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Spectral and structural studies of transition metal complexes of thiosemicarbazone

Tahani I.Kashar

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, (EGYPT)

E-mail : tahanikashar@yahoo.com

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ABSTRACT

Mononuclear transition metal complexes with ONS donor phenylhydrazoethylacetoacetate thiosemicarbazone ligand (H_2L) were prepared. On the basis of the results from various physico-chemical and spectral studies the ligand behaves as tridentate in all complexes. The solid state ESR spectrum of $[Cu(HL)Cl]H_2O$ complex shows an axial type symmetry with dx^2-y^2 ground state and an essentially square – planar geometry around the Cu(II) ion whereas for $[Co(HL)Cl]H_2O$ characteristic of tetrahedral geometry. TGA and DTA showed that the complexes are thermally stable decomposed above 250 °C. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Complexes;
IR;
ESR spectra;
Magnetic properties;
Conductivity;
Synthesis.

INTRODUCTION

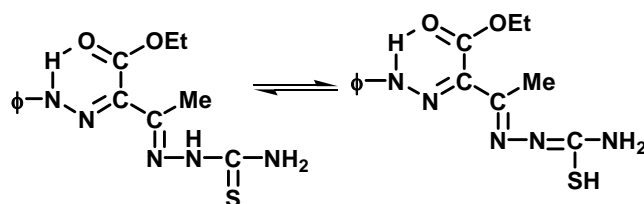
Thiosemicarbazones and their metal complexes present a wide range of bioactivities^[1,2]. Thiosemicarbazones are an important potential binding sites available for a wide variety of metal ions^[3-5]. The presence of various donor atoms and ability to change the denticity depending on the reaction conditions and starting reagents make thiosemicarbazones of various aldehydes and ketones a special category among organic ligands^[6]. Transition metal complexes of these compounds have been screened for their medicinal properties^[7] because they possess some degree of cytotoxic activity^[8] and possess a ranges of biological applications that include antitumor^[9] antifungal^[10], antiviral^[11], antibacterial and antimalarial activities^[12,13]. The complexes involving thiosemicarbazones have brown and orange colours resulting from the coordination of sulfur to the metal^[14].

In this paper we describe the synthesis, characterization and thermal (TGA and DTA) studies of some divalent metal ion complexes based on Schiff base derived from condensing phenylhydrazoethylacetoacetate with thiosemicarbazone (H_2L).

EXPERIMENTAL

All compounds and solvents used were pure chemicals from BDH or Aldrich and used as received.

The ligands used in the present investigation is phenylhydrazoethylacetoacetate thiosemicarbazone



Scheme 1 : The structure of the ligand

(H₂L) its formula given in Scheme 1

Preparation and characterization of the metal complexes

Metal chlorides of the divalent ions Cu(II), Ni(II), Co(II), Hg(II), Fe(III), Zn(II), Mn(II) and Cd(II) or AgNO₃ were mixed together in (1:1) mole ratios with the prepared ligand in absolute ethanol. The reaction mixture was refluxed on a water bath for 4 hours. The formed complexes were filtered off, washed several times with pure dry ethanol and dried in vacuo over anhydrous CaCl₂.

Measurements

Elemental analyses (C, H, N, Cl and S) were carried out at the microanalytical Unit of the University of Cairo. Metal ions were determined using atomic absorption with a Perkin Elmer (model 2380) spectrophotometer. The IR spectra were measured as KBr discs using a Perkin-Elmer 1430 infrared spectrometer (4000-200) cm⁻¹. Electronic absorption spectra in the 200-900 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. The thermal analyses (TGA and DTA) were carried out on a Shimadzu TG-50 and DT-30 thermal analyzers in the 27-800 °C range at a heating rate of 10 °C. min⁻¹. The magnetic susceptibilities were measured at room temperature

using the Gouy method with mercuric tetrathiocyanatocobaltate(II) as magnetic susceptibility standard; diamagnetic corrections were made using Pascal's constants¹¹. All solid ESR measurements at room temperature were carried out using Joel spectrometer model JES-FE 2XG equipped with an E101 microwave bridge. DPPH was used as a standard material. A Bibby conductimeter MCl was used for conductance measurements.

