

Synthesis and characterization of some new complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) with 2,3 and 3,4- di-(2'-thiophenyloxy) aniline

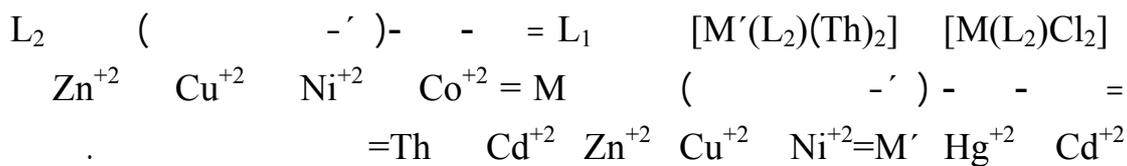
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[M(L₁)Cl₂]



DMSO (-) DMF

(-)

Abstract

A series of new complexes of the type [M(L₁)Cl₂], [M(L₂)Cl₂] and [M'(L₁)(Th)₂] where L₁=2,3-di-(2'-thiophenyloxy) aniline, L₂=3,4-di-(2'-thiophenyloxy)aniline, M=Co⁺², Ni⁺², Cu⁺², Zn⁺², Cd⁺² and Hg⁺², M'= Ni⁺², Cu⁺², Zn⁺² and Cd⁺², Th=thiophene carboxylate. The complexes were prepared and characterized by molar conductance, IR, UV/vis spectra studies, magnetic measurements and metal content analysis. Conductivity data in DMF for complexes (1-12) and DMSO for complexes (13-16) showed that all complexes are non-electrolyte. Magnetic moment and electronic spectra indicate that some of the complexes contain a tetrahedral and the other have octahedral environment.

Introduction

The reaction of metal complexes with thiophene and substituted thiophene were studied⁽¹⁻⁴⁾, and important mechanistic pathways were proposed. Some reaction include the π -coordination of thiophene either through one double bond⁽⁵⁾ or through the whole of its π system⁽⁶⁾. Alternatively, initial coordination through sulfur to form a S-bound complex, leading to insertion of the metal into the C-S bond, has been proposed.^(7,8)

A series of new thiophene amides containing a pyridine ring N-(2-pyridylmethyl)-3-thienyl-carboxamid has been synthesized and characterized. Single crystal x-ray structures have been determined for four of the new substances which show two distinct patterns of hydrogen-bonding. The crystal structure of the copper(II) complex of one of the ligands shows that the bonding is O, N in a square planar geometry with perchlorate ions in the axial position⁽⁹⁾.

Seven solid complexes of proportional mixed complexes (Eu^{+3} mixed with La^{+3}) of rare earth perchlorate with the 2-thiophene carboxylic acid and 1, 10- phenthroline were synthesized and characterized by Bao et al^(10,11).

The influence of the substituents (R) at the N^1 nitrogen of heterocyclic thiosemicarbazones $\{(\text{C}_4\text{H}_3\text{X})-\text{C}(\text{H})=\text{N}^3-\text{N}^2\text{H}-\text{C}^1(=\text{S})\text{N}^1\text{HR}; \text{X}=\text{O}, \text{Hftsc}; \text{X}=\text{S}, \text{Httsc}\}$ on the geometry of nickel(II) complexes was investigated. Furan-2-carbaldehyde thiosemicarbazones (Hftsc) have formed both trans $[\text{Ni}(\text{ftsc}-\text{N}-\text{R})_2](\text{R}=\text{Me}; \text{Et})$, and cis (R=Ph), square planar complexes unlike thiophene-2-carbaldehyde thiosemicarbazones (Httsc) which yielded only trans square planar complexes $[\text{Ni}(\text{ttsc}-\text{N}-\text{R})_2](\text{R}=\text{Me}; \text{Et}; \text{Ph})$ ⁽¹²⁾.

Han et al⁽¹³⁾ studied a series of organotin (IV) compounds of the type $[\text{R}_3\text{SnL}]_2$, R is Me (1), Bu (2), $[\text{R}_2\text{SnL}]_2$, R is Ph (3), Me (4), Bu (5), L is pyruvic acid thiophene-2-carboxylic hydrazone, and $[\text{R}_2\text{SnL}']$, R is Me (6), Bu (7), Ph (8), L' is salicylaldehyde thiophene-2-carboxylic hydrazone have been synthesized in 1:1 molar ratio. All compounds were characterized by elemental analysis, IR, ^1H , ^{13}C , ^{119}Sn NMR spectra.

