ORIGINAL ARTICLE

New bimetallic bisdithiocarbamate-based macrocyclic complexes; Preparation and spectral characterization

Aeed S.Al-Fahdawi[1], Hussain A.Al-Kafajy[1], Mohamad J.Al-Jeboori[2*], Herman Potgieter[3]

[1]Department of Chemistry, College of Science, University of Babylon, (IRAQ)
[2]Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, P.O. Box 4150, Adhamiya Baghdad, (IRAQ)
[3]School of Research, Enterprise and Innovation, Manchester Metropolitan University, Chester Street, Manchester, M1 5GD, (UK)
E-mail: aeedchemistry@yahoo.co.uk; mohamadaljeboori@yahoo.com; h.potgeiter@mmu.ac.uk

Abstract : The preparation of dinuclear transition metal(II) dithiocarbamate-based macrocyclic and their characterisation are described. The macrocyclic dithiocarbamate complexes were synthesised via a one pot reaction using; bis-secondary amine, CS_2, KOH and metal(II) chloride. The mode of bonding and over all geometries of the binuclear complexes were determined by IR, UV-Vis. NMR, mass spectral, magnetic moment, elemental analysis (C. H. N. S), metal content and molar conductance. These studies revealed the formation of binuclear macrocyclic complexes of the general formula $[M(L)]_2$ with tetrahedral geometries for Fe^{II}, Co^{II}, Zn^{II} and Cd^{II}, and square planer geometries with Ni^{II} and Cu^{II} complexes.   © **Global Scientific Inc.**

Keywords : Bisdithiocarbamates; Transition metal complexes; One-pot reaction; Structural study.

INTRODUCTION

Dithiocarbamate (dtc) species represents an interesting branch in the synthetic inorganic chemistry. This is due to the fact that dtcs can bind to the transition and representative metal ions. The important role of the dtcs is related to their ability to stabilize metal ion in a variety of oxidation states, and allowing the metal ion to adopt its preferable geometry[1]. Based on these facts, the chemistry of dtcs has been developed to give an unusual molecular architecture capable of encapsulating guest molecules in a selective manner. Dithiocarbamates are versatile ligands which have been extensively investigated with regard to their numerous applications in different areas such as medicine[2], and materials science[3], and in industrial applications[4]. Many works have described not only the preparation and characterisation of related complexes, but also their action against a range of tumours[5], fungi, bacteria, and other microorganisms[6]. In this paper, we report here a one-pot template preparation of new dimeric assemblies of dithiocarbamate-based complexes.

EXPERIMENTAL

Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Physical measurements

Elemental analyses (C, H, N and S) were carried out on a Heraeus instrument (Vario EL). Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as ATR uses a smart diamond ATR attachment on a Thermo - Nicolet FT-IR Spectrometer (AVATAR 320) in the range 4000-500 cm^{-1}, and as CsI discs using a Shimadzu 8300 FTIR spectrophotometer in the range 600-300 cm^{-1}. Electronic spectra were measured between 245-1000 nm with 10^{-3} M solutions in dimethylsulfoxide (DMSO) spectroscopic grade solvent at 25 °C using a Perkin-Elmer spectrophotometer Lambda. Mass spectra were obtained by positive Electrospray mass spectroscopy technique (ESMS). NMR spectra (^{1}H, ^{13}C, DEPT, ^{1}H-^{1}H COSY, ^{13}C- ^{1}H HMQC NMR) were acquired in DMSO-d6 solutions using a Jeol Lambda 400 MHz spectrometer with tetramethylsilane (TMS) for ^{1}H NMR. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic System Division).

SYNTHESIS

Preparation of the bis-amine precursor

The free bis-amine precursor namely *N, N'*-(1,4-phenylene)bis(2-(butylamino) acetamide) was prepared by two steps and as follows:

(a) Preparation of N, N'-(1,4-phenylene)bis(2-chloroacetamide)

