



Synthesis and Characterization of Some Transition Metal Complexes with Bis(o-aminophenyl)Disulfide Alkane Ligands

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Abstract

A series of new complexes of the type $[M(L)Cl_2]$ and $[M(L)]Cl_2$ where $M = Co(II), Ni(II)$ and $Cu(II)$, $L = L_1$ or L_2 ($L_1 = 1,2$ -Bis(o-aminophenyl)disulfide propane, $L_2 = 1,2$ -Bis(o-aminophenyl) disulfide butane), have been prepared in 1:1 (L:M) and characterized by molar conductivity, magnetic moment, FT-IR, 1H -NMR, UV-visible spectra studies and metal content analysis. Conductivity data in DMF and DMSO solution showed that some complexes are non-electrolyte and others are (1:1) (M:L) electrolytes. Magnetic moment and electronic spectra indicate that all complexes have a tetrahedral geometry except Ni(II) complexes which have a square planer geometry.

Keywords: 1,2-Bis(o-aminophenyl)disulfide derivatives, metal complexes.

1. Introduction

Benzothiazole is a preventative class of sulfur containing heterocyclic and involves a benzene ring fused to a thiazole ring [1,2]. The Benzothiazole ring system was originally found in various marine and terrestrial natural compounds, which is widely used as vulcanization accelerators, anti-oxidants, anti-inflammatory agents, enzyme inhibitors, fluorescent materials, and electroluminescent devices due to its highly pharmaceutical and biological activity [3,4]. There has been considerable interest in the study of organic ligands containing two or more different donor atoms because such ligands throw light on the nature of the metal ligands bonding [5]. The ability to tune the MN₂S₂ ligands by variations of M has resulted in a range of complexes, such as V^{4+} in $[V=O]^{2+}$, Fe^{2+} in $\{Fe(NO)\}_7$, Ni^{2+} , Pd^{2+} , Cu^{2+} , and Zn^{2+} [6]. The ability of the MN₂S₂ metalloligands to serve as monodentate as well as bidentate ligands to a single metal or as bridging bidentate ligands to two metals has led to multiple new compositions and various diverse structure forms [6]. Three new mono-nuclear complexes of nitrogen-sulfur donor set, formulated as $[Fe(L)Cl_2]$ (1), $[Co(L)Cl_2]$ (2) and $[Ni(L)Cl_2]$ (3), where $L = 1,3$ -bis(2-pyridyl methyl thio) propane were synthesized and isolated in their pure form. All the complexes were characterized by physico-chemical and spectroscopic methods. The structural analysis evidences isomorphous crystals with the

metal ion in a distorted octahedral geometry that comprises NSSN ligand donors with trans located pyridine rings and chlorides in cis positions. [7].

In all cases the ligand coordinates to the center metal ion through the imidazole and thiazole nitrogen atoms. The spiracyclic structure $[Co(btzc-SMe)_2]$, Btz = N-benzo-thiazole-2-yl) dithio carbamic methyl ester the ligand is a derivative of benzothiazole is anionic and behaves as bidentate, nitrogen and sulfur atoms are bonded to the center metal ion giving planar tricyclic chelates, where Co(II) is part of the six-membered ring [8].

In view of the reported interesting results and in continuation of our studies on transition metal complexes with sulfur, oxygen and nitrogen containing ligands [9-11]. We are presenting here the preparation of new ligands obtained from condensation of o-aminothiophenyl and 1,3-dibromopropane or 1,4-dibromobutane with sodium hydroxide in (2:1:2) molar ratio. Scheme-1 and their Co(II), Ni(II), Cu(II) and Zn(II) complexes.

2. Experimental:

2.1 Material and Methods:

All chemicals used were reagent grade from B.D.H or FLUKA companies, used as supplied. Melting point or decomposition temperature were determined on electrothermal digital melting point apparatus. Conductivity measurements were made on $10^{-3}M$

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solution of the complexes in (DMF) solvent at 25 °C using conductivity natural model 4070 Jenway. The chloride was determined using the method in Vogel [12]. IR spectra has been recorder on Shimadzu FT-IR –ATR from (400- 4000) cm^{-1} using KBr disc. Electronic spectra were recorded in DMF or DMSO (10^{-3}M) solutions on Shimadzu UV/vis recording UV-160 spectrophotometer at room temperature using 1cm quartz cell . The Magnetic measurements of the complexes were carried out at 25 °C on the solid state by Faraday's method using Bruker BM6 apparatus .Elemental analyses (C,H,N and S) were carried out using micro analytical techniques on perkin Elmer 2400(IEES) at ORDU universities. Metal estimation were don on PYEUNI-CAM SPg atomic absorption spectra –photometer. ^1H NMR spectra of the ligands were carried chemical shifts are reported in ppm relative to an internal standard of TMS .