RESULTS AND DISCUSSION

Characterization of the metal complexes

The analytical data of the prepared complexes with some physical properties are summarized in TABLE 1. The analytical data confirms well the general formula [M(HL)Cl]H₂O where M = Cu(II), Ni(II), Co(II), Fe(III), and Hg(II), [M(H₂L)₂]Cl₂ where M = Mn(II) and Cd(II). The zinc(II) complex has the formula [Zn(H₂L)Cl₂.H₂O] whereas the complex of silver has the following formula [Ag(HL)H₂O]. The complexes are insoluble in most common solvents but soluble in DMF and DMSO. Molar conductance indicates that the complexes have the formula [M(H₂L)₂]Cl₂ where M = Mn(II) and Cd(II) are electrolytes TABLE 1.

TABLE 1 : Elemental analyses of the ligand (H₂L) and its complexes

No.	Compound	Colour	M.P. °C	Λ _m μS	Found (calc.)%						μ _{eff.} B.M.	
					C	H	N	M	S	Cl		H ₂ O
1-	H ₂ L	Orange	210	5	51.1 (50.8)	5.0 (5.5)	22.7 (22.8)	-	11.2 (10.4)	-	-	-
2-	[Cu(HL)Cl]H ₂ O	Brown	245	20	37.1 (36.9)	3.5 (4.2)	15.8 (16.5)	8.2 (8.6)	6.8 (7.5)	7.9 (8.4)	3.9 (4.3)	1.8
3-	[Ni(HL)Cl]H ₂ O	Pale brown	240	15	36.4 (37.3)	4.4 (4.3)	16.1 (16.7)	14.2 (14.0)	7.2 (7.6)	9.5 (8.5)	4.0 (4.3)	dia
4-	[Co(HL)Cl]H ₂ O	Brown	265	30	37.3 (37.3)	3.6 (4.3)	16.0 (16.7)	13.9 (14.1)	6.9 (7.6)	7.8 (8.5)	4.1 (4.3)	3.6
5-	[Hg(HL)Cl]	Orange	250	32	29.8 (28.8)	3.0 (3.0)	13.6 (12.9)	36.2 (36.9)	5.8 (5.9)	6.7 (6.6)	-	dia
6-	[Fe(HL)Cl]Cl	Brown	230	80	36.2 (35.9)	3.5 (3.4)	17.0 (16.1)	13.5 (12.9)	7.1 (7.3)	16.0 (16.4)	-	5.2
7-	[Zn(H ₂ L)Cl ₂ .H ₂ O]	Orange	> 300	26	33.9 (33.8)	3.1 (4.1)	15.2 (15.2)	13.8 (14.2)	7.8 (6.9)	15.9 (15.4)	4.2 (3.9)	dia
8-	[Mn(H ₂ L) ₂]Cl ₂	Pale brown	> 230	180	42.7 (42.2)	3.8 (4.6)	20.1 (19.0)	7.0 (7.4)	8.2 (8.6)	9.2 (9.6)	-	5.8
9-	[Cd(H ₂ L) ₂]Cl ₂	Orange	250	170	39.7 (39.2)	3.7 (4.0)	17.7 (17.6)	14.3 (14.1)	9.0 (8.0)	7.9 (8.9)	-	Dia
10-	[Ag(HL).H ₂ O]	Brown	160	10	36.2 (36.1)	3.8 (4.2)	16.2 (16.2)	24.9 (25.0)	7.4 (7.4)	-	3.9 (4.2)	1.6

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'Hnmr and IR spectra

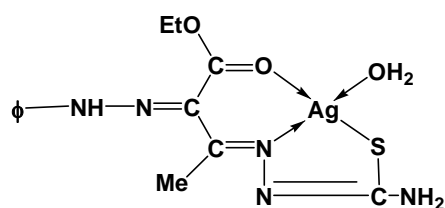
The ¹Hnmr spectra of the ligand in DMSO show peaks at 13.0, 9.6 and 9.0 ppm which may be assigned to NH—O, NH and NH₂^[15,16]. These peaks disappeared in D₂O spectra. Also multiplet bands appeared at 7-7.8 ppm may be due to aromatic ring protons^[17]. The triplet and quartet signals appeared at 2.2 and 3.8 ppm are assigned to CH₃ and CH₂ of the ester group and a singlet peak appeared at 2.4 ppm is assigned to CH₃ group.

