mass spectrum of ligand.



Removal of heavy metals from aqueous solutions

Compounds that have DTC groups work as strong chelating agents to capture heavy metal ions from aqueous solutions. This is because the DTC group acts as a Lewis base which has strong affinity toward Lewis acids like heavy metals, forming highly stable chelates. Due to this feature, DTC compounds are widely used in treatment of metal-contaminated wastewater by precipitation using chelating ligands [27, 28]. Chemical precipitation is affected by used precipitation reagent, the concentration and type of metal ions exist in the solution, and presence of other compounds which may cause inhibition of the reaction. One of the most important factors affecting chemical precipitation is pH [29]. So, The research was carried out at different pH values and temperature degrees to determine the efficiency of prepared ligand for removing Co(II), Ni(II), Zn(II), Hg(II) and Pb(II) ions from their aqueous solutions.

The efficiency of removing heavy metals under experimental conditions was calculated using the following formula [30]:

$$R(\%) = \frac{(C_o - C_f)}{C_o} \times 100 \qquad (1)$$

Where:

R(%): Removal efficiency of ions.

C0: The initial concentration of ions (ppm).

Cf: The final concentration of ions (ppm).

Through the experiments, The increasing in the removal efficiency resulting from the change of pH was significant in contrast to that caused by the change of temperature. The best removal efficiencies of Hg2+ ions was 99.18 at pH=7 and temperature of 35 ºC. With regard to Pb2+ ions, the best ratios were 100 % at (pH=6, 25 ºC) and (pH= 7, 35 ºC). The best removal efficiency of Co2+ ions was 98.82 at (pH=8, 35 ºC). As for Ni2+ ions, the best ratio was 99.93 at (pH=8, 25 ºC). The best removal efficiency of Zn2+ ions was 85.42 at (pH=8, 25 ºC). The results are summarized in Tables 4 and 5.

Table 4: Removal efficiency of ions by DTC ligand, 0.035 g per 30 ml of solution at 25 ºC and different values of pH for 2h time period.

Ion	Initial concentration in aqueous solution (mg/L)	Temperature ºC	pH	Remaining concentration in aqueous solution (mg/L)	Removal efficiency (%)
Hg^{2+}	100	25	6	11.73	88.27
			7	0.980	99.02
			8	1.240	98.76
Pb^{2+}	100	25	6	BDL*	100
			7	11.51	88.49
			8	31.36	68.64
Co^{2+}	100	25	6	68.52	31.48
			7	69.70	30.30
			8	1.180	98.82
Ni^{2+}	100	25	6	70.10	29.90
			7	73.76	26.24
			8	0.070	99.93
Zn^{2+}	100	25	6	26.67	73.33
			7	45.73	54.27
			8	14.58	85.42

*Below detection limits

Table 5: Removal efficiency of ions by DTC ligand, 0.035 g per 30 ml of solution at pH= 7 and different values of temperature for 2h time period.

Ion	Initial concentration in aqueous solution (mg/L)	pH	Temperature ºC	Remaining concentration in aqueous solution (mg/L)	Removal efficiency (%)
Hg^{2+}	100	7	15	1.390	98.61
			25	0.980	99.02
			35	0.820	99.18
Pb^{2+}	100	7	15	13.48	86.62
			25	11.51	88.49
			35	BDL*	100
Co^{2+}	100	7	15	69.54	30.46
			25	69.70	30.30
			35	68.79	31.21
Ni^{2+}	100	7	15	72.69	27.31
			25	73.76	26.24
			35	72.07	27.93
Zn^{2+}	100	7	15	50.33	49.67
			25	45.73	54.27
			35	35.30	64.70

*Below detection limits

Conclusions

This study showed that the prepared ligand is soluble in water and behaves as bidenetate at CS2 moiety with metal ions to form dithiocarbamate macrocyclic complexes. The general proposed molecular structure of these complexes is [M(L)(H2O)2]2, where M= Hg2+, Pb2+, Co2+, Ni+2 and Zn2+, and L is the ligand. They have octahedral geometry around CS2 group. The prepared ligand is good chelating agent for removal of Hg2+, Pb2+, Co2+, Ni2 and Zn2+ ions from their aqueous solutions. The pH is one of the most important factors affecting chelating process.

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