2.2. General procedure for the synthesis of the ligands [13](scheme 1)

2.2.1.1,3-bis (o-amino phenyl) disulfide propane (L₁):

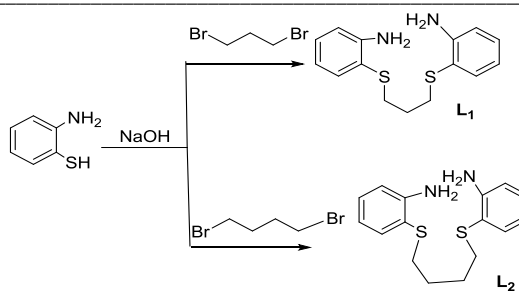
The mixture of 1,3-dibromo propane (0.2 g,0.1 mol) in ethanol (10ml) with an equivalent amount of (2-amino thiophenyl) (0.25g,0.2 mol) and NaOH (0.07g,0.2 mol) in ethanol (20 ml) was boiled under reflux for 6 hr., after cooling in room temperature .NaBr was removed by filtration then the solution has been evaporated to half volume , on cooling lift a Brown solid .the solid thus obtained , was filterd off ,washed with ethanol and diethyl ether then dried under vacuum for several hours .

2.2.2 1,4-bis (ortho amino phenyl)disulfide butane (L₂):

This ligand were papered by using similar procedure as above except using 1,4-dibromo butane (0.21g, 0.1 mol) in case (L₂).

2.3 General procedure for the synthesis metal complexes .

Ethanolic solution of (0.1 mole) of [L₁(0.29 g);L₂(0.30g)] was added to (0.1 mole) of metal chloride [CoCl₂.6H₂O(0.237g); NiCl₂.6H₂O (0.237g); CuCl₂.2H₂O (0.17g); ZnCl₂ (0.136g)]dissolved in (10 ml) ethanol , the reaction mixture was refluxed for 2 hours ,at room temperature give the precipitate which was filtered off, washed with ethanol and diethyl ether ,then dried under vacuum for 4 hours.



Scheme (1):Preparation the Ligands (L₁,L₂)

3. Results and Discussion

The synthetic route of the 1,3-di(o-amino pheny) disulfide propane or butane are depicted in Scheme(1) Bis-(o-amino phenyl) disulfide propane or butane were synthesized by the reaction of(o-aminothio phenyl) and 1,3-di bromo propane or 1,4-di bromo butane with sodium hydroxide in (2:1:2) molar ratio.

The complexes were prepared through direct reaction of the metal chlorides CoCl₂.6H₂O or NiCl₂.6H₂O or CuCl₂.2H₂O or ZnCl₂ with the above ligands in (1:1) molar ratio. The complexes are stable for long time ,non hydroscopic and colored solids .The metal complexes are in soluble in common organic solvents like chloroform carbon tetra chloride,hexane ,methanol,acetone. They are soluble in DMF or DMSO. The melting point,elemental analysis, conductance and magnetic measurements of complexes are listed in table(1) . The analytical data of the metal complexes show that all the metal chelates have 1:1 metal to ligand stoichiometry.

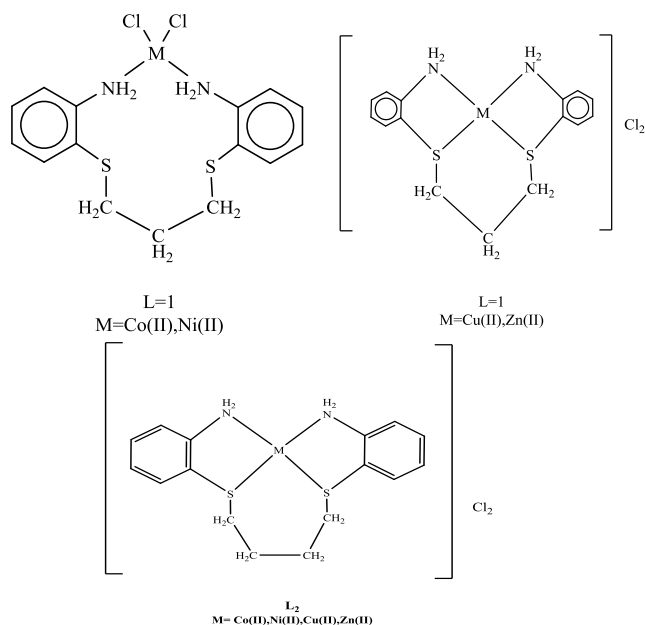


Figure (1):Preparation the Complexes

Table(1): The Physical properties and analytical of the ligand and their complexes

