Synthesis and Characterization of some Mononuclear Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes containing Bis-(2-thiophenelidene) thiosemicarbazone ligand

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Received: 2/2/2011; Accepted: 26/12/2011

Abstract:

A number of new complexes of the general formulaes $[M(L_1)_2Cl_2]$ and $[M(L_1)_2(\gamma\text{-pic})_2]Cl_2\{$ where L_1 = bis-(2-thiophenelidene) thiosemcarbazone; M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and $\gamma\text{-pic}$ = 4-methyl pyridine} have been prepared and characterized by molar conductance, magnetic properties and metal contents analysis, infrared, and electronic spectra. The electronic and magnetic susceptibility indicated that the complexes have distorted octahedral geometry either non regular for some complexes due to the differences in the two coordinated ligand and distorted copper complexes due to the above reason and also to Jahn teller effect.

تحضير وتشخيص بعض من معقدات Zn(II) و Cu(II) , Ni(II), Co(II) , Fe(II) , Mn(II) أحادية النوى المحتوية على ليكاند بس ـ (2 ثايوفنيليدين) ثايوسيميكاربازون

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ملخص البحث:

 $[M(L_1)_2Cl_2]$ تـم تحــضير عــدد من الــمعقدات الــجديدة ذوات الصيغ العامة $[M(L_1)_2Cl_2]$ [M(II) = M] (ف $[M(L_1)_2(\gamma-pic)_2]Cl_2$ و $[M(L_1)_2(\gamma-pic)_2]Cl_2$ و [M(II) = M] و [M(I

الالكترونية والعزم المغناطيسي بان المعقدات تمتلك بنية ثماني السطوح غير المنتظمة لبعض المعقدات بسبب كون الليكندين المتناسقين مختلفين والمشوهة لمعقد النحاس للسبب السابق فضلا عن تأثير يان تيلر.

Introduction:

Thiosemicarbazides are of current interest with respect to their biological activity and chemotherapeutic properties. In addition, these compounds have many applications especially as reagents for the microanalytical determination as well as their ability to form chelated complexes with transition metal ions [1-5].

Thiosemicarbazones and their metal complexes have been extensively studied during recent years mainly due to their various biological activities ^[6,7]. They usually acted as chelating ligands specially with transition metal ions, joint through the sulfur and azomethine nitrogen atoms ^[8].

A review was published by Lobana *et. al* ^[9,10] changing the attachment of the thiosemicarbazone moiety to the 3-position on the heteroaromatic ring often caused a decrease in biological activity. Thiosemicarbazones (TSC) have been synthesized by condensing substituted thiosemicarbazide with thiophene-2- carbxaldehyde. These thiosemicarbazones showed significant improvement in antiamobic activity^[11].

Intercalation of pyridine, 4-methylpyridine and 4-ethlpyridine into the interlayer spaces of Cu(II)-montmorillonite was investigated. The successful intercalation of these compounds through coordination to the interlayer Cu^{2+} cations was confirmed by powder X-ray diffractions and infrared spectroscopy of the products. The presented solid-gas intercalation of pyridine derivatives and in situ complex formation in the interlayer spaces of montmorillonite is a feasible way to prepare clay coordination-intercalation compounds which cannot be obtained in conventional ion-exchange reactions $^{[12]}$.

A new synthetic route to isothiocyanate-containing materials is presented. Eight isothiocyanate-4-methylpyridine (γ -picoline) compounds were prepared by refluxing metal powders with thiourea in γ -picoline^[13].

The present paper described the synthesis and characterization of L_1 = bis-(2-thiophenelidene) thiosemcarbazone , and the preparation of their new complexes with Mn(II), Fe(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) .

