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Design and Characterization of New Dinuclear Macrocyclic Dithiocarbamate Complexes by the Preparation of a Free Ligand Derived from Isopropylamine

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Abstract

The synthesis and structural characterization of new dithiocarbamate (DTC) ligand and some of its dinuclear transition metal complexes are described. The free dithiocarbamate ligand was prepared through several synthetic routes, including Schiff-base formation. The reaction of 2-aminopropane with terephthaldehyde leads to the formation of Schiff-base which is reduced by methanolic NaBH$_4$ to the corresponding secondary diamine. Diamine(N,N'- (1,4 phenylenebis (methylene)) bis(propan-2 amine)) reacts with (CS$_2$) in a basic solution of (KOH) to provide the corresponding bis(dithiocarbamate) free-ligand, which undergoes complexation with the appropriate metal (II) chloride to constitute macrocyclic complexes. Characterization of the ligand and its complexes was achieved by FTIR, UV-Vis, melting points, conductance, magnetic susceptibility, and ^{1}H, ^{13}C NMR spectroscopy. The analytical and spectroscopic data were employed to obtain the suggested geometries around metal centres. These studies revealed the formation of dinuclear macrocyclic complexes of the general formula $[M(L)]_2$ (where M= Mn$^{(II)}$, Fe$^{(II)}$, Co$^{(II)}$, Ni$^{(II)}$, Cu$^{(II)}$ and Zn$^{(II)}$), with tetrahedral geometries for Mn$^{(II)}$, Fe$^{(II)}$, Co$^{(II)}$ and Zn$^{(II)}$, and square planar geometry with Ni$^{(II)}$ and Cu$^{(II)}$ complexes.

Keywords: Dithiocarbamate (DTC) ligand, Dinuclear transition metal complexes, One-pot reaction

تصميم وتشخيص معقدات ثاني ثايوكاربميت جديده ثنائية النواة بواسطة تحضير ليكاند حر مشتق من ايزوبروبايل امين

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الخلاصة

تم تحضير وتشخيص ليكاند ثاني الثايوكاربميت جديد وبعض معقداته الفلزية الانتقالية ثنائية النواة . تضمنت طريقة تحضير الليكاند الحر لثاني الثايوكاربميت العديد من المراحل من خلال تشكيل قاعدة شيف. يؤدي تفاعل 2- امين بروبان مع الترفثالديهايد الى تكوين قاعدة شيف التي يتم اختزالها الى ثنائي الامين

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المقابل باستخدام بوروهايدريد الصوديوم الميثانولي. ثنائي الامين(N , N' _ (4,1 فينيلين ثنائي (ميثيلين))
ثنائي (بروبان –2 أمين)) يتفاعل بدوره مع الكابون ثنائي الكبريت في وسط قاعدي باستخدام هيدروكسيد
البوتاسيوم لتكوين الليكاند الحر الثنائي (ثاني ثايو الكاربميت) المقابل ثم يتم تعقيد الليكاند مع كلوريد الفلز
الثنائي التكافؤ لتكوين المعقدات الحلقية الكبيرة لثاني الثايوكاربميت.
تم تشخيص الليكاند ومعقداته بواسطة اطياف الاشعة تحت الحمراء واطياف الاشعة فوق البنفسجية والمرئية
[وقياس درجةFTIR, UV–Vis and ^{1}H, ^{13}C– NMR spectroscopyواطياف الرنين المغناطيسي]
الانصهار والتوصيلية المولارية والحساسية المغناطيسية. وضفت النتائج التحليلية والطيفية لايجاد الاشكال
الهندسية المقترحة حول مراكز الفلزات.اظهرت نتائج هذه الدراسات تكوين معقدات مخلبية كبيرة لثنائي
و[Zn$^{(II)}$,Mn$^{(II)}$] Co$^{(II)}$, Fe$^{(II)}$حيث اتخذت معقدات $[M(L)]_2$ الكاربميت ذات الصيغة العامة
الشكل الهندسي المربع المستوي[Ni$^{(II)}$,Cu$^{(II)}$]الشكل الهندسي الرباعي السطوح بينما اتخذت معقدات.

Introduction

Dithiocarbamates (DTCs) species are important organic molecules in chemistry science. They belong to the carbamate family in which the two oxygen atoms are substituted with sulfur atoms (Figure-1) that play an important role in coordination and have the ability to chelate transition metal ions and representative elements [1, 2]. The chelating abilities are attributed to their possession of two donor sulfur atoms in the ligands, which makes them useful ligands in both inorganic and bioinorganic chemistry. Researchers have been interested in studying dithiocarbamate compounds and identifying their properties, since they coordinate with most transition metals through double sulfur atoms to form stable compounds with a wide range of oxidation states [3].

Dithiocarbamates can behave as monodentate, bidentate chelating, or bidentate bridging ligands. This is due to the presence of the anionic (CS_2^-) moiety which has a wide range of binding modes upon complexation [4, 5]. The structural organization of the resulting metal complexes is determined by these binding properties [6]. Besides their complexation behavior, dithiocarbamates have myriad applications that range over a variety of scientific subjects, such as medicine [7,8], biological systems [9], materials science [10], and analytical chemistry [2], as well as industrial applications such as rubber vulcanization [11]. This property has encouraged a growing interest in their usage in environmental applications [12] and serving as herbicides [13] and fungicides [9] in agriculture. DTCs complexes have also shown diverse applications in nanoscience [14] and they are also applied in solar energy fields [15].

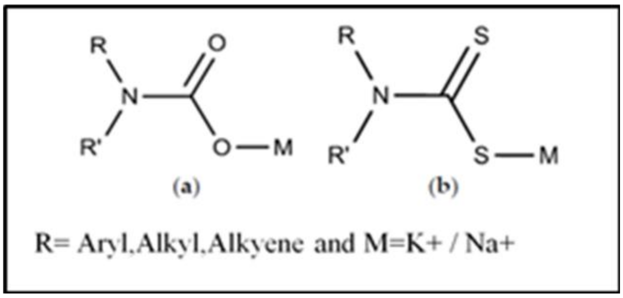

Figure 1 -Chemical struccture of (a)Carbamate ,(b)Dithiocarbamate.

Experime

Materials

2-Aminopropane, terephthalaldehyde, methanol (CH_3OH), potassium hydroxide (KOH), carbon disulphide (CS_2), and dimethyl sulfoxide (DMSO) were bought from B.D.H, Merck, Fluke, and Sigma-Aldrich, and used without additional purification. Solvents were purified by distillation.

Instrumentation

Melting points of all synthesized compounds were recorded on an Electro-thermal DMP-500 melting point device. FTIR was measured using Shimadzu (FT-IR) -8400S spectrophotometer in the

4000– 200 cm $^{-1}$ spectrum range. Spectra were performed as CsI and KBr discs. The electronic spectra for the ligand and its complexes were determined on a Shimadzu UV–Visible 160.A spectrophotometer, in DMSO solutions with 10^{-3} M. concentration. 1H– and 13C– NMR spectra were recorded on Bruker 400MHz SWISS.TS AG using DMSO and $CDCl_3$ as solvents. The metal content of the complexes was examined using a Nov (A.A) 350 atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded for 10^{-3}M solutions of the samples in DMSO as a solvent at room temperature using BC3020 professional benchtop conductivity meter. A magnetic susceptibility balance (Sherwood Scientific) was used to measure magnetic moments.

Methods Preparation of the Schiff-base 1,1'-(1,4-phenylene)bis(N- Isopropyl methane imine) (A)

Terephthaldehyde (0.5 g, 3.72mmol) was dissolved in absolute methanol (20mL) and then 4 drops of glacial acetic acid were added and stirred for 10 min. Isopropylamine (0.4 g, 7.45 mmol.) was added to the reaction flask with stirring, after which the mixture of the reaction was permitted to reflux for 6 hours. The product was achieved by evaporation of the solvent as a pale yellow crystal With the following characteristics; Yield: 0.7575g, (93.93%), m.p = 85-87 ºC.

IR data (cm^{-1}) : 3060 ν_{arom} (C-H), 2928 $\nu_{aliph.}$ (C-H), 1619 ν(C=N), 1437 and 1516 $\nu_{arom.}$ (C=C), (Figure-2).