complex no.	Structure	color	m.p	Analysis found (calc.) %						Molar Conductivity $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	μ_{eff}
				C	H	N	S	M	Cl		
L ₁	[C ₁₅ H ₁₈ N ₂ S ₂]	Brown	305 ^d	62.02 (60.11)	6.24 (6.6)	9.64 (9.22)	22.07 (22.05)
L ₂	[C ₁₆ H ₂₀ N ₂ S ₂]	Brown	291 ^d	63.11 (62.89)	6.62 (5.88)	9.20 (9.05)	21.06 (21.00)
1	[Co(L ₁)Cl ₂]	dark purple	240 ^d	42.86 (43.0)	4.31 (4.93)	6.66 (6.51)	15.25 (14.88)	14.02 (14.85)	16.86 (15.56)	23	Di
2	[Ni(L ₁)Cl ₂]	light green	293 ^d	42.89 (41.66)	4.31 (4.03)	6.66 (5.89)	15.26 (15.21)	13.97 (13.02)	16.87 (16.05)	25	Di
3	[Cu(L ₁)Cl ₂]	black	280 ^d	42.40 (42.01)	4.27 (3.99)	6.59 (6.21)	15.09 (14.89)	14.95 (15.01)	16.68 (16.05)	67	2.01
4	[Zn(L ₁)Cl ₂]	white	245- 247	42.21 (42.20)	4.25 (4.15)	6.56 (6.32)	15.02 (14.96)	15.32 (14.98)	16.61 (15.31)	78	Di
5	[Co(L ₂) Cl ₂]	violate	247- 250	44.24 (43.87)	4.64 (4.42)	6.45 (6.09)	14.76 (14.05)	13.56 (13.05)	16.32 (15.31)	85	4.80
6	[Ni(L ₂) Cl ₂]	Greenish white	279- 283	44.27 (43.68)	4.64 (4.19)	6.45 (6.22)	14.77 (14.10)	13.52 (13.33)	16.33 (15.56)	75	3.95
7	[Cu(L ₂) Cl ₂]	black	280 ^d	43.78 (43.11)	4.59 (4.43)	6.38 (5.88)	14.61 (14.0)	14.47 (14.33)	16.15 (16.05)	83	2.38
8	[Zn(L ₂) Cl ₂]	light gray	240 ^d	43.59 (43.08)	4.57 (4.17)	6.35 (5.68)	14.54 (13.98)	14.83 (14.60)	16.08 (15.80)	70	Di

3.1 Conductance measurements:

Were carried out to ascertain the electrolytic/non electrolytic nature of metal complexes, molar conductance values of complexes in 10^{-3} M DMF solution at room temperature suggest the nonelectrolytic nature for complexes (1,2) and (1:1) electrolytic nature for the complexes(3-8) [13,14]

3.2 Magnetic Susceptibility Measurements:

The Magnetic moment of the complexes at room temperature are (4.32-4.80) B.M. For Co(II) complexes (1,5) respectively, while for Ni(II) complex (2) is diamagnetic and complex (6) is (3.95)B.M, for Cu(II) complexes(3,7) are (2.01 - 2.38)B.M. suggest the presence of one unpaired electron, Zn(II) complexes (4,8) are diamagnetic. As the magnetic moment correlate very well with the mononuclear complexes [15].

3.3 Electronic Spectral Studies

The electronic spectra of ligand L₁ and L₂ in DMSO show the aromatic in tenses bands at 317 nm and 302 nm is attributed to benzene $\pi \rightarrow \pi^*$ transition and at 305 nm and 304 nm due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the amine group these

transitions are also found in spectra of complexes but they are shifted confirming the coordination of ligand to metal ions [16].

The spectrum of cobalt (II) complexes(1,5) show a bands (601-692) nm this is assigned to $^4A_2g \rightarrow ^2T_{1g}(p)$ transition, which is consistent with proposed tetrahedral symmetry of these complexes [17]. The diamagnetic nature of Nickel(II) complexes(2), while the complex (6) showed a bands at (588-696) and (412-430) nm were assigned to $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$ transition in a square planer environment around nickel ion [17].