Experimental:

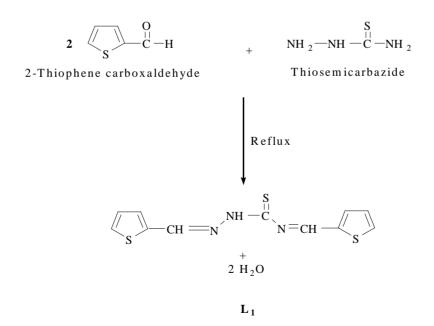
Physical measurement:

Electronic spectra were recorded on Shimadzu spectrophotometer UV-160 at room temperature, The measurements were recorded using a concentration of 10⁻³M of the two ligands and their complexes in N,N-dimethylformamide (DMF). Infrared spectra (4000-200 cm⁻¹) were recorded on a FTIR Brucker Tensor 27 co. spectrophotometer by KBr, CsI discs. Metal contents analyses were made on Shimadzu AA 670 atomic absorption spectrophotometer. The magnetic moments were carried out at 25°C on the solid states by Faraday method using Bruker BM6 instrument. The molar conductance of 10⁻³ M solution of metal complexes in (DMF) were measured at 25°C using Jenway 4070 conductivity meter. Melting point were determined on a Buchi 510 melting point apparatus and were uncorrected. The primary materials;

2-thiophene carboxaldehyde, thiosemisarbazide and all the metal salts that are used in the experiment were supplied (Fluka, BDH).

A . Preparation of the ligands:

The ligand L₁ has been synthesized according to the following procedure ^[14] .Treatment of 2-thiophene carboxaldehyde (2.24 g, 0.02 mol) in (10 ml) ethanol with thiosemicarbazide (0.91 g, 0.01 mol) in (10 ml) ethanol. Then the mixture was refluxed for 7 h. in presence of 2 ml conc. HCl, the (greenish yellow) solid was appeared then the mixture cooled and filtered off, washed with cold ethanol and dried in vacuum,recrystallization by propanol (Scheme(1)).



Scheme (1): Preparation and structure of the ligand L1

B. Preparation of the complexes:

A hot ethanolic solution of the ligand L_1 (0.56 g , 0.02 mol) and ethanolic solution of the corresponding metal salt {MnCl₂.4H₂O (0.19 g, 0.01 mol) or FeCl₂ (0.12 g , 0.01 mol) or CoCl₂.6H₂O (0.27 g , 0.01 mol) or NiCl₂.6H₂O (0.23 g , 0.01 mol) or CuCl₂.2H₂O (0.13 g, 0.01 mol and ZnCl₂ (0.13g , 0.01 mol)} in (20 ml) of ethanol were mixed together with stirring . The mixture has been refluxed for 4 hours , on cooling , a colored precipitate has been formed which was filtered off , washed with cold EtOH and dried under vacuum.

C. Preparation of the mixed ligand complexes:

The complex No.(2) was prepared by adding an excess of 4-methyl pyridine (0.07 g , 0.02 mol) dissolved in ethanol (10 ml) to (0.27 g , 0.01 mol) complex separately and refluxed for about 3 hours. On cooling a coloured precipitate has been formed which was filtered off, washed with cold EtOH and dried under vacuum, and the other complexes No.(4, 6, 10, 12) where prepared by applying the same procedure.

Results and discussion:

The complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the ligand L_1 =[bis-(2-thiophenelidene)thiosemcarbazone] were air stable solides and colored (Table 1). The molar conductivities of the complexes in DMF indicated the presence of two types of complexes , a nonelectrolytic nature (14-30 ohm⁻¹. cm².mol⁻¹)^[15] for Mn(II), Fe(II), Co (II), Ni(II), Cu(II) and Zn(II) complexes where as 1:2 electrolytes (135-167 ohm⁻¹. cm².mol⁻¹)^[16] for the mixed ligand complexes (Table 1).

IR spectra:

