Mono, di and trinuclear complexes Co^{+2},Ni^{+2}, Cu^{+2},Bi^{+3} and Sb^{+3} with bis-(n-butylthio)ethane

N.H.Buttrus[*] , F.T.Saied and S.W.Zeedan
Chem.Dept.College of Science,Mosul University

Received 18/12/2006 **Accepted** 04/04/2007

الخلاصة

يتضمن البحث تحضير ليكاند جديد بس-(n-بيوتيل ثايو) ايثان (L) من تفاعل ثنائي برومو ايثان و n- بيوتيل ثايوليت البوتاسيوم ، تم تحضير معقدات أحادية النوى بالتفاعل المباشر بين الليكاند أعلاه والأملاح الفلزية $CoCl_2.6H_2O$ و$NiCl_2.6H_2O$ و $CuCl_2.4H_2O$ وبنسبة ١:١ (فلز:ليكاند) ، بينما تم تحضير معقدات ثنائية النوى من تفاعل $SbCl_3$ أو $Bi(NO_3)_3$ مع الليكاند أعلاه وبنسبة (٢:٢) .اما المعقدات ثلاثية النوى ذوات الصيغة العامة $[M'_2M(L)_2X_6]Cl_2$ فقد تم تحضيرها من تفاعل $[M'_2(L)_2X_6]$ والأملاح الفلزية Co^{+2} و Ni^{+2} و Cu^{+2} وبنسبة مولية (١:١).

وقد تم تشخيص المركبات والمعقدات المحضرة بواسطة التحليل الفلزي ، أطياف الأشعة تحت الحمراء والمرئية وفوق البنفسجية والتوصيلية الكهربائية ، اضافة الى القياسات المغناطيسية.

Abstract

This paper describe the preparation of new ligand bis-(n-butylthio)ethane (L) from the reaction of dibromoethane and potassium-n-butylthiolate. Mono nuclear complexes were obtained by direct reaction of the above ligand with $CoCl_2.6H_2O$,$NiCl_2.6H_2O$ and $CuCl_2.4H_2O$ in 1:1 metal to ligand , while the dinuclear complexes were obtained from the reaction with $SbCl_3$ or $Bi(NO_3)_3$ in 2:2 metal to ligand. Trinuclear complexes of general formula $[M'_2M(L)_2X_6]Cl_2$ were obtained from the reaction of $[M'_2(L)_2X_6]$, $M'= Sb^{+3}$ or Bi^{+3} with metal chloride in 1:1 molar ratio, $M=Co^{+2}$, Ni^{+2} or Cu^{+2}.

The prepared complexes were characterized by metal analysis, IR,U.V-visible spectroscopy, conductivity and magnetic measurements.

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[*] Correspondence another

Introduction:

The coordination chemistry of thioether is an intensive area of study and numerous transition metal complexes of this group of ligands have been investigated(1-3). The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding(4).

The early/late heterobimetallics can be prepared from the so called metalloligands, in which bifunctional ligand is coordinated to a transition metal. In a second steps another transition metal is introduced. To date, various bifunctional ligands, like S/P(5-7),S/S(8,9),S/N(10,11) have been employed.

Abcl et al.(12) reported the preparation of dinuclear platinum (IV) complexes $[(PtXMe_3)_2\{(Me_2S)_2CHCH(SMe)_2\}]$ by treating the monomer chelate complexes $[PtXMe_3\{(Me_2S)_2CHCH(SMe)_2\}]$with equimolar amounts of $[(PtXMe_3)_4]$ X=Cl, Br or I). in the new complexes the ligand acts as double chelate towards the $PtXMe_3$ moieties .

Gürol et al.(13) report the synthesis of a new dithioglyoxime ligand and its mono-,tri- and penta-nuclear complexes of Co(II),Ni(II),Pd(II) , Cu(II) and Pt(II).

In view of these interesting results and as continuation of our comprehensive studies on the Co(II),Ni(II), Cu(II), Pd(II) and Pt(II) metal complexes with sulphur containing ligands(14-17), we describe here the reaction of metal chloride or nitrate with bis(n-butylthio) ethane ligand in different molar ratios.

Experimental:

All chemicals were of reangent grade and used as supplied from Fluka A.G.

IR spectra were recorded on a Perkin Elmer 580B IR spectrophotometer in the 4000-200 cm^{-1} range using CsI discs . The metal content were estimated spectrophotometrically using Shimdza Atomic absorption 670. Conductivity measurements were made on 10^{-3}M solutions of the complexes in dimethysulfoxide (DMSO) solvent at ambient temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV-Vis. Spectrophotometer UV-160 for 10^{-3}M solutions of the complexes in DMSO using (1 cm) quartz cell. The magnetic measurements were carried out at 25ºC on the solid by Faraday’s method using Burker BM6 .