Reaction of trans- $[\text{Ru}(\text{dppm})_2\text{Cl}_2]$ where (dppm= $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with thiophene-2-carbaldehyde thiosemicarbazone $\{\text{C}_4\text{H}_3\text{S}-\text{C}^2(\text{H})=\text{N}^3-\text{N}^2\text{H}-\text{C}^1(=\text{S})-\text{N}^1\text{H}_2, \text{H}_2\text{L}^1\}$ in the presence of Et_3N base formed a complex, $[\text{Ru}(\eta^3-\text{C}, \text{N}^3, \text{S}-\text{L}^1)(\eta^2-\text{P}, \text{P}-\text{dppm})(\eta^1-\text{P}-\text{dppm})](\text{L}^1 \text{ is dinegative thiophene-2-carbaldehyde thiosemicarbazone})$, with an unprecedented cyclometalation of a heterocyclic ring in Ru^{II} -thiosemicarbazone chemistry. The complexes have been characterized using analytical, spectroscopic, and single-crystal X-ray crystallographic⁽¹⁴⁾.

Complexes of Co(II) with two Schiff bases TEAB [2-hydroxy-4- $\{[2\text{-oxo-2-(thiophen-2-yl)ethylidene]amino\}$ benzoic acid] and TEPC [N-

[2-oxo-2-(thiophen-2-yl)ethylidene]pyridine-3-carboxamide] have been synthesized and characterized by using elemental analysis, magnetic susceptibility, mass spectra, ^1H , ^{13}C -NMR, IR and electronic spectral data. All these studies reveal the distorted octahedral Co(II) complexes ⁽¹⁵⁾.

The present paper describe the synthesis and characterization of 2,3-di-(2'-thiophenoyloxy)aniline and 3,4-di(2'-thiophenoyloxy)aniline and the preparation of their new complexes with Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2} salts.

Experimental

Physical measurement

Electronic spectra were recorded on Shimadzu UV/vis, spectrophotometer UV-160 at room temperature, The measurement were recorded using a concentration of 10^{-3} M of the complexes in DMF or DMSO. Infrared spectra with in the range ($4000\text{-}200\text{ cm}^{-1}$) were recorded on a FTIR Bruker Tensor 27co. spectrophotometer using CsI disc. Metal content analyses were made on Shimadzu AA 670 atomic absorption spectrophotometer. The magnetic moments were carried out at $2\text{ }^\circ\text{C}$ on the solid states by Faraday method using Bruker BM6 instrument. All magnetic susceptibilities values were corrected for diamagnetic contribution using Pascal's constant. The molar conductance of 10^{-3} M solution of metal complexes in Dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) was measured at 25°C using Jenway 4070 conductivity meter and a dip-cell with platinised electrodes.

Synthesis of 2,3 di (2'-thiophenoyloxy) aniline (L_1)

Treatment of 2-thiophene carboxylic acid (2.56g, 0.02mol) in 20ml ethanol and sodium hydroxide (0,08g, 0.02mol) in 20ml ethanol, with 2,3 dichloro aniline (0.16g, 0.01 mmol)⁽¹⁶⁾. Then the mixture was refluxed for 6h. under stirring. The light brown precipitate was obtained after evaporation of the solution to about 1/3 of its volume, which was filtered off, washed with cold ethanol and diethyl ether. Then dried under vacuum for several hours.

Synthesis of 3,4 di (2'-thiophenoyloxy) aniline (L_2)

It was prepare using 3,4-dichloroaniline by applying the above procedure.

Preparation of $[\text{M}(\text{L}_1)\text{Cl}_2]$ M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II).

A clear solution of the ligand 2,3-di(2'-thiophenoyloxy)aniline (0.345g, 1.0 mmol) in ethanol (30ml) was added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or ZnCl_2 or $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$ or HgCl_2 (1.0 mmol) in (10ml) ethanol, the reaction mixture was refluxed for 3 hours. Then the mixture was left for 24 hours, at room temperature to give the precipitate which was filtered off, washed with ethanol and diethyl ether, then dried under vacuum for 2 hours.

Preparation of $[\text{M}(\text{L}_2)\text{Cl}_2]$ M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II).

The complexes were prepared using the above procedure, with L_2 and the same metallic salts.

Preparation of $[\text{M}'(\text{L}_1)(\text{Th})_2]$ M= Ni(II), Cu(II), Zn(II), Cd(II).