The most important infrared spectra of the two ligands and their complexes are listed in Table 2. The IR spectra of the ligand showed band at 3202cm^{-1} in the ligand spectrum assigned to $\upsilon_{(NH)}$, this band has been shifted to lower frequency on complication [17]. Upon comparison it was shown that the $\upsilon_{(C=N)}$ was found to be splitted at $1610~\text{cm}^{-1}$ and $1606~\text{cm}^{-1}$ as we expected for the two type of C=N present in the complex . The two bands still splitted in the complexes and shifted to lower frequencies (Table 2) indicating the participation of azomethine nitrogen in coordination [18,19]. The spectra of the ligand showed band at the region 1173 cm due to $\upsilon_{(C=S)}$ in the spectra of some complexes this band undergoes little shift and appears at the range (1164-1172) cm which indicates that this band dose not involve in coordination, in the spectra of the other complexes this band appears at the range (1143-1158) cm showing that the coordination occurs through the sulfur of C=S bond with the metal ion [20]. The infrared spectra of γ -picoline ligand showed band

at 1625cm⁻¹ attributed to (C····N····C) group, this band was shifted to lower frequency (1562-1589) cm⁻¹ in the IR spectra of the complexes No. (2, 4, 6, 8, 10 and 12) indicating the coordination of this group with the metal ion^[21].

The other new bands in the range (418-459) cm⁻¹ in the spectra of the complexes were assigned to $\upsilon_{(M-N)}^{[22]}$ while the $\upsilon_{(M-N)}$ for (γ -picoline) ligand are in good agreement with the reported values of Nakamato which fall in the region (238-317) cm⁻¹ . The bands occurring at (350-390) cm⁻¹ and (269-303) cm⁻¹ have been assigned to the $\upsilon_{(M-S)}$ and $\upsilon_{(M-Cl)}$ modes, respectively. The spectrum of the ligand showed $\upsilon_{(N-N)}$ at (918-953) cm⁻¹ . The thiophene ring remained unchanged when passing from ligands to complexes at ≈ 837 cm⁻¹ $^{[20,\,22]}$.

Electronic spectra and magnetic moments:

The electronic spectral bands of the two ligands and their complexes, also the magnetic moment values for the complexes were listed in Table (3).

Manganese (II) complexes:

The electronic spectra exhibited band in the visible region at 26595, 26737 cm $^{-1}$,respectively for the two manganese (II) complexes these bands may be assigned to the transitions $^6A_1g \rightarrow ^4T_1g$ (G) and $^6A_1g \rightarrow ^4T_2g$ (P) ,respectively. The bands appeared at 30303, 32016 cm $^{-1}$ due to charge transfer $^{[23]}$. The magnetic moment values 5.87, 5.93 B.M for the manganese (II) complexes were in accordance with those having octahedral structure having five unpaired electrons .

Iron (II) complexes:

The electronic spectra of the two Fe(II) complexes showed a band in the visible region at 10131, 13089 cm $^{-1}$, respectively attributed to the $^5T_2g \rightarrow ^5Eg$ transition and could be assigned to octahedral structure $^{[23]}$. The values of the magnetic moment were 4.68, 4.85 B.M have been in well accordance with those having octahedral geometry .

Cobalt (II) complexes:

The magnetic moment of Co(II) complexes were 4.17, 4.68 B.M (the higher values were due to orbital contribution) indicating an octahedral geometry $^{[23\text{-}25]}$. The electronic spectra showed band in the positions (1) 10695, 10989 cm $^{-1}$, (2) 12886, 16181 cm $^{-1}$,(3) 15772, 18796 cm $^{-1}$, respectively for the two cobalt (II) complexes these bands may be assigned to the transition $^4T_1g(F) \rightarrow ^4T_2g(F)(\upsilon_1), ^4T_1g(F) \rightarrow ^4A_2g(\upsilon_2)$ and $^4T_1g(F) \rightarrow ^4T_1g(P)(\upsilon_3)$, respectively the fourth band was due to

the charge transfer $^{[23-25]}$. The bands appear at 33557, 35842 cm $^{\text{-1}}$ due to charge transfer .

The ligand field parameter B and the ligand field splitting energy (10Dq) in case of cobalt (II) complexes have been calculated, the values of B, β , ν_2/ν_1 suggested octahedral geometry for all the complexes ^[26]. Racah parameter gives useful information about the covalency in the metal – ligand bonds (when Racah parameter decreased the covalence character's of the bond between the metal ion and ligand increased). The value of Racah parameter explain clearly the position of electrons cloud near the metal ion or the ligand molecule i.e: the type of coordination bond between them ^[27].