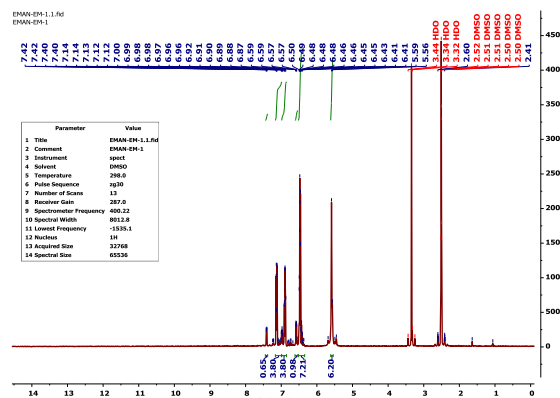
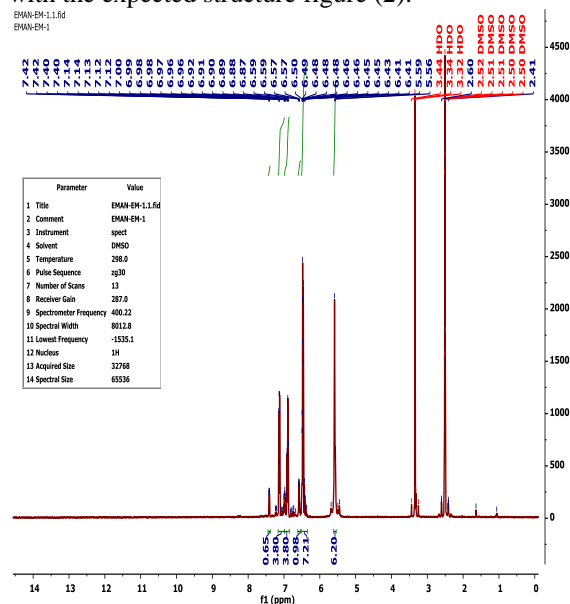
The electronic spectra of Cu(II) complexes (3,7) showed a band at (808-872)nm were assigned to $^2T_2 \rightarrow ^2E$ transition in tetrahedral environment [19].

The ligand used in this study coordinate to metal ions in bidentate fashion from nitrogen atoms with (1,2) complexes, while bidentate fashion from nitrogen and sulfur atoms with (3-8) complexes as shown in Figure.(1).

3.4 ¹H NMR data:

The ¹H NMR spectrum of the formation of ligands L₁ and L₂ observed by peak ratios in the ¹H-NMR spectra which was taken using DMSO-d₆

solvent show the following important signals in (ppm) unit. For L_1 δ (5.56- 6.49) indicate to NH_2 protons of bis(o-amino phenyl)disulphide , a multiple at δ (6.50- δ 7.42) due to aromatic protons and δ (2.41- δ 3.44) for alkyl protons. For (L_2) δ (5.00-600) indicate to NH_2 protons of bis(o-amino phenyl) disulphide,a multiple at δ (6.89- δ 7.43) indicate to aromatic protons, while δ (2.41-3.45) indicate to alkyl protons .The 1H NMR signals are in correlation with the expected structure figure (2). [19,20]



Fig(2): 1H NMR for a(L_1);b(L_2)

3.5 Infrared spectral studies:

The most important IR assignment of ligands and their complexes are listed in table1(2) the ligands L_1 and L_2 show in intense band due to $\nu(NH_2)$ of (o-aminothio phenyl) group at 3400 cm^{-1} and 3416 cm^{-1} . In all complexes this band has been shifted towards a lower frequencies and observed at (2956-3356) due to formation of the complexes^[21]. On the other hand, new band were appeared at $418\text{-}474\text{ cm}^{-1}$ in spectrum of complexes (1-8) due to ν (M-N) in these complexes.^[22]

The two bands observed at 750 and 744 cm^{-1} are attributed to $\nu(C-S)$ vibrations case of the ligands L_1 , L_2 respectively^[23]. In some complexes this band has shifted towards to lower frequency values ,while other complexes was shifted up ward^[24,25] table(2) .The IR spectrum for ligands and some complexes have been shown at figure (3).