NMR data (ppm), δH (400 MHz, $CDCl_3$): 8.39 (2H, s, C_4, $_4$`-H) , 7.79(4H, s, $C_6$, $_6$`,7, $_7$`-H) Ar-H, ,3.32 (2H,m,CH, $C_2$, $_2$`-H), 1.36 (12H, d, CH_3,C_1, $_1$`,3, $_3$`-H) (Figure-3).

δC(400 MHz,DMSO): 23.59 (CH_3, 4 C_1, $_1$`,3, $_3$`), 60.01 (CH, 2 C_2, $_2$`), 127.48 and 137.38(Ar- $C_{5,}$ $_5$` , 6, $_6$`,7, $_7$`), 157.22 (2 $C_{4,4}$`=N) (Figure-4).

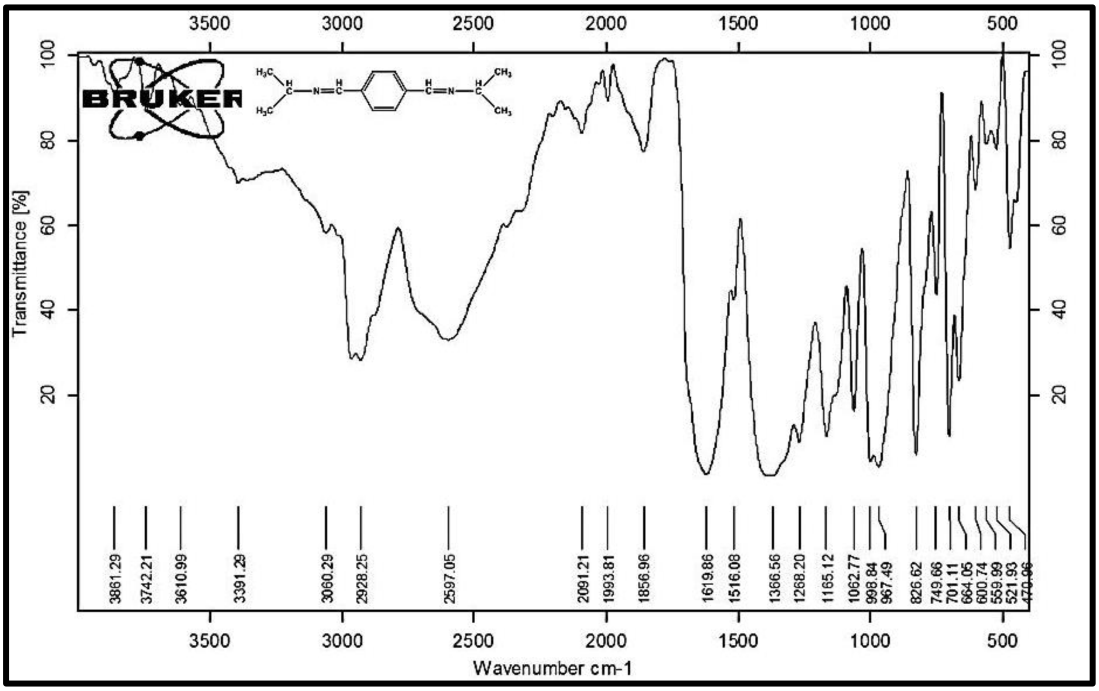

Figure 2 -FTIR– spectrum of Schiff-base 1,1'-(1,4-phenylene)bis(N- Isopropyl methane imine) (A)

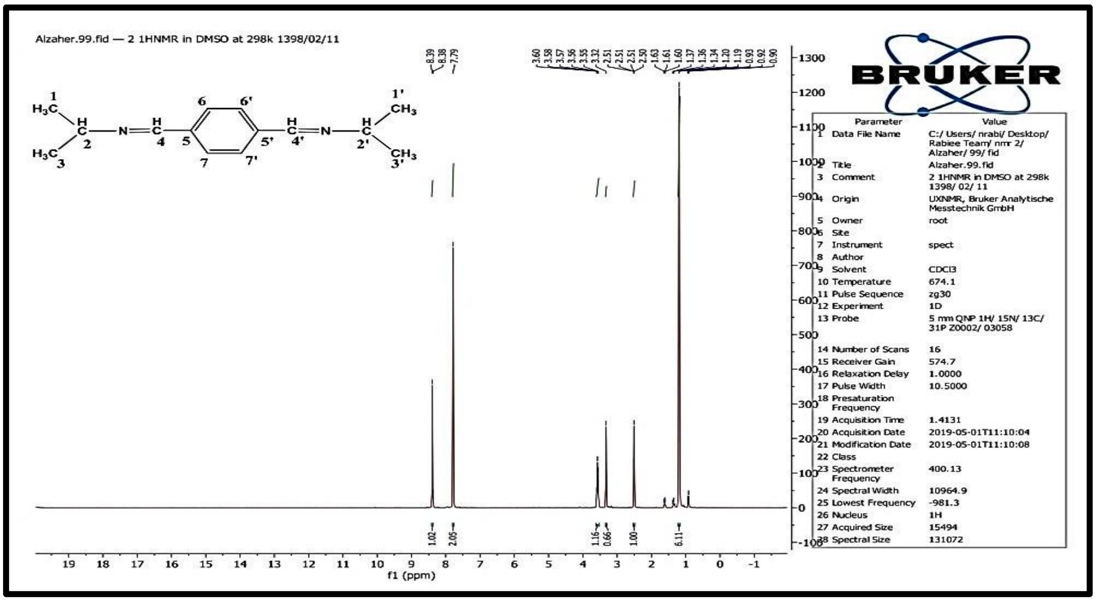

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Figure 3-^{1}H NMR spectrum of Schiff-base 1,1'-(1,4-phenylene)bis(N- Isopropyl methane imine) (A) in $CDCl_3$

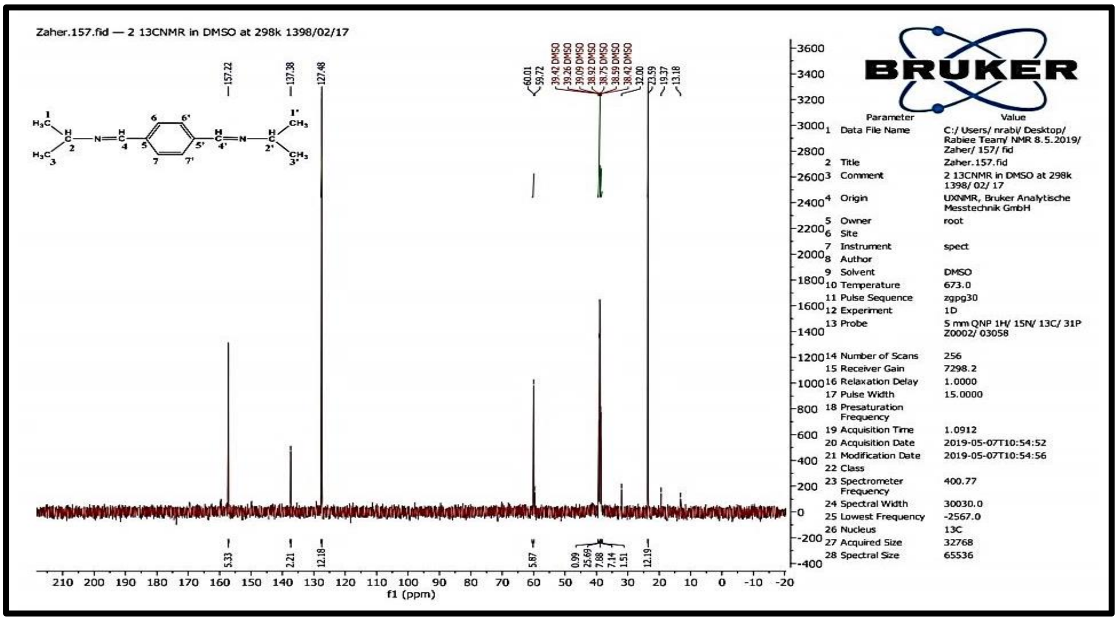

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Figure 4- ^{13}C NMR spectrum of Schiff-base 1,1'-(1,4-phenylene)bis(N- Isopropyl methane imine) (A) in DMSO

Synthesis of secondary amineN,N'-(1,4-phenylenebis(methylene)) bis(propan-2-amine) (B)

To a solution of 1,1'-(1,4-phenylene)bis(N-isopropylmethanimine) (A) (0.75g, 3.46mmol) dissolved in (30mL) of methanol, an excess, fivefold, $NaBH_4$ (1.31g, 6.93mmol) was added portion-wise with stirring for over 30 min. The reaction mixture was stirred well overnight at room temperature. Then, H_2O (200mL) was added and the product of diamine was extracted into CH_2Cl_2 (4 X 15mL). It was then washed again with water (200mL) and the organic layer was dried over anhydrous sodium sulfate (Na_2SO_4). The product was obtained after evaporating the solvent as a yellow oil. Yield: 0.65g, (88.55%). IR data (cm^{-1}) : 3463 ν(N–H), 3018 $\nu_{arom.}$(C–H), 2964 $\nu_{aliph.}$(C–H), 1514 $\nu_{arom.}$ (C=C), (Figure-5).