Nickel (II) complexes:

The two Ni(II) complexes exhibited magnetic moment values 3.07 and 3.12 B.M these values showed the presence of 2 unpaired electrons which lead to octahedral environment around Ni (II) ions , the high values of magnetic moment (from 2.87 B.M) were due to the orbital contribution [28]. The electronic spectra of the complexes showed three bands at (1) 10162-10183 cm $^{-1}$ (2) 15364-16792 cm $^{-1}$ and (3) 24038-26455 cm $^{-1}$ due to three spin allowed transitions $^3A_2g(F) \rightarrow ^3T_2g(F)(\upsilon_1), ^3A_2g(F) \rightarrow ^3T_1g(F)$ ($\upsilon_2)$ and $^3A_2g(F) \rightarrow ^3T_1g(P)$ ($\upsilon_3)$, respectively, indicating that the complexes had octahedral geometry, The ligand field parameter B and the ligand field splitting energy (10Dq) in case of nickel (II) complexes have been calculated, the values of B, $\beta, \, \upsilon_2/\, \upsilon_1$ suggested octahedral geometry for all the complexes $^{[26,27]}$.

Copper (II) complexes:

The magnetic moment of the Cu(II) complexes are 1.78 and 1.84 B.M which were due to the presence of one unpaired electron. The electronic spectra showed one band at which assigned to the ${}^2E_2g(F) \rightarrow {}^2T_2g$ transition in distorted octahedral structure around the Cu(II) ions ${}^{[29,30]}$.

As the spectra of Zn(II) complexes were not well resolved, there were not interpreted but they μeff values showed that they are diamagnetic as expected. On the basis of the above results the proposed structures for the metal (II) complexes were shown in Fig (1) .

 $M\text{=}\ Mn(II)\ , Fe(II)\ , Co(II)\ , Ni(II)\ , Cu(II)\ and\ Zn(II)$

Fig (1): Suggested structure of the complexes [M $(L_1)_2Cl_2$] and [M $(L_1)_2(\gamma$ - pic) $_2$]Cl $_2$

II. [6			9.	8.	7.	6. [S.	4.	3	2. [1				No.
	$[Zn(L_i)_2Cl_2]$	[Cu (L ₁) ₂ (y-pic) ₂] Cl ₂	[Cu(L ₁) ₂ Cl ₂]	[Ni (L ₁) ₂ (y-pic) ₂] Cl ₂	[Ni(L ₁) ₂ Cl ₂]	[Co (L ₁) ₂ (y-pic) ₂] Cl ₂	[Co(L ₁) ₂ Cl ₂]	[Fe (L ₁) ₂ (γ-pic) ₂] Cl ₂	$[Fo(L_1)_2Cl_2]$	[Mn(L ₁) ₂ (y-pic) ₂] Cl ₂	$[Mn(L_i)_2Cl_2]$	γ-pic		L	Compound
WILL	White	Green	Dark green	Dark green	Green	Brown	Dark brown	Brown	Brown	Pale brown	Brown	Brown	yellow	Greenish	Colours
289	241	303	216	255	294	223	206	271	263	247	213	145(B.b)		190	M.p °C
55	69	36	70	59	84	49	90	64	52	4	82	75		61	Yield
143	21	156	19	150	30	167	22	135	14	148	27	-		I	Molar conductance Ohm ⁻¹ .cm ² .mol ⁻¹
Zn Cl ₂	Zn Cl ₂	Cu Cl ₂ .2H ₂ O	Cu Cl _{2.2H2} O	Ni Cl ₂ .6H ₂ O	NiCl ₂ .6H ₂ O	Co Cl _{2.6} H ₂ O	Co Cl ₂ .6H ₂ O	FcCl ₂	FeCl ₂	MnCl ₂ ,4H ₂ O	MnCl ₂ ,4H ₂ O	1		1	Salts
7.32 (7.44)	9.41 (9.53)	7.13 (7.21)	9.91 (9.24)	6.62 (6.83)	8.53 (8.67)	6.64 (6.71)	8.56 (8.70)	6.32 (6.51)	8.15 (8.26)	6.22 (6.31)	8.03 (8.17)	1		1	Metal analysis found (calculated)%