Preparation of bis-(n-butylthio)ethane (L):

The ligand was prepared according to the following general method:

The reaction of potassium butyl thiolate {prepared in situ from the reaction of an equivalent amount of KOH (1.12g,0.02 mol) and n-butanethiol (1.80g,0.02mol) in ethanol (30cm^3)} with 1,2-dibromethane (1.87g,0.01 mol).The mixture was boiled under reflux for ca.6h.After cooling at room temperature, KBr was removed by filtration. The solution was reduced in volume to ca (10 cm^3) and on cooling to ca 5ºC. A white solid was formed, this was filtered off and dried under vacuum.

Preparation of [M(L)Cl$_2$]: M=Co(II),Ni(II),Cu(II)

$NiCl_2.6H_2O$,$CoCl_2.6H_2O$ and $CuCl_2.2H_2O$ salts were used to prepare the metal complexes. In each procedure (10 mmol) of the metal salt in (20 cm^3) ethanol and (10 mmol) of the ligand were mixed by stirring, a voluminous colored complex was precipitated , then the mixture was heated to reflux for 1h. to ensure the completion of the reaction. The solid thus obtained were filtered off, washed with ethanol, diethylether and dried under vacuum.

Preparation of [M$_2$´(L)$_2$X$_6$]: (M´=Bi(III),Sb(III),X=Cl,NO$_3$)

A solution of $Bi(NO_3)_3.5H_2O$ (0.89 g,2mmol) or $SbCl_3$ (0.44g, 2mmol) in ethanol (20 cm^3) was added drop by drop to a solution of bis-(n-butylthio) ethane (0.82g ,2 mmol) in ethanol (10 cm^3) with stirring. The resulting mixture was refluxed for 2h. The precipitation of the complex was aided by further digestion on water-bath for a bout 1h. The resulting precipitate was filtered, washed with ethanol and diethylether and dried under vacuum for several hours.

Preparation of [MM$_2$´(L)$_2$X$_6$]Cl$_2$:

(M=Co(II),Ni(II),Cu(II),M´=Bi(III),Sb(III),X=Cl or NO$_3$)

A clear solution of [M$_2$´(L)$_2$X$_6$] (1 mmol) in methanol (10 cm^3) was added to a solution of $CoCl_2.6H_2O$ or $NiCl_2.6H_2O$ or $CuCl_2.2H_2O$ (1mmol) in ethanol (10 cm^3). The mixture was stirred under reflux for ca 2h. the solid thus obtained was filtered off, washed with ethanol then diethylether and dried under vacuum for several hours.

Results and discussion:

Treatment of n-butanethiol with 1,2-dibromoethane in basic medium gives, after recrystallization 80% yield of the ligand bis-(n-butyl thio)ethane. Direct reaction of metal (II) chlorides with the above ligand gave mono-nuclear complexes of the type $[M(L)_2Cl_2]$. The complexes of the type $[M_2'(L)_2X_6]$ (M′=Bi(III) or Sb(III),X=Cl or NO_3) were prepared using similar reaction. New trinuclear complexes were prepared from the reaction of metal (II) chlorides with $[M_2'(L)_2X_6]$ complexes. The nucleophilicity of sulphur atoms in these complexes is responsible for the formation of these complexes. The physical properties of the solid complexes are tabulated in (Table 1). the complexes are quite stable in air and melt or decompose at above (191 ºC) they are insoluble in most organic solvent but soluble in DMSO.

The most important IR assignment of the complexes are listed in (Table 2). the most important band which appeared at 864 cm^{-1} due υ(C– S) stretching of the ligand is shifted to lower field in the $[M(L)Cl_2]$ and $[M_2'(L)_2X_6]$complexes. This is usually indicates the (C– S) group is involved in the coordination with metal atom through sulphur atom(18). Further support for the formation of new complexes is provided by the appearance of a new band with in the range 340-400 cm^{-1} range characteristic of bidentate ligand and a tentatively attributed to υ(M–S) , M=Co,Ni,Cu(14), further more the IR spectra of mononuclear complexes showed another band with in the 320-290 cm^{-1} range which may be due to υ(M– Cl)(15). In $[M_2'(L)_2X_6]$ and $[MM_2'(L)_2X_6]Cl_2$ complexes similar observation was found, except that in these complexes, the coordination occur through two sulphur atom from both ligands for the main element, while the transition metal coordinate to the four sulphur atom through the electron pair on the sulfur atoms forming tetradentate ring as shown in Fig 1.