To a mixture of 1,4-phenyldiamine (0.54 g, 5.0 mmol) in CHCl$_3$ (25 mL) was added a solution of KOH (0.59 g, 10.0 mmol) in H$_2$O (10 mL). Chloroacetyl chloride (1.13 g, 10.0 mmol) dissolved in CHCl$_3$ (25 mL)

was added dropwise with stirring to the mixture. After 15 minutes the solid was filtered off, and then washed with Et$_2$O (10 mL). Drying in *vacuo* gave a pink solid. Yield = 1.28 g, (98.1 %). IR (ATR cm^{-1}): 3258 ν(-CON-H), 3093 ν_{ar}(C-H), 2857 ν_{ali}(C-H), 1661 ν(C=O), 1620 δ(N-H), 1590 ν_{ar}(C=C). NMR data (ppm), δ_H (400 MHz, DMSO-d$_6$): 8.67 (br, 2H, N*H*), 7.52 (d of d, J_{HH}= 6Hz, J_{HH}= 3Hz, 2H, Ar*H*), 7.32 (d of d, J_{HH}= 6Hz, J_{HH}= 3Hz, 2H, Ar*H*), 4.24 (s, 4H, C*H*$_2$Cl).

(b) Preparation of secondary bis-amine N, N'-(1,4-phenylene)bis(2-(butylamino) acetamide)

An excess of butylamine (20 mL, 14.80 g, 20.23 mmol) was heated up to 40 °C, and then 2-chloro-*N*-[4-(2-chloro-acetylamino)-phenyl]-acetamide (4.24 g, 12.68 mmol) was added portion-wise with stirring. The mixture was stirred at 40 °C for 12 h. H$_2$O (200 mL) was added and the product extracted into CH$_2$Cl$_2$ (4 x 50mL), and then washed again with H$_2$O (200 mL) before drying over K$_2$CO$_3$. Filtration followed by solvent removal and heating at 40 °C in a vacuum gave yellow oil. Yield: (2.15 g, 96 %)[6,7]. IR (ATR cm^{-1}): 3348 ν(N-H), 3263 ν(-CON-*H*), 3030 ν_{ar}(C-H), 2925 and 2857 ν_{ali}(C-H), 1665 ν(C=O), 1620 δ(N-H), 1520 ν_{ar}(C=C). NMR data (ppm), δ_H (400 MHz, CDCl$_3$): 0.91 (t, J_{HH}= 7.33Hz, 6H), 1.33 (q of t, J_{HH}= 7.33Hz, 4H), 1.42 (t of t, J_{HH}= 7.33Hz, 4H), 1.60 (s, 2H) 2.65 (t, J_{HH}= 7.34Hz, 4H), 3.36 (t, J_{HH}= 15.28Hz, 4H), 7.24 (d, J_{HH}=15.28Hz, 4H) 9.33 (s, 1H); δ_C (100.63 MHz, CDCl$_3$): 14.02, 20.38, 32.33, 50.12, 53.07, 120.01, 133.98.

General one pot synthesis of the complexes

To a mixture of MeCN/H$_2$O (9:1 v/v) solution (10 mL) of the bis-secondary amine *N,N'*-(1,4-phenylene)bis(2-(butylamino) acetamide) (1 mmol) and 3.3 equivalents of KOH, was added in small portions a mixture of CS$_2$ (5.5 mmol) in a mixture of MeCN/H$_2$O (5 mL). The generated yellow solution was allowed to stir for 15 min at 0 °C, and then a solution of metal salt (1.25 mmol) in 2 mL of MeCN/H$_2$O (9:1), was added dropwise. The reaction mixture was allowed to stir under Argon at room temperature for 18 h, resulting in the formation of a solid mass which was filtered, collected and washed with a copious of methanol. The solid was then dried under vacuum. Elemental analysis data, colours, and yields for the complexes are given in (TABLE 1).

NMR data (ppm): [Zn(L)]$_2$; the ^{1}H and ^{13}C spec-

ORIGINAL ARTICLE

tra of the complex; δ_H (400 MHz, DMSO-d_6): 0.84 (t, J_{HH}=7.33Hz, 6H), 1.25 (m, 4H), 1.63 (m, 4H), 3.75 (t,4H), 4.58 (t, J_{HH}=7.34Hz, 4H), 7.72 and 7.50 (d, J_{HH}=15.28Hz, 4H) to each one, 9.95 (s, 2H): δ_C (100.63 MHz, DMSO-d_6): 13.66, 14.18, 19.38, 19.58, 28.20, 119.42, 164.75, 205.55.