NMR data (ppm), *δH (400 MHz, CDCl3)*: 6.53 (2H, s, N-*H*), 7.39 (4H, s, C6, 6`,7, 7`-*H*) Ar-*H*, 3.65(4H, s, CH2N, (C4, 4`-*H*)),2.71 (2H, m,CH, C2, 2`-*H*),1.00(12H, d, CH$_3$,C1, 1`,3, 3`-*H*) (Figure-6).

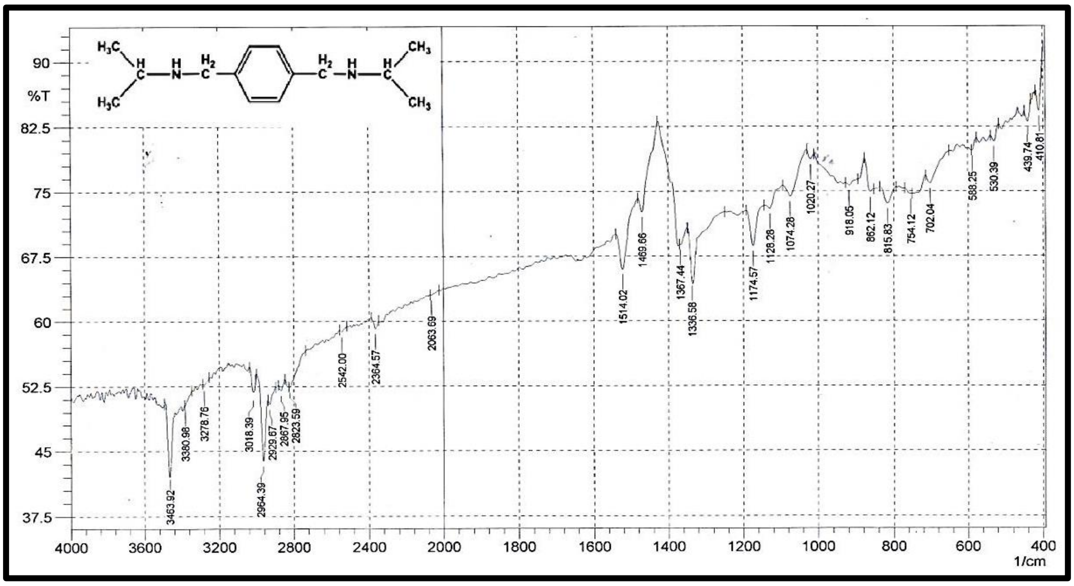
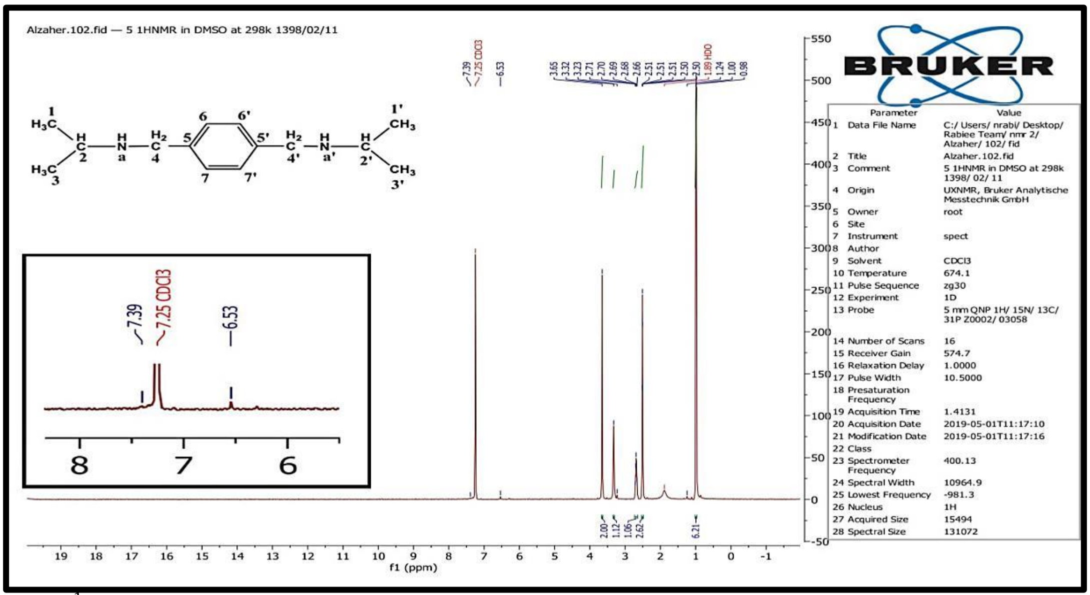


Figure 5 -FTIR^{-} spectrum of secondary amine N, N'-(1,4-phenylenebis(methylene)) bis(propan-2-amine) (B)



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13	Probe	5 mm QNP 1H/ 15N/ 13C/ 31P Z0002/ 03058
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24	Spectral Width	10964.9
25	Lowest Frequency	-981.3
26	Nucleus	1H
27	Acquired Size	15494
28	Spectral Size	131072

Figure 6- ^{1}H NMR spectrum of secondary amine N,N'-(1,4-phenylenebis (methylene)) bis(propan-2-amine) (B) in CDCl$_3$

Synthesis of potassium (1,4-phenylenebis(methylene)) bis (isopropyl carbamo dithioate) (L)

To a solution of bis-amine (B) (0.39g, 1.77 mmol) dissolved in methanol (10 mL), an excess of 2 equivalent KOH (0.19g, 3.54mmol) dissolved in 10ml of methanol was added gradually, and the resulted solution was permitted to stir under cold condition (0 °C) for 30 mins. Then, a solution of 2 equivalent carbon disulfide (0.26g, 3.54mmol) in 10 mL methanol was added dropwise to the reaction container and stirred for 6-7 hours until precipitation occurred. After evaporation of the solvent, a pale orange precipitate (potassium dithiocarbamate salt) was formed. The product was filtered off, washed with diethyl ether, and then dried at room temperature; Yield: 0.56g, (70. 59%), m.p = 300 - 307°C

IR data (cm^{-1}) : 1510 $\nu_{arom.}$ (C=C), 1422 ν (N^{-} CS$_2$), 1314,1270 ν (C–N) (Figure-9). NMR data (ppm), δH(400 MHz, DMSO): 7.17-7.31 (4H, m, C 6, 6`,7, 7` -*H*) Ar-*H*, 4.47(4H, s, CH2N, (C4, 4`-*H*)), 1.24 (12H, d,$CH_3$, C 1, 1`,3, 3` -*H*) (Figure-7).

