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Synthesis and characterization of Zn(II),Cd(II) and Hg(II) complexes with thioether ligands and their adducts with 1,10 phenanthroline

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الخلاصة

يتضمن البحث تحضير معقدات ومركبات جديدة ذوات الصيغ العامة $[M(L)(SBu^n)_2]$ و $[M(L)(SFur)_2]$ و $[M(L)(SBu^n)_2(phen)]$، $[M(L)(SFur)_2(phen)]$ حيث L= سز-بس-1،2-(ثايوفنيل) اثيلين، SBu^n= 1-بيوتان ثايول، SFur=2- فيوران ميثان ثايول،، phen =1،10 - فينانثرولين، M =Zn(II)،Cd(II) و Hg(II) في الوسط القاعدي.

تم تشخيص المعقدات ومركبات الإضافة بقياسات الامتصاص الذري والتوصيلية الكهربائية وقياسات الأطياف الالكترونية وطيف الأشعة تحت الحمراء وقياسات الوزن الجزيئي. وبناءاً عليها اقترحت الأشكال الرباعية السطوح حول الأيون الفلزي في المعقدات والثمانية السطوح في مركبات الإضافة .

Abstract

New complexes of general formula $[M(L)(SBu^n)_2]$,$[M(L)(SFur)_2]$ and adducts $[M(L)(SBu^n)_2(phen)]$, $[M(L)(SFur)_2(phen)]$,where L=Cis-bis-1,2-(phenylthio)ethylene, SBu^n= 1-butanethiol, SFur=2-furanmethanthiol, phen=1,10 phenanthroline, M=Zn(II),Cd(II) and Hg(II) have been prepared in basic medium. The complexes and adducts were characterized by atomic absorption, conductivity measurements ,spectral (IR and electronic) and molecular weight measurements studies. Tetrahedral environment around the metal ions in the complexes and octahedral geometry in the adducts were suggested according to the above measurements.

Introduction:

The past decade has seen period of intense activity in the study of the complexation of transition metal and main group metal ions with crown thiolate and thioether ligands(1-4).

Reaction of Hg(II) salts with thioether carboxylic acids $o\text{-}C_6H_{11}\{CH(SCH_2COOH)_2\}_2$ and $PhCH(SCH_2COOH)_2$ in water were found to lead to the decomposition of these ligands and the formation of $Hg(SCH_2COOH)_2$ and the aldehydes $o\text{–}C_6H_4(CHO)_2$ and PhCHO respectively. The x-ray structure of $Hg(SCH_2COOH)$ were studied by Bromlett et al.(5), they were showed that the complex had a linear -S-Hg-S- moiety.

The reaction of TiX_4 ($X = Cl^-$ or Br^-) with tripodal ligands $MeC(CH_2SMe)_3$ or $MeC(CH_2SeMe)_3$ (L) in CH_2Cl_2 produced extremely the moisture sensitive complexes [TiX(L)]. These were characterized by physico-chemically and also by variable temperature $^{1}H_{1}$ ^{31}C and ^{77}Se NMR spectroscopy. They were showed that (L) behaved as bidentate chelating ligands in all the complexes (6).

The preparation and analysis of di,tri and tetra aryl thioether have been achieved from the reaction of di,tri and tetra haloethers with their respective thiophenol XC_6H_4SH (X = H or NH_2). The products were treated with $ZnCl_2$ or $CdCl_2$ or $Hg(OAc)_2$ in different molar ratio to yield mono or dinuclear complexes $[MLX_2]$ and $[M_2LX_4]$ respectively (7).

The crystal structures for a series of homo leptic complexes involving the three group 12 family members with the crown thioether 1,4,7-trithiacyclodecane ($10S_3$) have been reported by Helm et al.(8) they have been showed that the ligand coordinated in tridentate fashion and readily formed bis complexes with the d^{10} metal ions Zn(II),Cd(II) and Hg(II).