The IR spectra for the free ligand differ from those of their complexes and provide significant indications regarding the bonding sites of the ligand. IR spectral assignments of the ligand and the complexes are listed in (TABLE 2). The IR spectra of the ligand show strong band at 3300 and 3260 Cm⁻¹ due to ν_{NH2} and ν_{NH} respectively. The band at 1700 Cm⁻¹ is assigned to ν_{C=O}^[18]. A strong band at 1580 Cm⁻¹ corresponds to ν_{C=N} vibration^[19] but ν_{C=S} appeared at 1040 Cm⁻¹. The band appeared at 900 cm⁻¹ is assigned to ν_{N-N} vibration^[20].

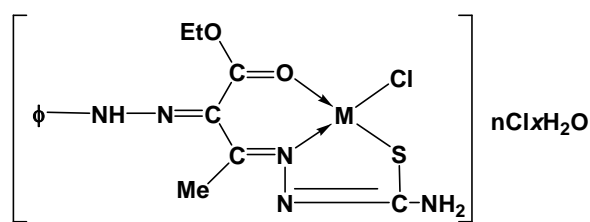
TABLE 2 : Important I.R. spectral bands of the ligand (H₂L) and its complexes

No.	Compound	ν _{OH}	ν _{NH2}	ν _{SH} ν _{NH}	ν _{C=O}	ν _{C=N}	ν _{C=S}	ν _{N-N}	ν _{M-O}	ν _{M-N}	ν _{M-S}	ν _{M-Cl}
1-	H ₂ L		3420	3300 3260(m)	1700(s)	1580	1040(s)	900(m)	-	-	-	-
2-	[Cu(HL)Cl]H ₂ O		3340 (br)		1685(s)	1600(s) 1560(s)	-	920(w)	510(m)	450(m)	375(s)	350(w)
3-	[Ni(HL)Cl]H ₂ O	3700- 3100 (br)	3300 (br)		1695(s)	1610(s) 1565(s)	-	915(w)	510(w)	570(s)	375(s)	330(w)
4-	[Co(HL)Cl]H ₂ O		3440(s)	3370(s)	1695(s)	1620(s) 1570(s)		915(m)	510(m)	470(m)	385(s)	330(m)
5-	[Hg(HL)Cl]		3440(s)	3260(s)	1695(s)	1610(s) 1560(s)	-	910(m)	510(m)	460(m)	420(m)	385(s)
6-	[Fe(HL)Cl]Cl		3430(s)	3260(s)	1695(s)	1610(s) 1560(s)	-	915(m)	510(m)	470(s)	375(s)	330(m)
7-	[Zn(H ₂ L)Cl ₂ .H ₂ O]	3600- 3400 (br)	3280(s)	3160(s)	1695(s)	1620(s)	1070(s)	915(m)	510(m)	470(m)	390(s)	320(m)
8-	[Mn(H ₂ L ₂)Cl ₂		3430(s)	3260(s)	1690(s)	1590(s)	1040(s)	910(m)	510(w)	470(s)	385(s)	330(m)
9-	[Cd(H ₂ L ₂)Cl ₂		3440(s)	3260(s)	1690(s)	1610(s)	1040(s)	910(m)	510(w)	470(m)	420(m)	380(s)
10-	[Ag(HL).H ₂ O]	3700- 3100 (br)		3260(s)	1680(s)	1600(s) 1565(s)	-	915(m)	510(m)	450(w)	375(s)	

s : strong m : medium w : weak br : broad



[Ag(HL)H₂O]