RESULTS AND DESICCATION

Chemistry

Dithiocarbamate macrocyclic complexes were prepared from the bis-secondery amine, N, N'-(1,4-phenylene)bis(2-(butylamino) acetamide), separated by aromatic amides spacer. This spacer conferred a degree of rigidity upon the formation of ligand, thus play a role in pre-organising it for self-assembly. Attempts to isolate the free ligand were unsuccessful. Therefore, a one pot approach was implemented to obtain metal complexes. In this approach, the resulting bis-secondary amine was reacted with a base, carbon disulphide and metal(II) chloride salt to yield the bis-metallic macrocyclic complexes. In these template reactions the metal centres play a key role in the assisted self-assemblies forming bimetallic dithiocarbamate macrocyclic complexes. The bis-amine precursor N, N'-(1,4-phenylene)bis(2-(butylamino) acetamide) (Scheme 1) was synthesised in almost quantitative yield via two steps; (i) preparation of the N, N'-(1,4-phenylene)bis(2-chloroacetamide), which based on the dehalogination reaction using two equiva-

lents of chloroacetyl chloride and one equivalent of p-phenylenediamine in chloroform solvent to give the alkyl chloride starting material. n-Butylamine was reacted with alkyl chloride to give the secondary amine, N, N'-(1,4-phenylene)bis(2-(butylamino) acetamide).

The compounds were characterised by elemental analysis, IR, ^{1}H and ^{13}C NMR spectra. The IR spectrum for the bis-amine shows characteristic bands due to the ν(N–H), ν(C=O) amide and ν(C=C) functional groups (see Experimental section). The ^{1}H NMR spectrum shows a characteristic peak at δ= 1.60 ppm, which attributed to ($N_{a,a'}$-*H*) protons. Resonances at δ= 2.65 and 3.36 ppm assigned to ($C_{4,4}$'-*H*) and ($C_{5,5}$'-*H*), respectively. These signals are appeared as expected downfield, due to their attachment to the withdrawing groups (C=O and N-H). The ($N_{b,b}$'-*H*) signal for the amide segment is detected as expected, as singlet, at resonance δ= 9.33 ppm. The ^{13}C-NMR shows the chemical shift for the C=O of the amide moiety appears as expected at δ= 170.04 ppm, assigned to ($C_{6,6}$').

Metal-directed self-assembly of the desired dinuclear macrocyclic complexes [M(L)]$_2$ (where M=Fe[II], Co[II], Ni[II], Cu[II], Zn[II] and Cd[II]) was performed via the initial reaction of the bis-amine with potassium hydroxide and carbon disulphide in MeCN/H$_2$O medium (this was to generate the potassium bis-dithiocarbamate salt that was not usually isolated), Scheme 1. The complexes are air stable solid, completely soluble in DMSO. The new dinuclear macrocyclic complexes

M=Fe[II], Co[II], Ni[II], Cu[II], Zn[II] and Cd[II]
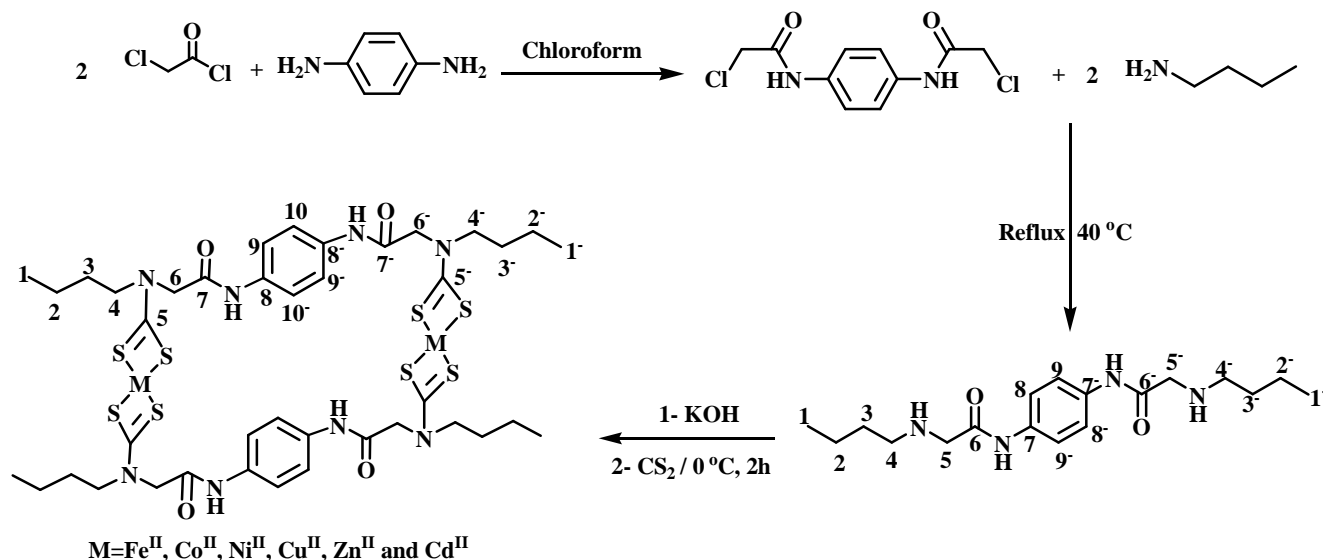
Scheme 1 : Synthesis route of complexes [M(L)]$_2$, where M= Fe[II], Co[II], Ni[II], Cu[II], Zn[II] and Cd[II]