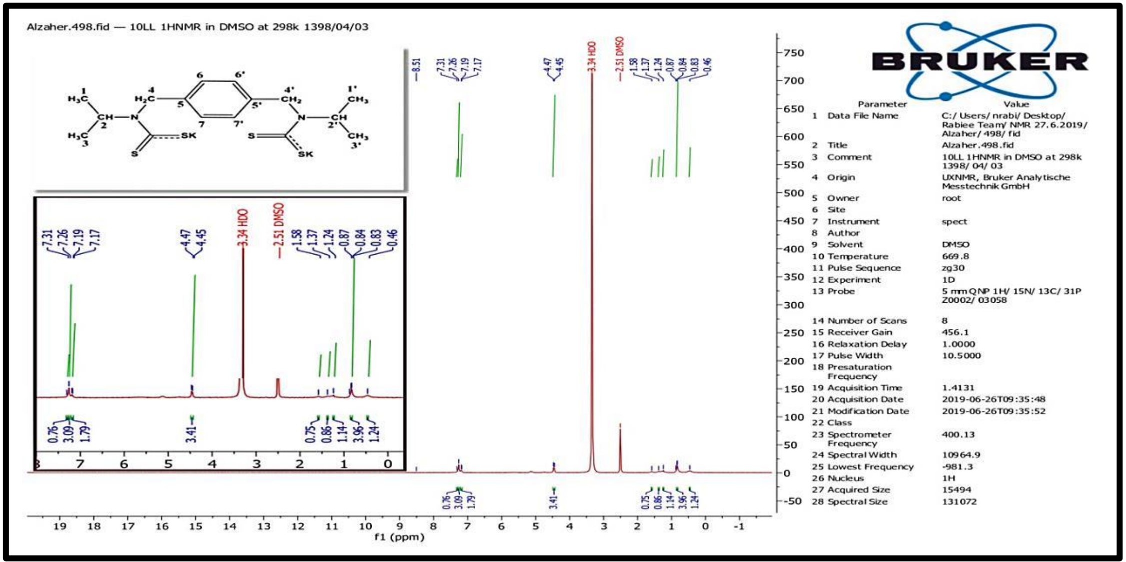


Figure 7- ^{1}H NMR spectrum of potassium (1,4-phenylenebis(methylene)) bis (isopropyl carbamo dithioate) (DTC) L in DMSO

General synthesis of the complexes

A general method was used to prepare the required metallic dithiocarbamates complexes, as follows.

A solution of 1 mmol of the metal chloride salt, dissolved in methanol (10mL), was added portion-wise to a warm solution of the potassium dithiocarbamates ligand (1mmol) dissolved in methanol (15mL). Then the mixture was stirred and heated under reflux for 4 h at 63 ^{o}C. A solid product was accumulated, which was filtered off, washed by excess methanol, and dried at room temperature to give the required dithiocarbamates - complex. All the complexes were prepared in the ratio of 1:1 metal-ligand. Colors, yields, metal content, and molar conductivity for the complexes are listed in (Table- 1).

1H-NMR spectrum of $[Zn(L)]_2$ in $CDCl_3$ showed peaks at δH (400MHz, $CDCl_3$):

3.71 (8H, s, CH_2–N, (C4, 4`,C10, 10` -*H*)), 2.76 (4H, m, CH , (C2, 2`,C8, 8` -*H*)), 7.30-7.38 (8H, d, C 5, 5`,6, 6`,11, 11,` 12, 12` , -*H*) Ar-*H*, 1.24 (24H, d,CH_3 , C 1, 1`,3, 3`, 7, 7`,9, 9`, -*H*) (Figure-8).

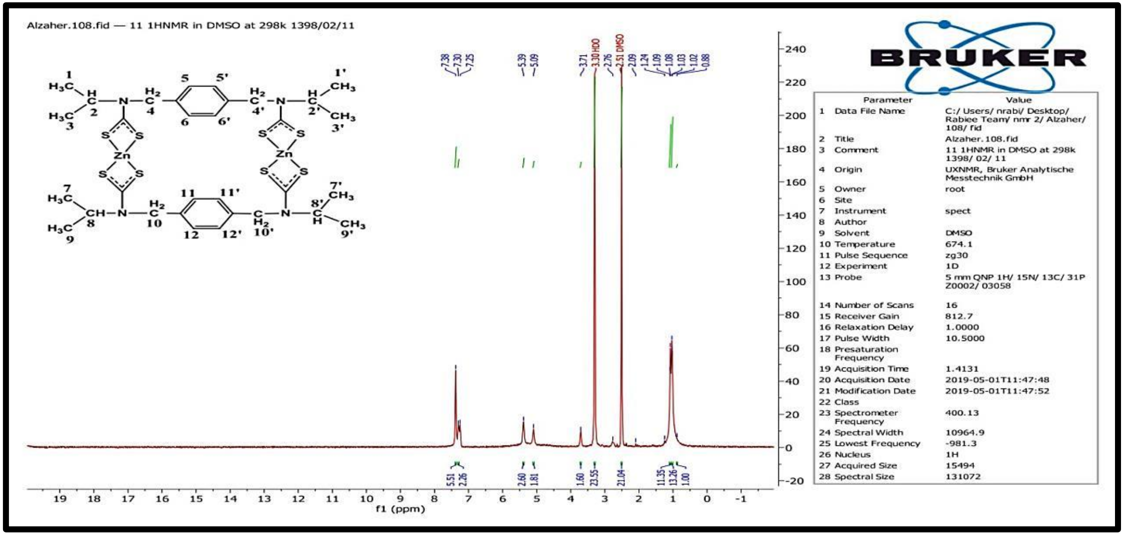


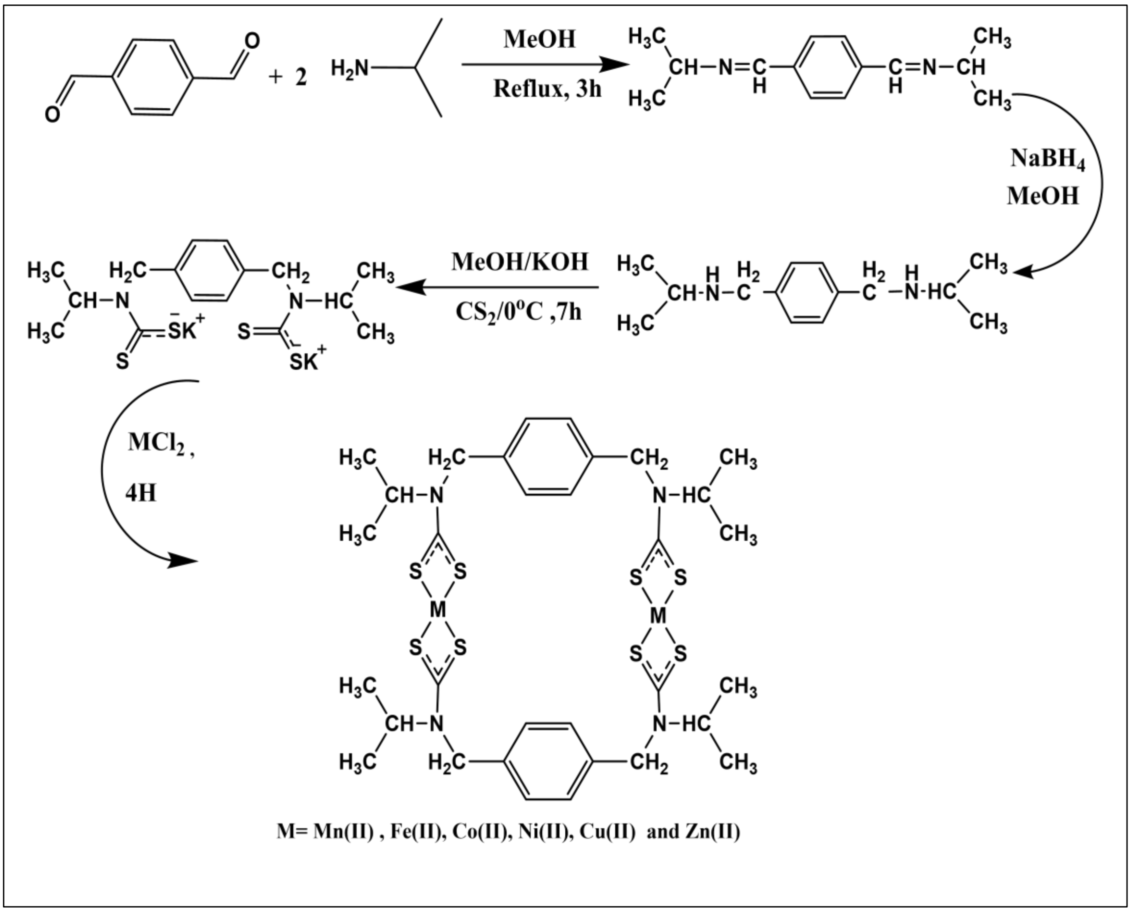
Figure 8-^{1}H NMR spectrum of $[Zn (L)]_2$ complex in DMSO

Results and Discussion

The reaction of terephthaldehyde with propan-2-amine in a mole ratio of 1:2 obtained the required Schiff-base, which was reduced in methanolic media to the corresponding secondary amine using sodium borohydride ($NaBH_4$). The resulted secondary- amine was reacted with CS_2 in a mole ratio of 1:2. Then, the (DTC) ligand was isolated in a good yield, as illustrated in (Scheme -1). The generated bimetallic dithiocarbamate macrocyclic complexes were obtained from the reaction of the ligand with the selected metal(II) salt in 1:1 mole ratio. In this process, the metal(II) ion assumed a key role in the self-assembly of the desired macrocyclic dinuclear complexes.