[M (HL) Cl] H₂O

Where

M = Cu, Ni, Co, Hg and Fe

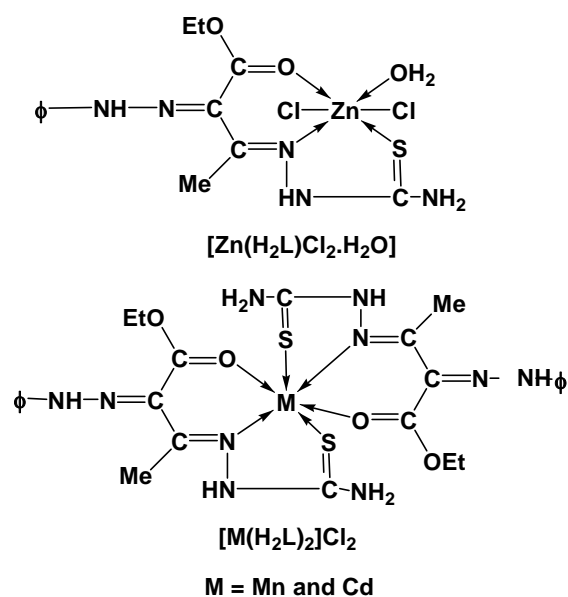
n = 0 for Cu, Ni, Co and Hg

= 1 for Fe

X = 0 for Hg and Fe

= 1 for Cu, Ni and Co

In the spectra of the Cu(II), Ni(II), Co(II), Fe(III), and Hg(II) complexes, the band assigned to ν_{C=S} of the free ligand disappears providing strong evidence for ligand coordinated around the metal ion in its deprotonated form (HL⁻)^[21]. The νC=O is shifted to higher wavenumber and the νC=N is shifted to lower frequency. These results indicate that the metal ions are bonded to the ligand molecule through covalent bonding and coordination bond to the azomethine nitrogen and carbonyl oxygen in the complexes^[22-24]. This denotes that the hydrazone acts as monobasic tridentate towards the Cu(II), Ni(II), Co(II), Fe(III),



and Hg(II) complexes. In the spectra of the Mn(II) and Cd(II) and Zn(II) complexes, the band assigned to $\nu_{C=S}$ of the free ligand are shifted to higher frequency indicating that these group coordinated to the metal. The bands of ν_{N-N} appeared at higher frequency in all complexes compared to the free ligand confirming the coordination to the metal. Medium bands at $\approx 510 \text{ cm}^{-1}$ corresponding to ν_{M-O} [25] and the bands at $470-450 \text{ cm}^{-1}$ and $390 - 375 \text{ cm}^{-1}$ in the spectra of the complexes were attributed to the ν_{Cu-N} and ν_{Cu-S} vibrations [26], Hence the infrared spectra indicate coordination through the N-S chelating system. In the spectra of Ag(I) and Zn(II) complexes the presence of water molecules is confirmed by the presence of the broad bands at $3454-3400 \text{ cm}^{-1}$ due to ν_{OH} of water molecules associated with the complex. The band at 3340 cm^{-1} and the two weaker bands around 840 and 720 cm^{-1} , which can be assigned to OH rocking and wagging modes of vibrations, confirm the coordination of water molecules to the metal ions.

Electronic absorption spectra and magnetic moment

The electronic absorption spectra of the complexes under study are summarized in TABLE 3. The electronic spectra of thiosemicarbazone show bands at $41,000$ and $31,740 \text{ cm}^{-1}$ assignable to $\pi-\pi^*$ and $n-\pi^*$ transitions respectively [27]. These bands are slightly shifted upon complexation. The shift of the $\pi-\pi^*$ bands to longer wavelength region in complexes is the result of the C=S bond being weakened and the conjugation

system enhanced on complexation [28,29]. The $n-\pi^*$ bands in the complexes has shown a blue shift due to donation of lone pair of electrons to the metal and hence the coordination of azomethine with a reduction of intensity. The band in the $27,000 - 20,760 \text{ cm}^{-1}$ range involves phenoxy $O \rightarrow M$ (II) transitions [30]. The Cu(II), Co(II), Ni(II) and Fe(III) complexes has a broad d-d combination band in the range $15,000 - 17,000 \text{ cm}^{-1}$ and appears as a shoulder on the intraligand and charge transfer bands. For asquare planar complex with $d_{x^2-y^2}$ ground state, three transitions are possible viz, $d_{z^2} - d_{x^2-y^2}$, $d_{xy} - d_{x^2-y^2}$ and $d_{xz} - d_{yz}$.

TABLE 3 : Electronic spectral assignments of the ligand and their complexes

Compounds	$\pi-\pi^*$	$n-\pi^*$
H ₂ L	41,000	31,740
[Cu(HL) Cl]H ₂ O	43,650	31,980 26,970
[Ni(HL) Cl]H ₂ O	42,060	31,410 27,000
[Co(HL) Cl]H ₂ O	39,390	32,010 26,860
[Hg (HL) Cl]	41,760	31,290 25,705
[Fe(HL) Cl]Cl	43,290	31,650 26,520
[Zn(H ₂ L) Cl ₂ .H ₂ O]	43,240	31,260 25,670
[Mn(H ₂ L) ₂]Cl ₂	42,300	31,800
[Cd (H ₂ L) ₂]Cl ₂	42,400	31,380
[Ag (HL) H ₂ O]	41,760	31,830 20,760

The room temperature magnetic moments per metal atom are given in TABLE 1. The values of μ_{eff} for copper complex 1.8 B.M are expected for square-planar geometry but for cobalt complex 3.6 B.M indicating the tetrahedral structure. The values of μ_{eff} showed that the nickel complex is diamagnetic, similar to the red square-planar dimethylglyoximate complex of nickel (II). The value for Fe(III) complex are those expected for square planar geometry but for Mn(II) complex are octahedral.