A solution of $[\text{M}(\text{L}_1)\text{Cl}_2]$ (1.0 mmol) in dimethylformamide (15 ml) were added to a solution of sodium thiophen 2-carboxylate (0.15g, 2.0 mmol) in ethanol (10 ml) (prepared from the reaction of an equivalent amount of NaOH (0.04g, 0.01mol) and (1.28g, 0.01mol) thiophene carboxylic acid in ethanol (40ml). The mixture was stirred under reflux for 3 hours and during which time a precipitate formed. The mixture was cooled at room temperature and the filtration solid was washed with ethanol and diethyl ether, then dried under vacuum.

Results and discussion

The complexes were prepared through a direct reaction of the ligands 2,3 di(2'-thiophenoyloxy) aniline (L_1) or 3,4 di(2'-thiophenoyloxy) aniline (L_2) with an ethanolic solution of metal (II) chloride gave complexes of the type $[\text{M}(\text{L}_1)\text{Cl}_2]$ and $[\text{M}(\text{L}_2)\text{Cl}_2]$, while the complexes of the type $[\text{M}'(\text{L}_1)(\text{Th})_2]$ were prepared from the reaction of sodium thiophene carboxylate with complex type $[\text{M}(\text{L}_1)\text{Cl}_2]$, where $\text{M}=\text{Co}^{+2}$, Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} and Hg^{+2} ; $\text{M}'=\text{Ni}^{+2}$, Cu^{+2} , Zn^{+2} and Cd^{+2} ; $\text{Th}=\text{Thiophene carboxylate}$.

In general all the prepared complexes are colored, stable in air at room temperature and they are soluble in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The physical properties of complexes are listed in Table 1. The molar conductance in 10^{-3} M solution in DMF are in the (10-30) $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ range indicating a non-electrolytic nature of the complexes. This is inconsistent with the stoichiometry assumed for the complexes on the basis of analytical data.

IR spectra

The most important IR assignments of the ligands and its complexes are listed in Table 2. The characteristic bands in the infrared of the ligands occur at 690 cm^{-1} due to the stretching vibration of $\nu(\text{C-S})^{(17)}$. In the

complexes (2,8,10) this band show decreasing in the frequencies, indicating that it is involved in the coordination with metal ions Table 2.

The IR spectra is showed band at 3076 cm^{-1} and 3076 cm^{-1} in the ligands assigned $\nu(\text{NH}_2)$. These bands remained almost constant upon coordination with the metal ion⁽¹⁸⁾, which indicates that this group is not involved in the coordination.

The IR-spectra of the ligands showed a band at 1556 cm^{-1} and 1560 cm^{-1} assigned to carbonyl group $\nu(\text{C}=\text{O})$. The spectra of the complexes(1-12) showed stretching vibration at $1588\text{-}1663\text{ cm}^{-1}$, which indicated that the carbonyl group are involved in the coordination with metal ions⁽¹⁹⁾.

The IR spectra of the Zn(II) complex (15) showed intenes bands at 1597 and 1421 cm^{-1} assigned for asym. $\nu(\text{COO})$ and for sym. $\nu(\text{COO})$ respectively. The magnitude of ΔV ($\Delta V = \nu_{\text{asym}} \text{COO} - \nu_{\text{sym}} \text{COO}$), were 220 cm^{-1} suggested bidentate bonding of carboxylic group to Zinc ion, while the IR spectra of complexes (13, 14, 16) showed bands at 1562 , 1523 , 1562 cm^{-1} and 1390 , 1385 , 1387 , cm^{-1} assigned for asym. $\nu(\text{COO})$ and for sym. $\nu(\text{COO})$ respectively. The magnitude of ΔV ($\Delta V = \nu_{\text{asym}} \text{COO} - \nu_{\text{sym}} \text{COO}$), were in the range $148\text{-}175\text{ cm}^{-1}$ suggested monodentate bonding of carboxylic group to metal ions⁽²⁰⁾.

The infrared of the complexes show a new bands at $400\text{-}478\text{ cm}^{-1}$ assigned to $\nu(\text{M-O})$ ⁽²¹⁾, while the complexes (1-12) show band at $(253\text{-}298)\text{ cm}^{-1}$ assigned to $\nu(\text{M-Cl})$ ⁽²²⁾. The complexes (8,10) show band at $(392, 365)\text{ cm}^{-1}$ assigned to $\nu(\text{M-S})$.

Further more IR spectra for complexes (13-16) doesn't show any absorption belong to $\nu(\text{M-Cl})$, which means the absence of chloride ions in the complexes, that was proved by sodium fussion test.

Electronic Spectra

The electronic spectra of the complexes were recorded as 10^{-3} M solution in DMF, DMSO and the results are presented in Table 2.