However, in all bismuth complexes, the nitrate groups being coordinated to bismuth as monodentate ligand(19). This is evident from the fact that doubly degenerate IR active fundamental modes are split into υ_1 at 1290 and 1510 cm^{-1} respectively in nitrate complexes(20).

The U.V-Visible spectra of the compound and complexes were recorded as 10^{-3} M solution in DMSO and the results are presented in (Table 2). the broad observed in the range 33120-36000 cm^{-1} are due π- π* or n- π* within the ligand, while new addition band was observed in the compounds (4 and 5) were in the range 28300-26500 cm^{-1}. this can be attributed to charge transfer from filled ligand orbitals to the vacant Sb or Bi orbitals(21).

The values of magnetic moment of Co(II) complex [1] is 4.15 B.M. The electronic spectrum of Co(II) show abroad band at 17211 cm^{-1} due to $^4A_2 \longrightarrow {}^4T_1p(\upsilon_3)$ transition as a result of spin orbit coupling , similar to those reported for $[CoCl_4]^{-2}$ and $[CoI_4]^{-2}$ suggesting a tetrahedral geometry for Co(II) complex(22).

The Ni(II) complex [2] show a magnetic moment of 3.97 B.M, this value agree well with a high spin configuration and indicate the presence of tetrahedral environment(23). The electronic spectra of Ni(II) complex show band at 15625 cm^{-1} which correspond to the transition $^3T_1(F) \longrightarrow {}^3T_1(p)$ (υ_3) in tetrahedral environment.

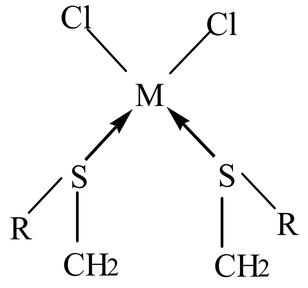
The Cu(II) complex [3] show a magnetic moment of 2.00 B.M. the electronic spectrum showed a bonds at 12886 cm^{-1} which correspond to the transition $^2T_2 \longrightarrow {}^2E$ and another band at 29000 cm^{-1} correspond to charge transfer respectively. This shows that the Cu(II) complex have tetrahedral geometry (23) .

The electronic spectra of the complexes $[MM_2'(L)_2X_6]Cl_2$ [6-11] are listed in (Table 2). The magnetic moment values of the complexes [6 and 9] are (2.10,2.31 B.M) at room temperature, this suggest the presence of one unpaired electron which reveal the spin nature of the complexes. The electronic spectra of Co(II) complexes [6 and 9] show the presence of broad bands in the range 13297-18726 cm^{-1} which are assigned to the $^2A_1g \longrightarrow {}^2Eg$ transition and another band at 26041-27000 cm^{-1} which correspond to charge transfer, these values suggest square planar geometry around the Co(II) complexes. The diamagnetic nature, together with the electronic spectral bands indicate a square-planar geometry around the nickel (II) complexes (No. 7 and 10). The appearance of the bands at 15500-16722 or 20800-25600 cm^{-1} were assigned to $^1A_1g \longrightarrow {}^1A_2g$ transition in a square planar(24) environment around nickel with D_4h symmetry.

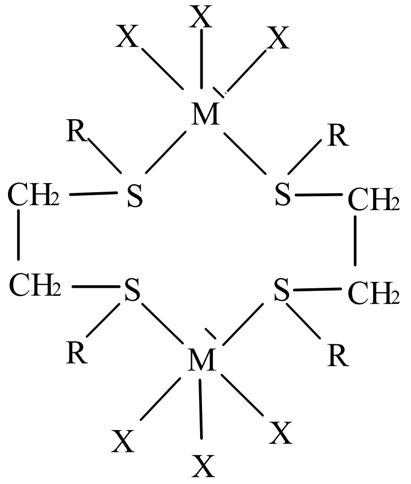
The magnetic moments of Cu(II) complexes [8 and 11] has been found to be (2.01 and 1.98 B.M). this correspond to the presence of one unpaired electron in the complexes.

In the Cu(II) complexes, the observed bands at 16000-17100 cm^{-1} which were assigned to $^2B_1g \longrightarrow {}^2A_1g$ and $^2B_1g \longrightarrow {}^2Eg$ transition in distorted square planar complexes(25).