Table(2): Electronic and Infrared spectral data of Ligands and complexes

No.	Band maxima (λ_{max}) nm	$\nu(C-S)$	$\nu(M-N)$	$\nu(-NH_2)$	Yield %
L_1	316	746_m	3400_s	73.5
L_2	302	744_s	3416_m	72.6
1	344,601,673	748_s	418_w	3252_s	87
2	305,610,687	750_s	455_w	3365_s	61.4
3	327,392	759_s	422_w	3356_s	73
4	371,525,606	746_s	424_w	3240_m	94
5	324,610,692	748_s	422_w	2956_w	82
6	306,610,696	746_s	474_m	3284_s	91
7	332,429	750_m	472_w	3335_s	85.6
8	403,588,640	746_m	470_w	3240_w	64.6

S=strong, m=medium, w= weak

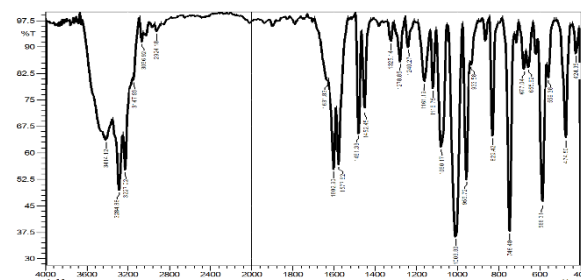
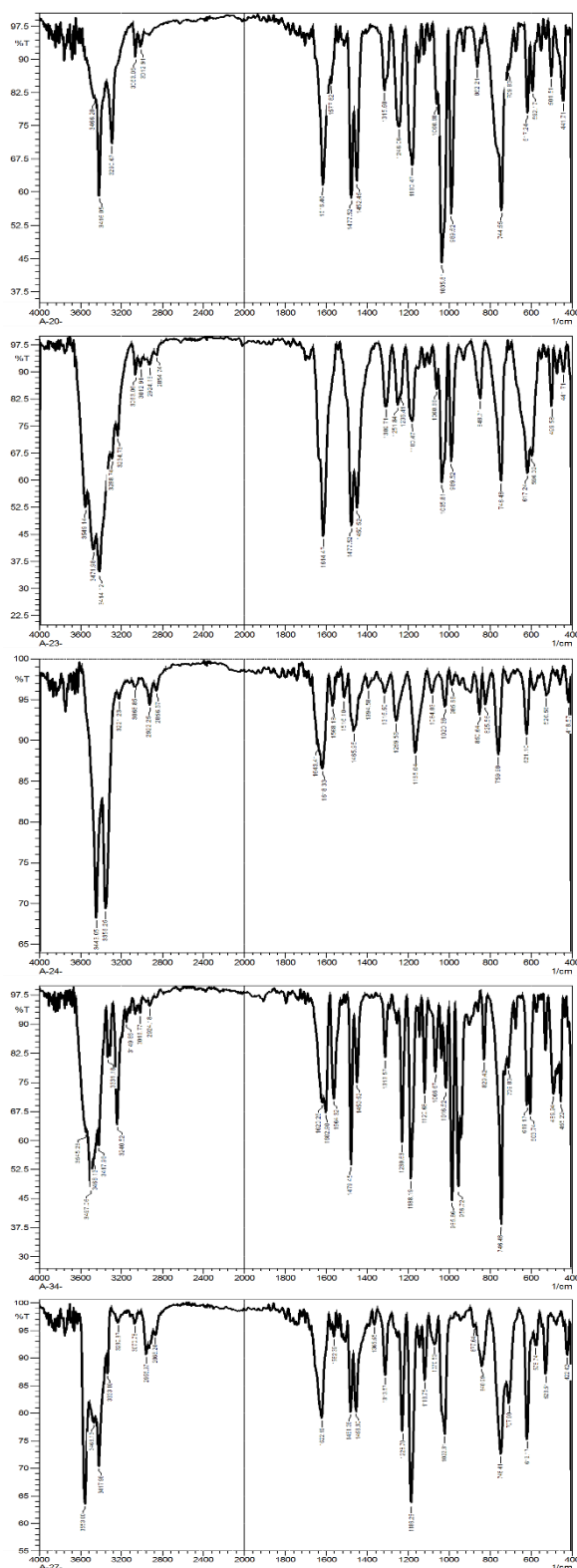


Fig (3):IR-Spectra of (a)L¹;(b) complex 3,(c) complex 4 (d)L²;(e) complex 5,(f) complex 6

Conclusion:

By choosing proper experimental condition, the present investigation was made to synthesized 1,3 and 1,4-bis (o-aminothiophenyl)disulfide propane or butane and their complexes with Co(II),Ni(II),Cu(II) and Zn(II). From the result , discussion and analysis data it is conformed 1:1 stoichiometry and the electronic spectral data suggest that the Ni(II) complexes have square planer geometry where as Co(II) ,Cu(II) and Zn(II) complexes have tetrahedral geometry.

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