In view of the above important results, we have prepared some new complexes of general formula $[M(L)(SBu^n)_2]$, $[M(L)(SFur)_2]$ (where L= Cis-bis-1,2-(phenylthio)ethylene), and their adducts with 1,10-phenanthroline of general formula $[M(L)(SBu^n)_2(phen)]$ and $[M(L)(SFur)_2(phen)]$, (where M=Zn(II),Cd(II) and Hg(II)).

Experimental:

1. Chemicals

All chemicals as reagent grade (BDH,Fluka) were used as supplied. All solvents were dried by standard methods(9).The ligand L= Cis-bis-1,2-(phenylthio)ethylene were prepared according to literature method(10).

2. Physical Measurements

Melting point or decomposition temperature were determined by a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra within the range 4000-400 cm^{-1} were recorded on a Burker Tensor 27 Spectrophotometer and Perkin-Elmer 580B spectrophotometer in the 4000-200 cm^{-1} range, as KBr or CsI discs. Electronic spectra were measured with a Shimadzu UV/Vis.recording UV-160 spectrophotometer at room temperature, using a concentration of 10^{-3} M in N,N'-dimethyl formamide (DMF) solution. Conductivity measurements have been carried out with an electrical conductivity measuring set model PCM3-Jenway using 10^{-3}M in(DMF) solution at room temperature. The metal content (Zn &Cd) was estimated spectrophotometrically using Shimadzu AA670, while (Hg) were measured by Titrimetry by complex formation method(11).Molecular weight of all complexes were measured in dimethyl sulfoxide (DMSO) using cryoscopic method(12).

Preparation of complexes:

1. Preparation of [M(L)($SBu^n)_2$] complex:

(2.71g, 0.001mol) mercuric chloride in ($20cm^3$) ethanol have been treated with (0.24g,0.001mol) cis-bis-1,2-(phenylthio)ethylene in ($20cm^3$) ethanol and equivalent amount of KOH (0.11g,0.002mol) and (0.24g,0.002 mol) 1-butanethiol in ($20cm^3$) ethanol. The mixture was stirred under reflux for 2 hours.The resulting solution was reduced in volume to about half of its original volume and on cooling a solid was obtained which was filtered off, washed with water,ethanol followed by diethylether and then dried under vacuum.

The same procedure has been followed to prepare Zn(II) and Cd(II) complexes.

2. Preparation of [M(L)$(SFur)_2$] complex:

Similar procedure was applied.

3. Preparation of [M(L)$(SBu^n)_2$(phen)] complex:

(0.62 g, 0.001 mol) of [Hg(L)$(SBu^n)_2$] in (20 cm^3) propanol solution was mixed with an ethanolic solution of (0.17 g,0.001 mol) 1,10 phenanthroline. The mixture was refluxed for 1 hour, after cooling the mixture was filtered off, washed with diethylether and then dried under vacuum.

The same procedure has been followed to prepare Zn(II) and Cd(II) complexes.

4. Preparation of [M(L)$(SFur)_2$(phen)] complex:

Similar procedure was applied.

Result and discussion

The reaction of metal chloride or acetate with the ligand cis-bis-1,2-(phenylthio)ethylene (L) and 1-butanethiol (SBu^n) or 2-furanmethanthiol (SFur) in ethanol yielded complexes of general formulas $[M(L)(SBu^n)_2]$ and $[M(L)(SFur)_2]$. Further reaction of the prepared complexes with 1,10-phenanthroline resulted in the formation of the adducts of the general formulas $[M(L)(SBu^n)_2(phen)]$ and $[M(L)(SFur)_2(phen)]$.