were characterised by elemental analysis, IR, ES MS, electronic spectra and ^{1}H and ^{13}C NMR spectroscopy. Where necessary, full assignments of peaks in the ^{1}H and ^{13}C NMR spectra were made using two-dimensional ^{1}H-^{1}H COSY and ^{13}C- ^{1}H HMQC NMR. All attempts to isolate crystals suitable for X-ray single crystal diffraction analysis were unsuccessful. The analytical data (TABLE 1) agree well with the suggested formulae. The molar conductance of the complexes in DMSO solutions is indicative of their non-electrolytic nature[7].

FTIR and mass spectra for complexes

The important infrared bands of complexes with their assignments are collected in TABLE 2. The IR spectra of the dinuclear macrocyclic gave evidence for the formation of the dithiocarbamate functions and their coordination to the metal ions. Bands at 1494-1463 cm^{-1}, which resulted from the stretching vibrations of the C-N-S bonds, have a wave umber that are intermediate when compared to those reported for C-N single bonds at 1250-1350 cm^{-1} and C=N double bonds at 1630-1690 cm^{-1}, suggesting a partial delocalization of π-electron density within the dithiocarbamate functions[8]. For the CS$_2$ groups two bands were observed; ν(CS$_2$) asymmetric at 1112-1110 and 1034-1005 cm^{-1} and one band for the symmetric ν(CS$_2$) around 1005-969 cm^{-1}. This is characteristic for an anisobidentate chelation mode of the ligand to the metal atoms[9,10]. At lower frequency the complexes exhibited two sets of bands around 345 and 391cm^{-1}, which are assigned to

the ν(M-S) vibration mode, and supporting the anisobidentate chelation mode of the ligand[3].

The electrospray (+) mass spectrum of Ni^{II}-complex gave ion peak at m/z = 1084.5 (4 %), which assigned for the parent ion peak (M)$^+$=(C$_{40}$H$_{56}$N$_8$ Ni$_2$O$_4$S$_8$)$^+$. The spectrum displays the observed and theoretical isotope distribution pattern of the molecular ion peaks for the complex. Peaks detected at 988.2 (4%) and 666.7 (35%) assigned to [M-(Ni$_2$)]$^+$ and [M-{(Ni$_2$)+(CH$_3$)$_2$(CH$_2$)$_8$(CO)$_2$N$_2$CS$_2$}]$^+$, respectively.

UV-Vis spectral data for the complexes, and magnetic susceptibility

The electronic spectra of the Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} complexes exhibited various extents of bathochromic shift of bands related to the ligand field $\pi \to \pi^*$ and n $\to \pi^*$ transitions (TABLE 2). Bands in the range of 321-437 nm related to the charge transfer transition (CT)[11-13]. The magnetic moment value of the Fe(II) complex, as well as the other analytical data, are in agreement with tetrahedral structures[14]. The Fe(II) complex in DMSO solutions indicating further coordination to solvent molecules. The Fe-complex in DMSO displays additional bands in the d-d region at 491 and 663 nm, due to ^{5}A$_2$g→T$_2$g and ^{5}T$_2$g→^{5}Eg, characteristic for distorted octahedral Fe(II) complexes[15]. The Co-complex displays additional bands in the d-d region at 460 and 636 nm, related to ^{4}A$_2$$^{(F)} \to$ ^{4}T$_2$$^{(F)}$ and ^{4}A$_2$$^{(F)} \to$ ^{4}T$_1$$^{(F)}$, characteristic for tetrahedral geometry around Co atom[16]. The magnetic moment of