Physico-chemical studies showed the formation of four coordinate complexes of the general formula $[M(L)]_2$ (where M= Mn$^{(II)}$, Fe$^{(II)}$, Co$^{(II)}$, Ni$^{(II)}$, Cu$^{(II)}$ and Zn$^{(II)}$), illustrated in (Scheme -1).

The complexes are air-stable, solid, and totally dissolvable in DMSO but not in common organic solvents. The new ligand and its dinuclear macrocyclic complexes were characterized by FT-IR, 1HNMR, electronic spectra (UV-Visible), melting point, magnetic measurement, and conductance. As can be observed in (Table -1), the analytical data agree with the suggested formulas. The conductivity measurements of all complexes in DMSO solutions are demonstrative of their non-electrolytic nature.



Scheme 1: Synthetic route of of potassium (1,4-phenylenebis(methylene)) bis (isopropyl carbamo dithioate) (DTC) L and its complexes

Table 1-The Physical Properties of the Metal(II) Complexes

Metal ion	*Colour*	*Yield (%)*	*m.p. ºC*	*M%*	*$\varepsilon M(\Omega^{-1}cm^{2}$ $mol^{-1})$ in DMSO*
Mn^{II}	Pink-brown	49.90	200*	6.95 (6.45)	17.3
Fe^{II}	Dark green	39.30	235*	6.42 (6.54)	12.08

Co^{II}	green	39.43	295*	6.64 (6.86)	10.9
Ni^{II}	Dark grey	44.55	297*	6.97 (6.83)	11.3
Cu^{II}	Dark brown	28.60	263*	7.83 (7.31)	6.04
Zn^{II}	white	20.58	$>$ 300	7.67 (7.49)	2.5

*=Decomposed

FTIR spectra for the complexes

The most significant infrared bands for (DTC) L and its complexes together with their assignments are described in (Table-2) and shown in Figure-9. The FTIR spectra of the dinuclear-macrocyclic complexes provided evidence of the formation and coordination of the dithiocarbamate functions with the metal(II) ions. The bands resulting from the stretching vibrations of the N- CS_2 bonds in the range 1459-1475 cm^{-1} have a wave number which is intermediate between the values observed for C-N single bond (1270-1377 cm^{-1}) and C=N double bonds (1619cm^{-1}), suggesting a partial delocalization of (π-electron) density within the dithiocarbamate functions [16]. For the (CS_2) groups, the asymmetric vibrations of the CS_2 fragment appeared between 1059 and 1065 cm^{-1} and the symmetric band ν(CS_2) was observed at 999-901cm^{-1}, assuring the anisobidentate chelation mode of the DTC ligand to the metal atoms [17].

The vibrational bands were observed in the region 474 – 420 cm^{-1} in the spectra of all DTC complexes and related to the presence of ν(M-S), hence assuring that the sulfur atoms of the DTC ligand are coordinated to the metal center moiety and supporting the anisobidentate chelation mode of the DTC ligand [18].

Table 2-FT-IR spectral data (wave number cm^{-1}) of DTC complexes

Comp.	**ν_{ali}(C–H)**	**ν_{ar}(C=C)**	**ν (N– CS_2)**	**δ (CH_2)**	**ν (C–N)**	**ν_{as}(CS_2) ν_s(CS_2)**	**ν (M–S)**
L	2970	1510 ,1556	1458,1422	1377	1314,1270	1065,999 and 961	–
$[Mn(L^2)]_2$	2974	1511	1460	1407	1337,1264	1061,1021 and 963	448
$[Fe(L^2)]_2$	2974,2930	1500	1459	1413	1338,1253	1060,958	433
$[Co(L^2)]_2$	2973,2931	1510	1459	1414	1339,1244	1065,970 and 903	420
$[Ni(L^2)]_2$	2972	1545	1475	1416	1339,1257	1059,962 and901	420
$[Cu(L^2)]_2$	2975,2930	1512	1474	1414	1337,1271	1060,964 and902	430
$[Zn(L^2)]_2$	2975,2932	1515	1460	1412	1337,1254	1061,956 and903	443

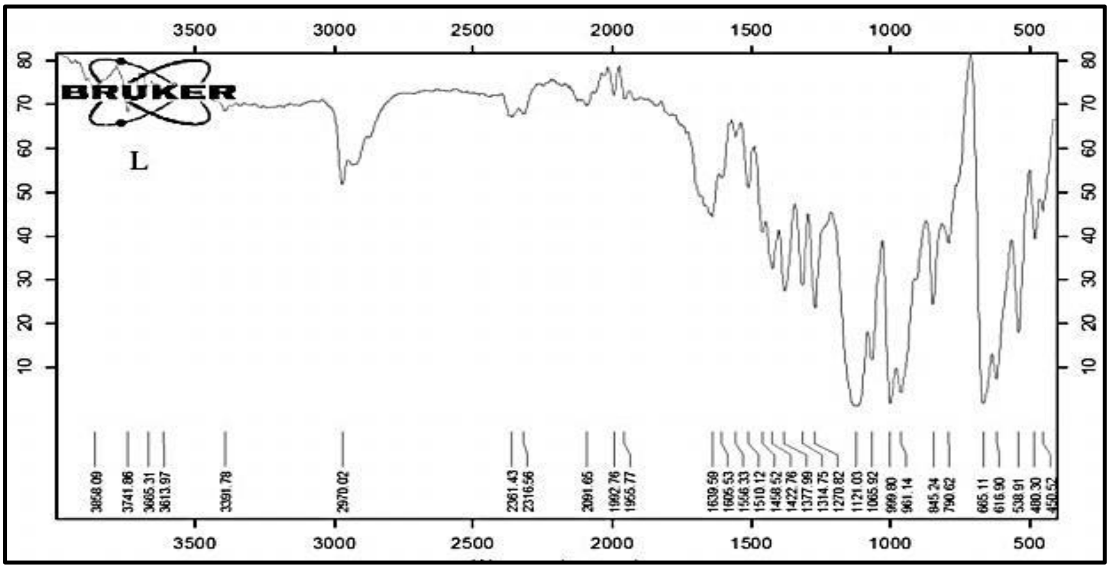


Figure 9-FTIR⁻ spectrum of potassium (1,4-phenylenebis(methylene)) bis (isopropyl carbamo dithioate) (DTC) L