The e.s.r spectra

The e.s.r spectrum of a solid complex [Cu(HL)Cl]H₂O at R.T shows an axial type symmetry with $d_{x^2-y^2}$ ground state and an essentially square-planar geometry around the Cu(II) ion [31,32] which is in agreement with electronic spectrum data. The g_{\parallel} value for this complex shows considerable covalent bond character [33]. The g-values are

g_{\parallel}	g_{\perp}	g_{iso}
2.19	2.04	2.09

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The e.s.r spectrum of the complex $[\text{Co}(\text{HL})\text{Cl}]\text{H}_2\text{O}$ characteristic of a monomeric species, high spin d^7 configuration-Eight lines were observed in the high field region from the hyper fine interaction of the unpaired electron spin ^{59}Co ($I = 7/2$, 100% abundant) the line width save anisotropic. The spectrum exhibits two features assigned to $g_{\parallel} = 2.4$ with $A_{\parallel} = 135\text{G}$ and $g_{\perp} = 2.03$ with $A_{\perp} \geq 25\text{G}$ characteristic of tetrahedral^[30] geometry, $g_{\parallel} > g_{\perp} > 2.0023$, indicating $dx^2 - y^2$ ground state^[34].

Thermal analyses DTA and TGA

Thermal behaviour of the ligand and Cu(II), Co(II) and Zn(II) complexes were investigated by thermogravimetric studies TABLE 4. Phenylhydrozoethylacetoacetate thiosemicarbazone is thermally stable up to 210 °C, the sharp endothermic peak at 220 °C is due to melting. The content of a component in a complex changes with its composition and structure. Thus, the content of such component can be determined based on the mass losses of these components in thermogravimetric plots of the complex^[35,36]. Therefore, the thermogravimetric analysis (TGA, DTA)(50-800) for prepared complexes were recorded to distinguish between the coordinated and

hydrated water and to give an insight into the thermal stability of the studied complexes. The DTA curves in the 50-150 °C range show that Cu(II) and Co(II) complexes are thermally stable up to 50 °C when dehydration begins, this fact characterized by endothermic peaks within 50-150 °C range corresponding to the loss of hydrated water^[37]. In Zn(II) complex the endothermic peak was observed at 150-250 °C corresponding to the loss of coordinated water. The decomposition proceeds above 300 °C when the organic constituents of the complexes start releasing at 400-600 °C finally leaving metal oxide.

CONCLUSION

The molecular structures of the material are evaluated. The ligand behaves as tridentate in all complexes. ESR spectrum of $[\text{Cu}(\text{HL})\text{Cl}]\text{H}_2\text{O}$ complex shows an axial type symmetry with $dx^2 - y^2$ ground state and an essentially square-planar geometry around the Cu(II) ion whereas for $[\text{Co}(\text{HL})\text{Cl}]\text{H}_2\text{O}$ characteristic of tetrahedral geometry. TGA and DTA showed that the complexes are thermally stable decomposed above 250 °C.

REFERENCES

TABLE 4 : Thermal analyses TG and DTA of the ligand and some complexes

Compound	t.g.		d.t.a		Assignment
	Temp.c	%wt. loss	peak	Temp.c	
H_2L	250	85.89	Endo.	220	Melting
	550-650	6	Endo.	500	Decomposition
$[\text{Cu}(\text{HL})\text{Cl}]\text{H}_2\text{O}$	50-150	5	Exo.	50-150	Dehydration
	150-330	46.28	Endo.	246	Melting
	400-650	20.47	Exo.	550	Decomposition
			Exo.	600	Decomposition
$[\text{Co}(\text{HL})\text{Cl}]\text{H}_2\text{O}$	50-150	5	Exo.	120	Dehydration
			Endo.	230.76	
	150-330	61.32	Exo.	260	
			Endo.	320	Decomposition
400-660	18.78	Exo.	400	Decomposition	
		Exo.	600	Decomposition	
$[\text{Zn}(\text{H}_2\text{L})\text{Cl}_2.\text{H}_2\text{O}]$	150-250	4.5	Exo.	150-200	Loss of one coordinated water
	250-300	19	Endo.	255	Loss of chlorine
			Exo.	340	Decomposition
400-550	10	Exo.	650	Decomposition	

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