TABLE 1 : Colours, yields, melting points, (C, H, N, S) analysis, and molar conductance values complexes

Metal ion	Colour	M.P. °C	Yield (%)	Found (Calca%)					$\Lambda_M(\Omega^{-1} cm^2 mol^{-1})$
				M%	C	H	N	S	
Fe^{II}	Red	293-295	46.72	9.95	44.41	5.29	10.42	23.70	22.4
				(10.33)	(44.44)	(5.22)	(10.36)	(23.73)	
Co^{II}	Dark red	308*	56.89	10.77	44.26	5.22	10.23	23.65	23.9
				(10.84)	(44.18)	(5.19)	(10.31)	(23.59)	
Ni^{II}	Green	330*	44.82	10.69	44.11	5.16	10.27	23.57	20.7
				(10.80)	(44.20)	(5.19)	(10.31)	(23.60)	
Cu^{II}	Orange	328*	52.39	11.66	43.74	5.18	10.19	23.48	11.8
				(11.59)	(43.81)	(5.15)	(10.22)	(23.39)	
Zn^{II}	White	192-294	54.24	11.94	43.71	5.18	10 22	23.23	6.8
				(11.89)	(43.66)	(5.13)	(10.18)	(23.31)	
Cd^{II}	White	223-225	59.38	18.70	40.21	4.80	9.45	21.46	10.1
				(18.83)	(40.23)	(4.73)	(9.38)	(21.48)	

*= Decomposed

ORIGINAL ARTICLE

this complex is typical for tetrahedral structure[17]. The Ni(II) and Cu(II) complexes in DMSO solutions indicated further coordination to solvent molecules. The spectra of the Ni(II) and Cu(II) complexes display bands in the d-d region, which are characteristic of distorted octahedral complexes[16]. The magnetic moment value of the Ni(II) and Cu(II) complexes, as well as the other analytical data, are in agreement with their square planar structures[3,11,17]. The electronic spectra of the $[Zn(L)]_2$ and $[Cd(L)]_2$ complexes exhibited bands related to ligand field and $L \rightarrow M$ charge transfer[16]. These complexes are diamagnetic as expected (d^{10} system)

and normally prefer tetrahedral coordination.

^{1}H-, ^{13}C-, and DEPT-NMR

The ^{1}H NMR spectrum for $[Zn(L)]_2$ displays chemical shift at δ= 0.84 ppm (6H, t, J_{HH}=7.33 Hz) assigned to ($C_{1,1}$'-H). The signal at δ= 1.25 ppm (4H, m) and δ= 1.63 ppm (4H, m) assigned to ($C_{2,2}$'-H) and ($C_{3,3}$'-H) protons, respectively. The chemical shift at δ= 3.75 ppm (4H, t) attributed to ($C_{4,4}$'-H). The spectrum displays chemical shift at δ= 4.58 ppm (4H, t, J_{HH}=7.34 Hz) assigned to ($C_{6,6}$'-H) protons. These signals are shifted to downfield compared with that detected in the

TABLE 2 : FTIR spectral data (wave number) cm^{-1} of bisdithiocarbamate-based complexes

Comp.	ν (N-H)	ν_{ar}(C-H)	ν_{ali}(C-H)	ν(C=O)	δ (N-H)	ν_{ar}(C=C)	ν(N- CS$_2$)	δ (CH$_2$)	$\nu_{as,s}$(CS$_2$)
$[Fe(L)]_2$*	3297	3023	2957, 2870	1670	1609	1550, 1514	1484	1428	1111, 1005 and 969
$[Co(L)]_2$	3284	3024	2925	1670	1609	1559 1513	1477	1408	1112, 1034 and 1005
$[Ni(L)]_2$	3290	3028	2956, 2868	1671	1610	1510	1494	1433	1112, 1010 and 970
$[Cu(L)]_2$	3273	3028	2956, 2889	1669	1609	1513	1484	1429	1111, 1009 and 969
$[Zn(L)]_2$	3263	3030	2952, 2870	1665	1610	1520	1463	1403	1110, 1021 and 970
$[Cd(L)]_2$	3281	3030	2956, 2870	1674	1610	1514	1484	1406	1112, 1005 and 970