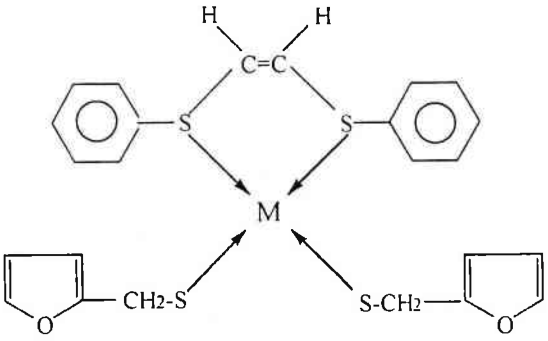
The analytical and physical data of the complexes and adducts (Table 1).Revealed the proposed formula of the complexes. The values of the molar conductance were in the range of (7-22) Ω^{-1} mol^{-1} cm^2 in N,N′-dimethylformamide solution indicated that the complexes and adducts behaved as non-electrolytes(13).Table 2, showed the characteristic infrared spectral bands of the free ligands and their complexes. The most significant information on the geometry of these complexes comes from the analysis of the double bond $\upsilon_{(C=C)}$, thiophenyl $\upsilon_{(C-S)}$ and thiolate $\upsilon_{(C-S^-)}$ absorption region. Stretching frequencies of these functional groups are closely related to the way in which they are coordinated to the metal atom(14).

The complexes did not showed any $\upsilon_{(SH)}$ band in the region 2390-2600cm^{-1}(15) .The characteristic bands in the infrared spectra of the free ligands were observed at 1660,1290 and 670 cm^{-1} due to $\upsilon_{(C=C)}$, $\upsilon_{(C-O-C)}$ and $\upsilon_{(C-S)}$ respectively(16). In the complexes the bands $\upsilon_{(C=C)}$ and $\upsilon_{(C-O-C)}$ were found at the same frequencies indicating that they have been not involved in coordination with the metal ions.

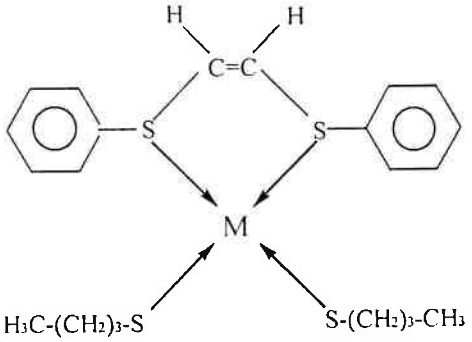
The IR spectra of the complexes, showed a lowering in the frequencies of $\upsilon_{(C-S)}$ indicating that this group was involved in coordination (Table 2), $\upsilon_{(C-S)}$ of furfuryl and butane ligands were found at 820-918 cm^{-1} which mean that they were involved in coordination(17). The infrared of these complexes showed new bands at 380-400 cm^{-1} assigned to $\upsilon_{(M-S)}$(18) .Furthermore the IR spectra of the adducts showed similar observation, except that of 1,10-phenanthroline ligand was found to coordinate to the metal via azomethine nitrogen donor sites, further support for this coordination was provided from the new band at about 480-500 cm^{-1},which tentatively assigned to $\upsilon_{(M-N)}$(19). The absence of any band due to $\upsilon_{(M-Cl)}$ or $\upsilon_{(M-OAc)}$ in the complexes indicated the absence of the chloride or acetate ion in the complexes .This observation was also confirmed by sodium fusion test.

The UV/visible spectra of the complexes were similar to one another but different from those of ligands (Table 2). The broad band observed in the rang (23584-36231) cm^{-1} was due to π-π^* transition in the free ligands, where as new additional band was observed for all complexes and adducts in the range (19531-24038) cm^{-1}. This can be attributed to the charge transfer transition from the field ligand orbitals to the vacant metal orbitals(20).

On the basis of the above discussions , the following structures for the metal complexes were proposed as shown in Fig 1.