9. 8 10. w 00 .7 6. in 4 12 -12. [Zn (L₁)₂ (γ-pic)₂] Cl₂ [Cu (L₁)₂(y-pic)₂] Cl₂ $[Co(L_1)_2(\gamma-pic)_2]Cl_2$ [Fe $(L_1)_2(\gamma-pic)_2$] Cl_2 $[Mn(L_1)_2(\gamma-pic)_2]$ Cl_2 [Ni(L₁)₂(y-pic)₂] Cl₂ $[Cu(L_1)_2Cl_2]$ $[\operatorname{Zn}(L_1)_2\operatorname{Cl}_2]$ $[\operatorname{Fe}(L_1)_2\operatorname{Cl}_2]$ [Ni (L₁)₂ Cl₂] $[C_0(L_1)_2Cl_2]$ $[Mn(L_1)_2 Cl_2]$ Compound Ligand γ-pic 3144 3179 3161 3153 3172 3134 (HN) a 3170 3153 3149 3147 3178 3136 3202 ١ 1608, 1579 1578, 1573 1595, 1580 1596, 1588 1597, 1581 1585, 1579 1588, 1583 1583, 1577 1595, 1588 1586, 1584 1610, 1606 1601, 1582 1597, 1583 U(C-N) U(CNC) for y-pic 1580 1574 1567 1573 1589 1562 1625 ١ 1 1 ۱ 1148 1143 1146 1169 1148 1158 1169 1171 1172 1170 1173 1155 12 1 (C=S) Thiophene ring 837 831 833 857 834 837 837 24 832 850 836 837 837 (N-N) 947 939 918 930 939 951 939 952 926 939 939 953 942 ۱ 435, 452 419, 442 408, 446 432, 446 410, 428 420, 438 (N-M) 457 436 428 418 459 434 I for y-pic (N-W) 277 270 317 248 238 259 I 1 I U (M-S) 355 370 360 390 385 376 ۱ ١ I ı ı ı (M-CI) 277 303 285 269 293 290 ı ı I I I

Table (2): Selected I.R bands and their assignment in cm⁻¹.

Table (3): Magnatic moment and electronic spectral data of the complexes.

12.	E	10.	9.	.∞	7.	6.	5.	4.	က	2.		No.
$[Zn(L_1)_2(\gamma-pic)_2]Cl_2$	$[Zn(L_1)_2Cl_2]$	$[Cu(L_1)_2(\gamma-pic)_2]Cl_2$	$[Cu(L_1)_2Cl_2]$	$[Ni(L_1)_2(\gamma\text{-pic})_2]Cl_2$	$[Ni(L_1)_2Cl_2]$	$[Co(L_1)_2(\gamma\text{-pic})_2]Cl_2$	$[C_0(L_1)_2Cl_2]$	$[Fe(L_1)_2(\gamma-pic)_2]Cl_2$	$[Fe(L_1)_2Cl_2]$	$[Mn(L_1)_2(\gamma-pic)_2]Cl_2$	$[Mn(L_1)_2Cl_2]$	Compound
Diamagnetic	Diamagnetic	1.78	1.84	3.12	3.07	4.68	4.17	4.85	4.68	5.87	5.93	μ _{eff} B.M (25 C)
31056, 34722	31645, 32051	11792, 26455	13089, 30303	10183, 16792, 24038, 30487	10162, 15364, 26455, 31645 755.53	10989, 16181, 18796, 33557 134.00	10695, 12886, 15772, 35842	10131, 32894	13089, 33333	26595, 30303	26737, 32016	λ max (cm ^{-l})
-		1	1	685.4	755.53	134.00	228.46		-		1	В
	1		1	0.66	0.73	0.13	0.23	1	1	1	1	β
	1	I		1.64	1.51	1.47	1.20	1	1	I	1	υ ₂ / υ ₁
1	1	1		10183	10162	10989	10695	-	1	1		10 Dq
		1		12219	12194	19780	19251	I	i	•	-	υ ₂ /υ ₁ 10 Dq C.F.S.E

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