*= ν(Fe-S), 378 and 364 cm^{-1}

TABLE 3 : UV-Vis spectral data of bisdithiocarbamate-based complexes in DMSO solutions and magnetic moment

Comp.	Concen. mol/L	Band Position λ_{nm}	Wave number (cm^{-1})	Extinction coefficient ε_{max} (dm^3 mol^{-1} cm^{-1})	Assignment	μ_{eff} (B.M) per atom
$[Fe(L)]_2$	1×10^{-5}	266	37594	10000	Intra-ligand $\pi \rightarrow \pi$*	3.45
	1×10^{-5}	374	26738	30000	CT	
	1×10^{-5}	491	20367	10000	$^5A_2g \rightarrow T_2g$	
	1×10^{-3}	663	15083	40000	$^5T_2g \rightarrow ^5Eg$	
$[Co(L)]_2$	1×10^{-5}	272	37593	69000	Intra-ligand $\pi \rightarrow \pi$*	3.9
	1×10^{-5}	321	16447	20000	CT	
	1×10^{-5}	460	21739	5000	$^4A_2g^{(F)} \rightarrow ^4T_2g^{(F)}$	
	1×10^{-4}	638	14903	700	$^4A_2g^{(F)} \rightarrow ^4T_1g^{(F)}$	
$[Ni(L)]_2$	1×10^{-5}	262	38168	90000	Intra-ligand $\pi \rightarrow \pi$*,	Diamagnetic
	1×10^{-5}	326	30675	20000	n $\rightarrow \pi$*	
	1×10^{-5}	368	27174	10000	CT	
	1×10^{-5}	477	20964	8000	$^1A_1g^{(F)} \rightarrow ^2B_2g^{(F)}$	
	1×10^{-4}	631	15848	200	$^1A_1g^{(F)} \rightarrow ^1A_2g^{(F)}$	
$[Cu(L)]_2$	1×10^{-5}	271	36900	150000	Intra-ligand $\pi \rightarrow \pi$*	1.6
	1×10^{-5}	437	22883	50000	CT	
	1×10^{-4}	674	14837	200	$^2B_1g \rightarrow ^2A_1g$	
$[Zn(L)]_2$	1×10^{-5}	267	37878	170000	Intra-ligand $\pi \rightarrow \pi$*	Diamagnetic
	1×10^{-3}	450	22222	50	CT	
$[Cd(L)]_2$	1×10^{-4}	268	37313	off-scale	Intra-ligand $\pi \rightarrow \pi$*,	Diamagnetic
	1×10^{-4}	271	36630	off-scale	n $\rightarrow \pi$*	
	1×10^{-4}	280	35714	off-scale	CT	

ORIGINAL ARTICLE

secondary amine (see Experimental section). This may be due to the redistribution of the negative charge of the dithiocarbamate moiety, upon complexation, to the carbonyl group resulting in the deshielding of the (-CH$_2$) group (C$_{6,6}$'-*H*). Also they are shifted down filed because of their attachment between two drawing groups (C=O and N-H). The N-H signal f the amide group appeared at δ= 9.95 ppm. This peak is shifted downfield, compared to that detected in the bis-amine. This may due to its attachment to the electron withdrawing groups (carboxylic group and aromatic ring).

The ^{13}C NMR spectrum of [Zn(L)]$_2$, shows the chemical shift of the amide moiety, (C$_{7,7}$'), as expected downfield at δ= 164.75 ppm. The spectrum gave one peak at chemical shift 205.55 ppm assigned to CS$_2$ moiety, indicating the CS$_2$ carbons are equivalent. The downfield appearance of the carbon of CS$_2$ is due to the alleviation of excess electron density, which results in a drift of electron density towards the metal centre through the thioureide bond from the nitrogen atom, and supporting the bidentate coordination fashion of the dithiocarbamate to metal centres[18].