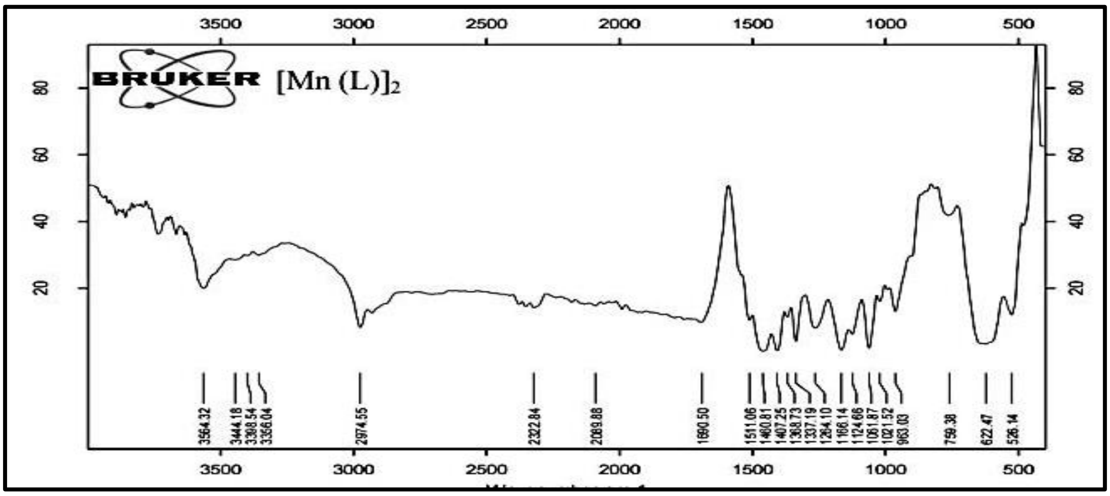


Figure 10-FTIR⁻ spectrum of $[Mn(L)]_2$

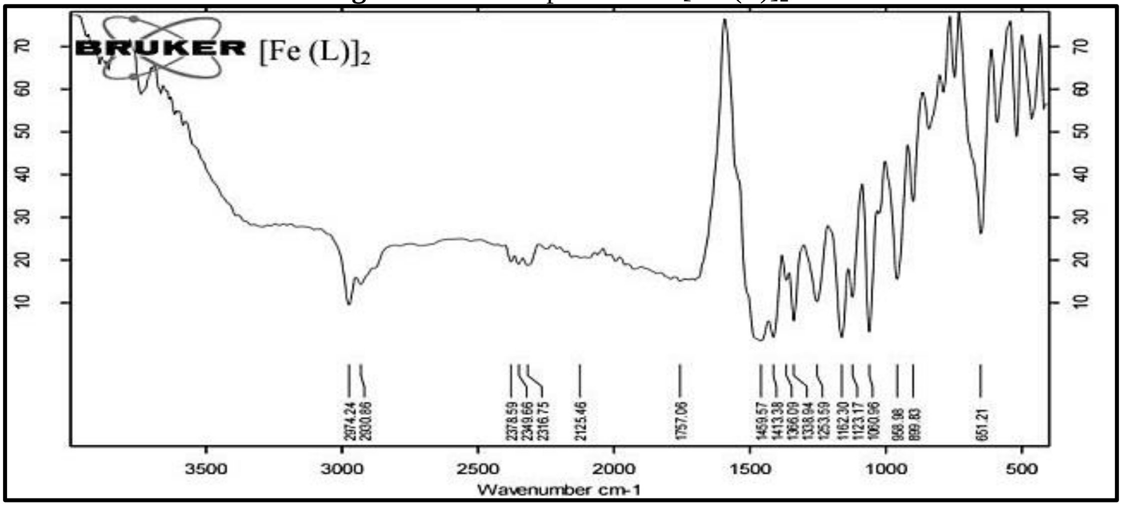


Figure 11-FTIR⁻ spectrum of $[Fe(L)]_2$

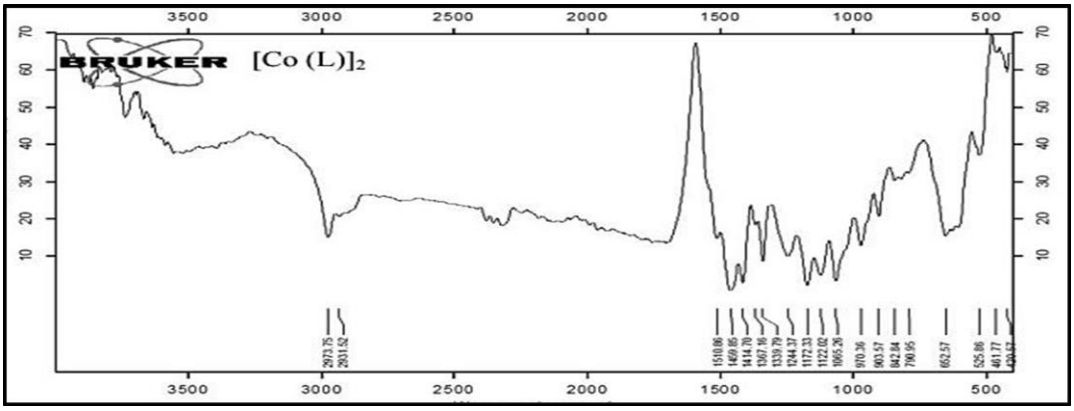


Figure 12-FTIR^{-} spectrum of [Co(L)]$_2$

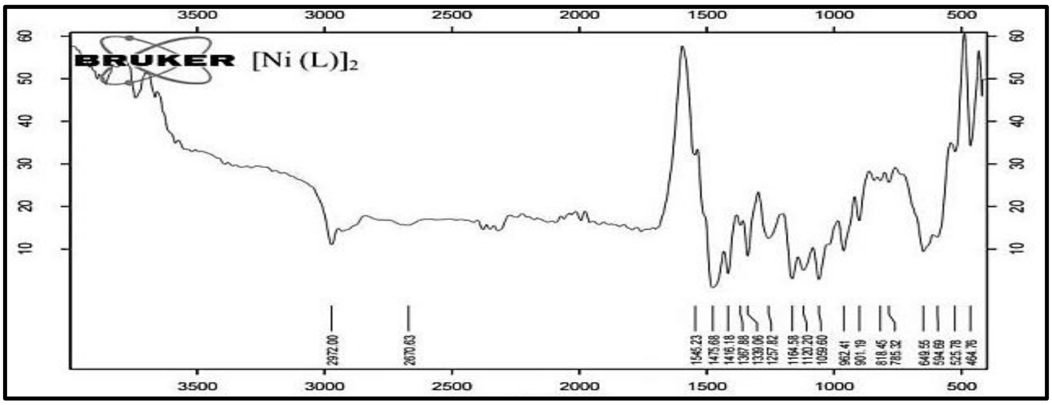


Figure 13-FTIR^{-} spectrum of [Ni(L)]$_2$

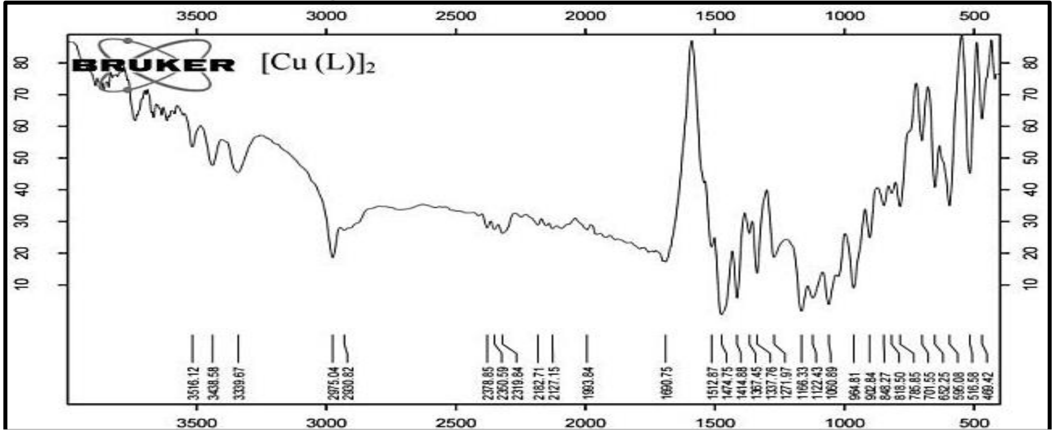


Figure 14-FTIR^{-} spectrum of [Cu(L)]$_2$

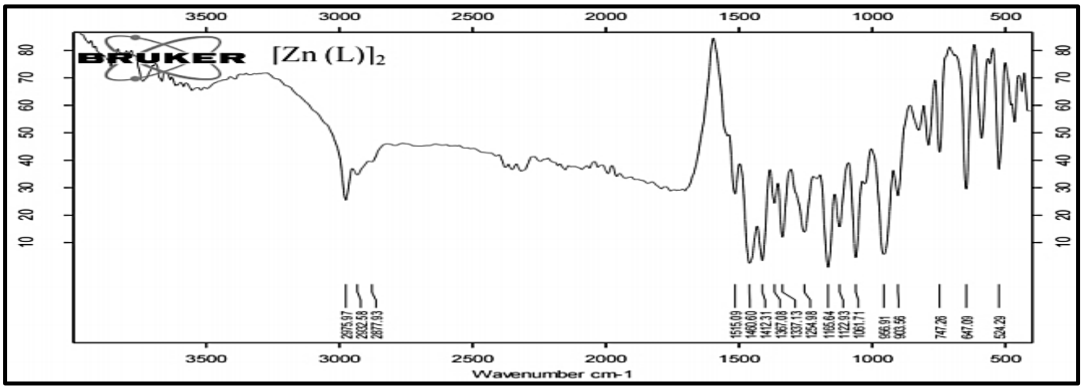


Figure 15-FTIR^{-} spectrum of [Zn(L)]$_2$

Electronic$^-$ spectra and magnetic moments

The UV−Vis spectral data of DTC ligand spectra show peaks 277 and 345nm assigned to π → π* and n → π* transitions, respectively [19,20], as shown in Figure-16. The electronic spectra of the DTC complexes [M (L)]$_2$ (where; M$_=$Mn$^{(II)}$, Fe$^{(II)}$, Co$^{(II)}$, Ni$^{(II)}$, Cu$^{(II)}$, Zn$^{(II)}$) in DMSO solutions exhibited various bands around 325-265 nm related to the ligand field π → π* transitions [19,20] . Bands at 343- 435 nm in L complexes were ascribed to the n → π* and charge transfer (CT) transitions [21,22].