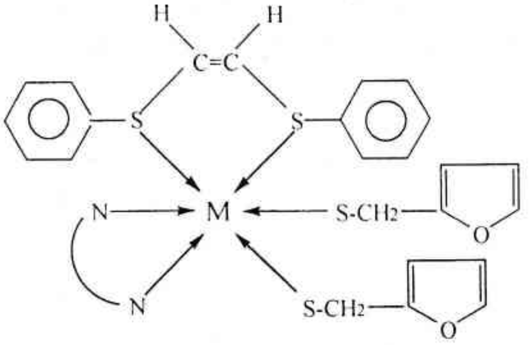


$[M(L)(SFur)_2]$

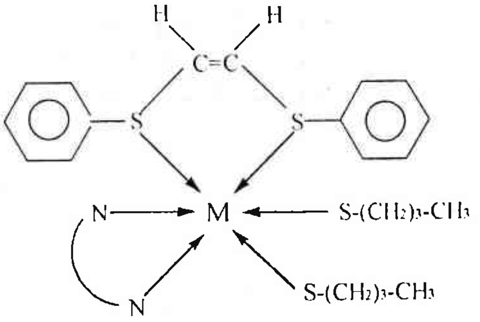


$[M(L)(SBu^n)_2]$

M= Zn(II),Cd(II) and Hg(II)



$[M(L)(SFur)_2(phen)]$



$[M(L)(SBu^n)_2(phen)]$

M= Zn(II),Cd(II) and Hg(II)

=1,10 phenanthroline

Fig 1: Suggested structure of the complexes
where L=Cis-bis-1,2-(phenylthio)ethylene

Table 1: Analytical and some physical properties of the complexes and adducts

No.	Complex	Colour	M.P (°C)	Yield (%)	Molar conductivity $\Omega^{-1}.cm^{2}.mol^{-1}$	% Metal Found (calc.)	Molecular weight Found (calc.)
1	$[Zn(L)(SBu^{n})_2]$	Yellow	234*	87	12	13.39 (12.76)	487.88 (480.93)
2	$[Cd(L)(SBu^{n})_2]$	White	250	81	7	21.01 (20.75)	534.91 (520.84)
3	$[Hg(L)(SBu^{n})_2]$	Gray	156	80	15	32.19 (30.99)	623.09 (610.77)
4	$[Zn(L)(SFur)_2]$	Brown	217*	95	13	16.04 (15.83)	406.52 (400.74)
5	$[Cd(L)(SFur)_2]$	Brown	138	77	9	24.78 (24.31)	453.56 (430.50)
6	$[Hg(L)(SFur)_2]$	Green	184*	72	10	37.02 (36.78)	541.74 (532.75)
7	$[Zn(L)(SBu^{n})_2(phen)]$	Yellow	153	92	16	9.78 (9.18)	668.1 (660.43)
8	$[Cd(L)(SBu^{n})_2(phen)]$	Yellow	202	94	18	15.71 (15.52)	715.13 (700.15)
9	$[Hg(L)(SBu^{n})_2(phen)]$	Pink	210	80	17	24.97 (23.88)	586.74 (577.75)
10	$[Zn(L)(SFur)_2(phen)]$	Brown	190	85	16	11.14 (10.93)	633.78 (621.98)
11	$[Cd(L)(SFur)_2(phen)]$	Brown	106	83	20	17.73 (16.32)	721.96 (563.98)
12	$[Hg(L)(SFur)_2(phen)]$	Brown	143*	75	22	27.78 (27.01)	710.94 (705.19)

* = decomposition temperature

Table 2:Electronic and infrared data of the ligands and its metal complexes and adducts

No.	υ(C -S)	υ(C -S)	υ(M-S)	υ(M–N)	U.Vvis
1	915	619	376	---	22727,36231
2	911	643	360	---	24038, 34246
3	918	633	400	---	17793, 22321
4	885	668	370	---	36231
5	859	643	395	---	31055, 34965
6	884	622	400	---	30487,33112
7	867	641	370	480	23584, 34965
8	861	637	390	485	23584, 33112
9	918	628	380	492	19531,10570,32467
10	866	641	---	480	33783,43103
11	820	637	---	500	32258,42735
12	883	621	---	490	34482

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