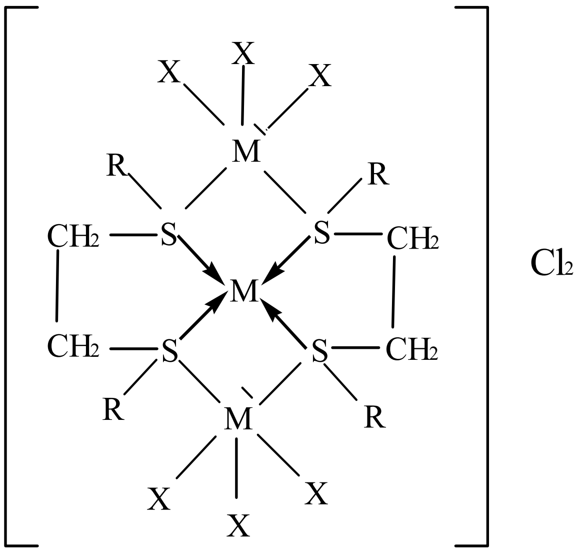
The ligand used in this study, coordinate to the metal ions in a bidentate fashion from both sulfur atoms forming mononuclear complex in 1:1 molar ratio and dinuclear complex in 2:2 molar ratio while for trinuclear complexes the central metal ion coordinate to sulfur atom in tetradentate fashion as shown in Fig 1.



(1-3)



(4-5)



(6-11)

R= $CH_3CH_2CH_2CH_2$
M′ = Sb(III) or Bi(III)
M = Co(II),Ni(II),Cu(II)
X = Cl or NO_3

Fig 1: Suggested structure for the prepared compounds and complexes

Table 1: Physical properties of the ligand and their metal complexes

No.	Complex	Colour	m.p (°c)	Analysis % found (calc.)		Λ ohm^{1}.cm^{2}.mol^{-1}	Meff (B.M)
				M′=(Bi,Sb)	M = (Co,Ni,Cu)		
	Ligand (L)	Milky	49-51	----	----	10	----
1	$[Co(L)Cl_2]$	Dark green	199 d	----	17.49 (17.56)	14	4.15
2	$[Ni(L)Cl_2]$	Pale green	207 d	----	17.39 (17.48)	12	3.97
3	$[Cu(L)Cl_2]$	Green	191 d	----	18.59 (18.65)	15	2.00
4	$[Sb_2(L)_2Cl_6]$	White	271	28.00 (28.05)	----	18	----
5	$[Bi_2(L)_2(NO_3)_6]$	Pale yellow	235 d	34.65 (34.77)	----	16	----
6	$[CoSb_2(L)_2Cl_6]Cl_2$	Pale green	252	24.31 (24.39)	5.69 (5.90)	78	2.10
7	$[NiSb_2(L)_2Cl_6]Cl_2$	Greenish yellow	224 d	24.29 (24.40)	5.79 (5.88)	70	Dia.
8	$[CuSb_2(L)_2Cl_6]Cl_2$	Dark yellow	276 d	24.21 (24.28)	6.12 (6.33)	75	2.01
9	$[CoBi_2(L)_2(NO_3)_6]Cl_2$	Pink	262 d	31.35 (31.38)	4.39 (4.42)	80	2.31
10	$[NiBi_2(L)_2(NO_3)_6]Cl_2$	Pale green	233 d	31.40 (31.42)	4.35 (4.40)	76	Dia.
11	$[CuBi_2(L)_2(NO_3)_6]Cl_2$	gray	247	31.19 (31.28)	4.71 (4.75)	85	1.98

Table 2: IR and electronic spectral data of the free ligand and its compounds and complexes

No.	Selected IR bands (cm^{-1})			Electronic spectra (cm^{-1})
	υ(C–S)	υ(M–S)	υ(M–Cl)	
L.	$864_{(m)}$	----	----	33600
1	$837_{(m)}$	$380_{(m)}$	$320_{(m)}$	17211
2	$841_{(m)}$	$370_{(S)}$	$295_{(S)}$	15625
3	$840_{(m)}$	$385_{(m)}$	$310_{(m)}$	12886,29000
4	$845_{(m)}$	$340_{(S)}$	$320_{(S)}$	26500,34400,36000
5	$836_{(S)}$	$350_{(S)}$	----	28300,33120,35500
6	$839_{(S)}$	$340_{(w)}$,$400_{(m)}$	$320_{(w)}$	13297,14600,26041
7	$836_{(S)}$	$350_{(w)}$,$390_{(m)}$	$300_{(m)}$	15500,25600
8	$833_{(m)}$	$340_{(m)}$,$380_{(S)}$	----	16000
9	$828_{(m)}$	$350_{(m)}$,$400_{(m)}$	----	18726,27000
10	$827_{(m)}$	$360_{(w)}$,$400_{(w)}$	----	16722,20800
11	$830_{(w)}$,	$350_{(w)}$,$390_{(m)}$	----	171000

s= strong, m = medium , w = weak.

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