The electronic spectrum of the Mn(II) $^-$ complex exhibited a weak-absorption , low-intensity band in the d-d region assigned for $^6A_1^{(F)} \rightarrow {}^4T_1^{(G)}$, which is a feature for tetrahedral geometry around the Mn atom [23]. The magnetic moment of Mn(II) in [Mn$^{(II)}$(L)]$_2$ complex 6.05 B.M. is typical for a high spin referring to tetrahedral arrangement of Mn$^{(II)}$ion [19].

The Fe(II)$^-$complex spectrum pointed out a peak in the (d-d) region at 525nm ascribed to $^5E_1 \rightarrow {}^5T_2$ transition, and the value of μeff is 4.54 B.M. This magnetic moments value indicates tetrahedral geometry about Fe(II) ion[24,25]. The Co (II)$^-$complex displayed bands in the d-d visible region at an average of 564 and 645nm. These bands could be attributed to $^4A_2^{(F)} \rightarrow {}^4T_1^{(F)}$ transitions [17,18]. The magnetic moment value of μeff 4.76 B.M for the green Co (II) complex is in agreement with tetrahedral structures [19]. The Ni(II)$^-$complex presented peaks in the (d-d) region at 651 nm and 674 nm assigned to d-d transition type($^1A_1g^{(F)} \rightarrow {}^1B_1g^{(F)}$and $^1A_1g^{(F)} \rightarrow {}^1A_2g^{(F)}$), respectively, with its dimagnatic behaviour confirming square planar arrangement around the Ni$^-$ atom [18, 23, 25]. The Cu(II)$^-$complex gives two (d-d) absorption bands at 769 nm and at an average of 791nm, 839 nm, corresponding to $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2A_1g$ transitions, respectively. Cu-complex gave μeff value of 1.85 B.M, which is in agreement with square planar structures geometry about metal center [17,23]. The spectrum of the Zn(II) $^-$ complex presented bands around 278, 382, and 435 nm attributed to π →π* and n→ π* and charge transfer, respectively. As expected, this complex is dimagnatic and the metal usually prefers tetrahedral coordination [18,22,24].

Table 3-UV$^-$Vis spectral data of (DTC)L and complexes in DMSO solutions

Comp.	Band Position λnm	Wavenumber (cm^{-1})	Extinction coefficient εmax (dm^3.mol^{-1}.cm^{-1})	Assignment.	μeff (B.M)
L	277 345	36101 28985	1951 61	π → π* n → π*	-
[Mn(L)]$_2$	296 350 515	33783 28571 19417	2328 216 31	π → π* (C.T) $^6A_1^{(F)} \rightarrow {}^4T_1^{(G)}$	6.05
[Fe(L)]$_2$	276 343 525	36231 29154 19047	1716 260 4	π → π* (C.T) $^5E_1 \rightarrow {}^5T_2$	4.54
[Co(L)]$_2$	276 307 321 353,364 564,645(average)	36231 32573 31152 28328,27472 17730,15503	1882 1347 1511 872,909 16,37	π → π* (C.T) $^4A_2^{(F)} \rightarrow {}^4T_1^{(F)}$	4.76
[Ni(L)]$_2$	265, 285 325 371, 388 651 674	37735, 35087 30769 26954, 25773 15360 14836	526, 364 1717 283, 328 31 32	π → π* (C.T) $^1A_1g^{(F)} \rightarrow {}^1B_1g^{(F)}$ $^1A_1g^{(F)} \rightarrow {}^1A_2g^{(F)}$	dimagnatic
[Cu(L)]$_2$	272 354	36764 28248	844 57	π → π* n → π*	1.85

	410 769 791,839(average)	24390 13003 12642,11918	178 9 11, 9	(C.T) $^2B_1g\rightarrow{}^2B_2g$ $^2B_1g\rightarrow{}^2A_1g$	
$[Zn(L)]_2$	278 382 435	35971 26178 22988	2076 106 165	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ (C.T)	dimagnatic

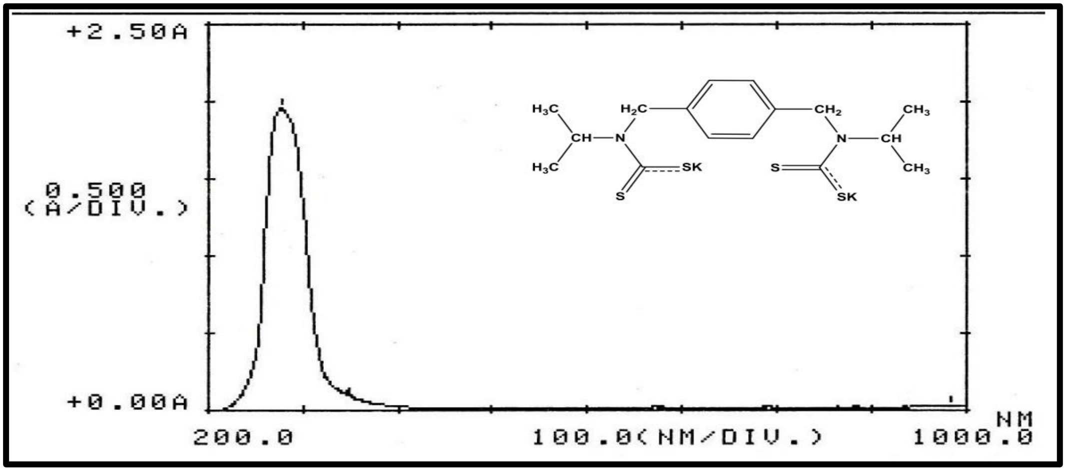


Figure 16-The electronic spectrum^{-} of potassium (1,4-phenylenebis(methylene)) bis (isopropyl carbamo dithioate**)** **(**DTC**)** **L**