The electronic spectra of Co(II) complexes (1 and 7) show a bands in the visible region $15015\text{-}16892\text{ cm}^{-1}$ are generally correspond, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition which is consistent with tetrahedral geometry⁽²³⁾.

The Ni(II) complexe (2 and 8) shows three bands at $11965\text{-}12920$, $14970\text{-}15432$ and $23722\text{-}23364\text{ cm}^{-1}$, which are assigned to ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_2\text{g}(\text{F})(\nu_1)$, ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{F})(\nu_2)$ and ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{P})(\nu_3)$ transition respectively. This shows that the structure is an octahedral geometry⁽²⁴⁾. While the Ni(II) complex (13) show a band at 14620 cm^{-1} are due to the transition from ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ in tetrahedral geometry⁽²⁵⁾.

The electronic spectra of Cu(II) (3,9 and 14) showed bands at 12987 , 13587 and 13736 cm^{-1} respectively correspond to the transition ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ for distorted tetrahedral geometry around Cu(II)⁽²⁶⁾.

Magnetic Susceptibility measurements

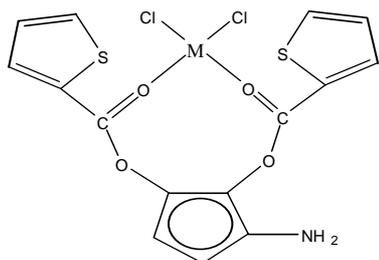
The magnetic moment of the complexes are given in Table 1. The Co(II) complexes (1 and 7) have magnetic moments of (4.17,4.09) B.M which are related to tetrahedral geometry⁽²⁷⁾.

The Ni(II) complexes (2 and 8) have magnetic moments of (2.93,2.80) B.M which correspond to octahedral geometry⁽²⁸⁾, while the nickel complex (13) has magnetic moments of 3.36 B.M suggest tetrahedral geometry⁽²⁹⁾.

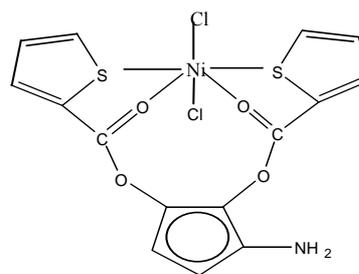
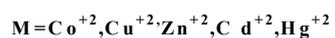
The magnetic moment of Cu(II) complexes (3,9 and 14) have been found to be (2.19, 1.84 and 1.71)B.M, this corresponds to the presence of one unpaired electron in the complexes⁽³⁰⁾.

As the spectra of Zn(II), Cd(II) and Hg(II) complexes are not well resolved, they are not interpreted but they μ_{eff} value shows that they are diamagnetic as expected.

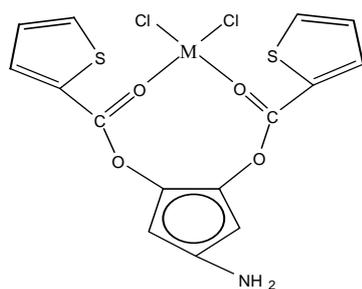
On the basis of the above discussion we propose the following structures for the metal(II) complexes as shown in Fig. 1.



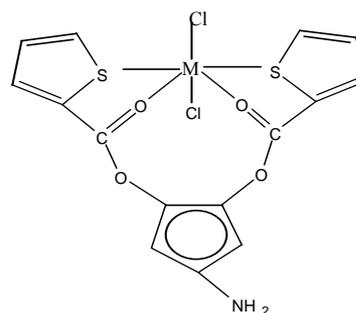
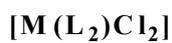
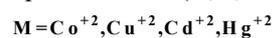
Complexes No. (1,3,4,5,6)



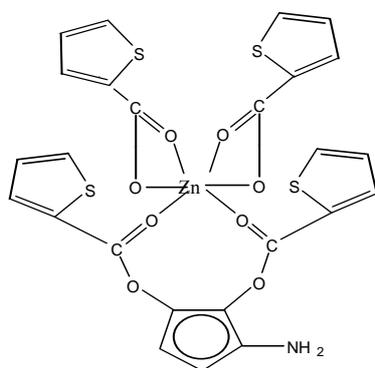
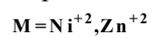
Complex No. (2)



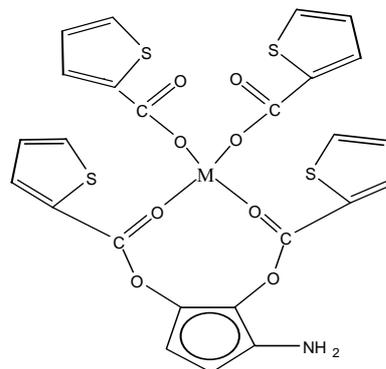
Complexes No. (7,9,11,12)