DEPT ^{13}C NMR spectrum for [Zn(L)]$_2$, shows important signals at δ= 14.18, 19.38, 19.57 and 28.20 ppm assigned to (C$_{2,2}$'), (C$_{3,3}$'), (C$_{4,4}$') and (C$_{6,6}$'), respectively. These peaks were enhanced in the negative direction (down), and therefore assigned to (-CH$_2$) group. The other signals between δ= 117.80-119.43 ppm, assigned to (C$_{9,9}$',$_{10,10}$'). These signals enhanced in the positive direction (up), and therefore assigned to (-CH). No signals around 140.0-220 ppm may assigned to (C$_{7,7}$') and (C$_{5,5'}$) are detected. These signals are related to a quaternary carbon which is not shown in the spectrum.

CONCLUSION

The synthesis and characterisation of some bimetallic dithiocarbamate macrocyclic complexes are descried. Attempts to isolate the free ligand from the reaction mixture were unsuccessful. Therefore, a one-pot reaction approach using the bis-amine-compound, CS$_2$, KOH and metal chloride, was used to isolate the required bimetallic dithiocarbamate macrocyclic complexes. The mode of bonding and overall structure of the complexes were determined by physico-chemical and spectroscopic methods. These results revealed the preparation of four coordinate complexes.

REFERENCES

[1] S.Singh, N.Bhattacharya, Subrato.; J.Organomet. Chem., **700**, 69-77 **(2012)**.

[2] C.Bolzati, E.Benini, M.Cavazza-Ceccato, E.Cazzola, E.Malago, S.Agostini, F.Tisato, F.Refosco, G.Bandoli; Bioconjug.Chem., **17(2)**, 419-28 **(2006)**.

[3] H.A.Hasan, E.I.Yousif, M.J.Al-Jeboori; Global J.Inorg.Chem., **3(10)**, 1-7 **(2012)**.

[4] P.B.Hitchcock, A.G.Hulkes, M.F.Lappert, Z.Li; Dalton Trans., **2004(1)**, 129-36.

[5] H.Tlahuext, R.Reyes-Martinez, G.Vargas-Pineda, M.Lopez-Cardoso, H.Hopfl; J.Organomet.Chem., **696**, 693-701 **(2011)**.

[6] A.Normah, N.Farahana, B.Ester, H.Asmah, N.Rajab, A.Halim; Res.J.Chem.Environ., **15**, 544-549 **(2011)**.

[7] E.Canpolat, M.Kaya; J.Coord. Chem., **31(7)**, 511-515 **(2005)**.

[8] G.Faraglia, S.Sitran, D.Montagner; Inorg.Chim. Acta, **358**, 971-980 **(2005)**.

[9] M.J.Al-Jeboori, A.Al-Jeboori Fahad, M.A.R.Al-Azzawi; Inorg.Chim.Acta, **379(1)**, 163-170 **(2011)**.

[10] B.F.Johnson, K.H.Al-Obalidi, J.A.Mecleverty; J.Chem.Soc.A, **19**, 1668-1670 **(1969)**.

[11] P.K.Pandey, A.K.Pandey, A.N.Mishra, K.K.Ojha, S.R.Kumar; Indian J.Sci.Res., **3(1)**, 119-122 **(2012)**.

[12] L.Ronconi, L.Giovagnini, C.Marzano, F.Bettı'o, R.Graziani, G.Pilloni, D.Fregona; Inorg.Chem., **44**, 1867-1881 **(2005)**.

[13] R.N.Jowitt, P.C.H.Mitchell; J.Chem.Soc.A, **1970**, 1702-1708.

[14] M.J.Al-Jeboori, H.H.Al-Tewel, R.M.Ahmad; Inorg.Chim.Acta, **363**, 1301-1305 **(2010)**.

[15] M.J.Al-Jeboori, A.J.Abdul-Ghani, A.J.M.Al-Karawi; J.Coord.Chem., **62(16)**, 2736-2744 **(2009)**.

[16] S.M.Mamba, A.K.Mishra, B.B.Mamba, P.B.Njobeh, M.F.Dutton, E.Fosso-Kankeu; Spectrochim.Acta, part A., **77(3)**, 579-87 **(2010)**.

[17] R.S.Lakshmi, M.K.Sesha, G.Siva Reddyc, B.J.Reddyd, R.L.Frostd, T.Endoe; Spectrochim. Acta, Part A, **77**, 11-15 **(2010)**.

[18] S.Srinivasan, K.Ramalingam, C.Rizzoli; Polyhedron, **33**, 60-66 **(2012)**.