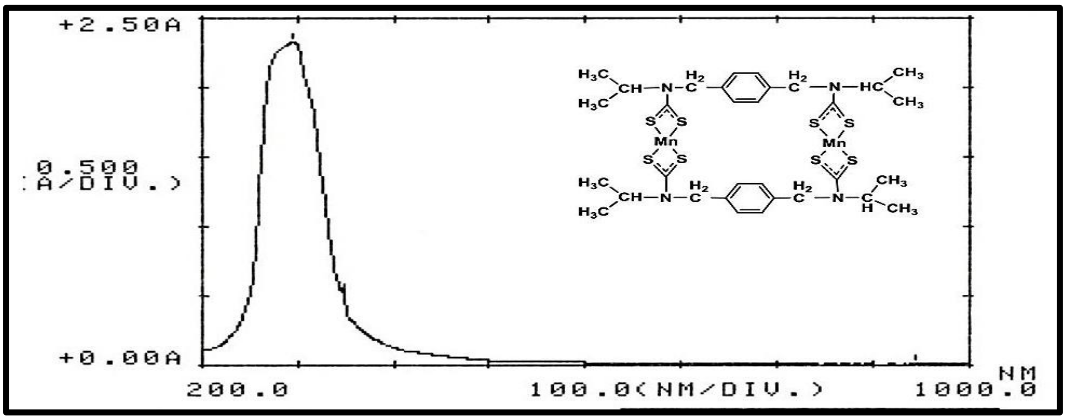


Figure 17-The electronic spectrum^{-} of **[**Mn**(L)]**$_2$

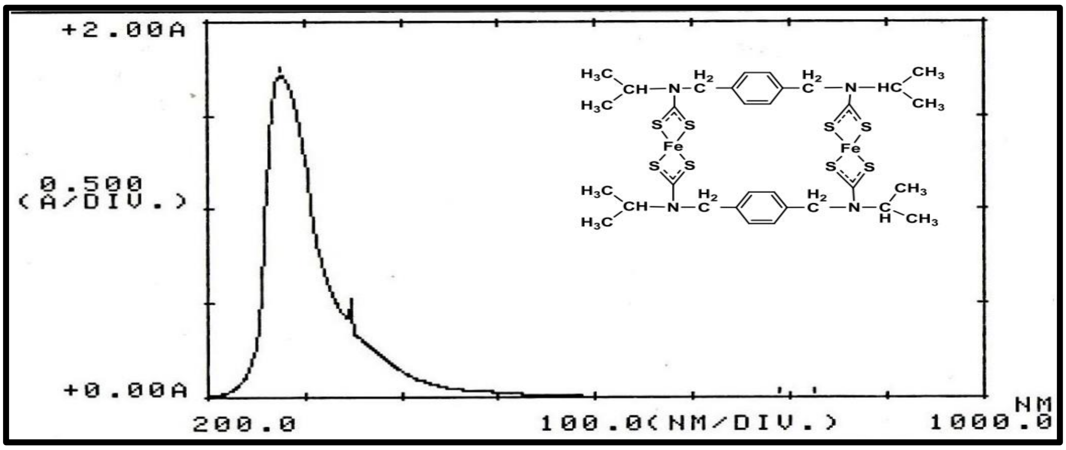


Figure 18-The electronic spectrum of $[Fe(L)]_2$

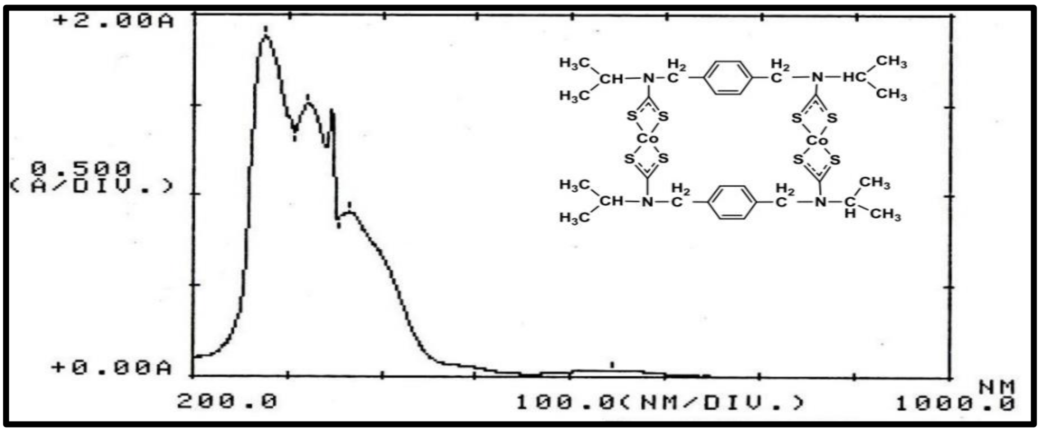


Figure 19-The electronic spectrum of $[Co(L)]_2$

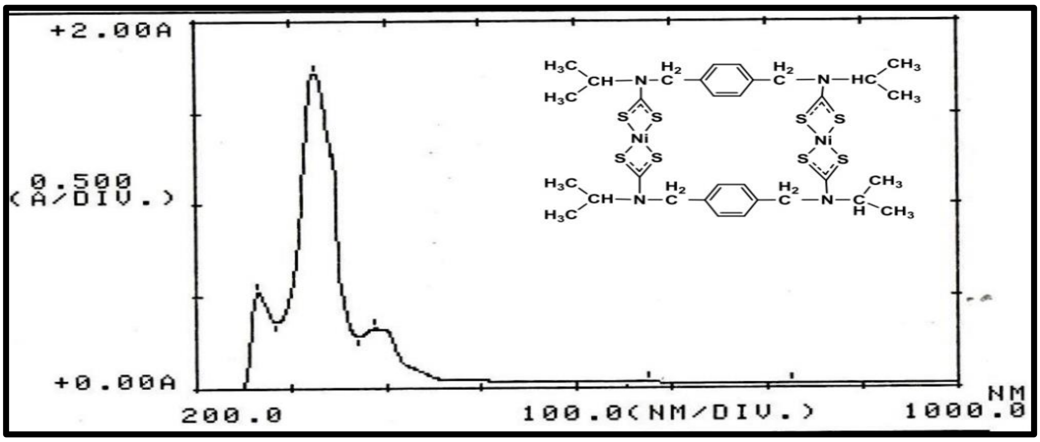


Figure 20-The electronic spectrum of $[Ni(L)]_2$

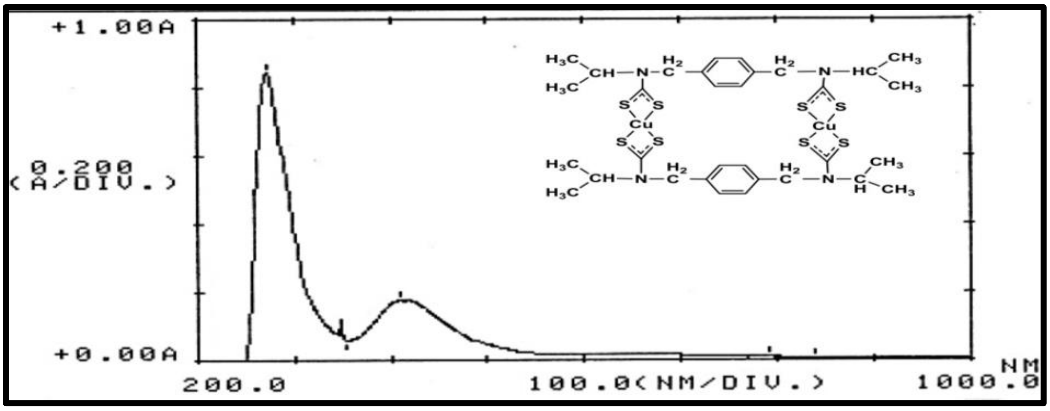


Figure 21-The electronic spectrum of $[Cu(L)]_2$

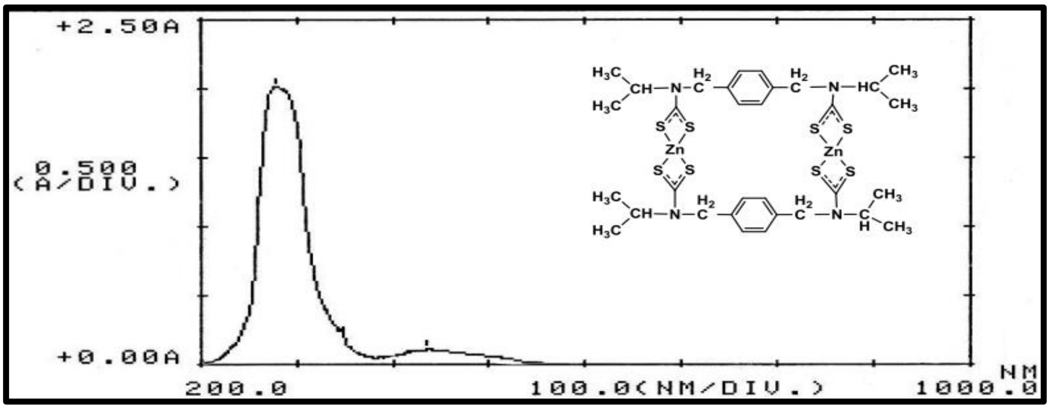


Figure 22-The electronic spectrum of $[Zn(L)]_2$

Conclusions

The synthesis and characterization of a new DTC-bidentate chelating ligand and some of its bimetallic macrocyclic complexes are discussed. The ligand was afforded via three steps. This included the formation of Schiff-base and the corresponding bis-amine. Then, bis(dithiocarbamate) free-ligand was provided, which was employed to produce a series of DTC-complexes, characterized using different spectroscopic (NMR, FT-IR and UV-Vis) techniques. The spectroscopic data indicated the formation of four-coordinate complexes. The bonding mode and the complexes' overall geometry were identified using physico-chemical and spectroscopic methods. The prepared complexes displayed two types of geometries in the solid and solution states, which are divided according to their physico-chemical measurements into; tetrahedral geometries for $Mn^{(II)}$, $Fe^{(II)}$, $Co^{(II)}$ and $Zn^{(II)}$ and square planar geometries with $Ni^{(II)}$ and $Cu^{(II)}$ complexes.

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