Complexes No. (8,10)



Complex No. (15)



Complexes No. (13,14,16)

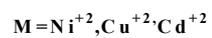


Fig 1: Possible structure of the complexes

Table 1: Physical properties of ligand and their complexes

No.	Complexes	Colour	M.p (°c)	Yield (%)	Analysis found (calc.)% M	Λ $\text{Ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$	μ_{eff} (B.M)
L ₁	(C ₁₆ H ₁₁ N ₁ O ₄ S ₂)	Pale brown	220	70	-----	-----	-----
L ₂	(C ₁₆ H ₁₁ N ₁ O ₄ S ₂)	Light brown	243	65	-----	-----	-----
1.	[Co(L ₁)Cl ₂]	violet	292 ^d	52	12.41(12.11)	24	4.17
2.	[Ni(L ₁)Cl ₂]	Pale green	290 ^d	81	12.38(12.40)	25	2.93
3.	[Cu(L ₁)Cl ₂]	Dark blue	288 ^d	79	13.27(13.52)	32	2.19
4.	[Zn(L ₁)Cl ₂]	Pale brown	270 ^d	73	13.62(13.60)	29	-----
5.	[Cd(L ₁)Cl ₂]	Pale brown	278 ^d	48	-----	28	-----
6.	[Hg(L ₁)Cl ₂]	Pale yellow	320 ^d	40	-----	31	-----
7.	[Co(L ₂)Cl ₂]	Pale violet	135	53	12.41(12.52)	17	4.09
8.	[Ni(L ₂)Cl ₂]	pale green	196	48	12.38(12.31)	26	2.80
9.	[Cu(L ₂)Cl ₂]	Dark green	148	72	13.27(13.18)	27	1.84
10.	[Zn(L ₂)Cl ₂]	Pale yellow	142	54	13.62(13.70)	22	-----
11.	[Cd(L ₂)Cl ₂]	yellow	271	67	-----	17	-----
12.	[Hg(L ₂)Cl ₂]	Pale yellow	142	49	-----	30	-----
13.	[Ni(L ₁)(Th) ₂]	Pale green	310 ^d	60	-----	20*	3.36
14.	[Cu(L ₁)(Th) ₂]	Dark green	190	53	-----	19*	1.71
15.	[Zn(L ₁)(Th) ₂]	Pale yellow	180	40	-----	22*	-----
16.	[Cd(L ₁)(Th) ₂]	yellow	260 ^d	50	-----	16*	-----

d =Decomposition temperature

*=soluble in DMSO

Table 2: Electronic and infrared spectral data of ligand and their complexes

No.	Band maxima(cm^{-1}) λ_{max}	IR spectral bands (cm^{-1})				
		$\nu(\text{C-S})$	$\nu(\text{C=O})$	$\nu(\text{M-Cl})$	$\nu(\text{M-O})$	$\nu(\text{M-S})$
L ₁	-----	690 _m	1556 _s	-----	-----	-----
L ₂	-----	689 _m	1560 _s	-----	-----	-----
1	15015,16447,34483	691 _m	1603 _s	277 _w	444 _m	-----
2	11965,14970,23722	674 _w	1588 _s	293 _w	517 _m	-----
3	13587,29586,32895	692 _m	1603 _s	290 _w	498 _w	-----
4	25000,32468	691 _w	1616 _s	285 _w	494 _m	-----
5	32680,35971	690 _w	1639 _s	253 _w	482 _w	-----
6	33557,43077	690 _w	1618 _s	269 _w	478 _w	-----
7	15015,16892,32680	690 _w	1629 _s	298 _w	469 _m	-----
8	12920,15432,23364	675 _m	1655 _s	283 _w	471 _w	392 _m
9	12987,24038	690 _w	1663 _s	277 _w	463 _m	-----
10	23148,32051	670 _m	1616 _s	285 _w	469 _m	365 _m
11	25225,34722	690 _m	1626 _s	298 _w	482 _m	-----
12	32051,34247	688 _w	1629 _s	276 _w	478 _w	-----
13	14620,29412	690 _w	-----	-----	478 _m	-----
14	13736,31056	690 _w	-----	-----	498 _w	-----
15	31056,34722	690 _w	-----	-----	459 _m	-----
16	32722,34014	690 _w	-----	-----	480 _w	-----

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