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Preparation and Investigation of some Transition Metal Complexes with α,α-Diphenyl-α-Hydroxy Thiourea

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Abstract

In this research a new complexes have been prepared with some first transition elements, which have ageneral formula $[M(L_1)_2X_2]$ (where M = Manganese (II), iron(II) cobalt(II) nickel(II) copper (II) and zinc (II). L_1 = α,α-Diphenyl-α-hydroxy thiourea X = Cl^-, NO_3^-) Two types of metal salts were used (chloride and nitrate) for preparation,The complexes have been characterized by metal analysis (metal 100%) molar conductance measurements, magnetic susceptibility measurements, IR, electronic spectral studies.

Keywords: α,α-Diphenyl-α-hydroxy acetic acid, thiourea, transition metal.

الخلاصة

تم في هذا البحث تحضير معقدات جديدة لبعض عناصر السلسلة الانتقالية الاولى والتي تمتلك الصيغة العامة $[M(L_1)_2X_2]$ (حيث M = حديد(II) ، منغنيز(II) ، خارصين (II) ، نحاس (II) ، نيكل (II) و كوبلت (II) ، L = α،α- ثنائي فنيل-α- ثايويوريا هيدروكسي X= Cl^- ، NO^-_3) استخدم نوعان من املاح العناصر الانتقالية في التحضير (الكلوريدات والنترات) وكل هذه المعقدات شخصت بالتحليل الدقيق للعناصر وقياسات التوصيلية الكهربائية والقياسات المغناطيسية وقياسات الاشعة تحت الحمراء والطيف الالكتروني ، وتم التوصل إلى الشكل الفراغي المتوقع لهذه المعقدات والذي هو ثماني السطوح.

Introduction

The chemistry of thiourea and its derivative (amide ligands) has received considerable attention in view of their variable bonding modes. promising biological applications, structural diversity and ion-sensing ability(1,2,3,4).

They have been used as drugs possessing a wide variety of biological activities against bacteria, fungi and certain type of tumors and they have been a useful models for bioinorganic processes(5,6).

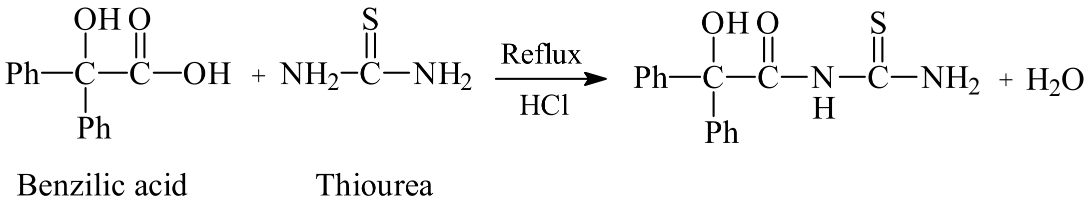
These types of ligands have been highly interested due to the presence of several potential donor atoms, their flexibility and their ability to coordinate in either the natural or deprotonated forms(7,8,9).

In view of the above applications the present work included the synthesis and spectroscopic studies of several transition metals complexes with (α,α-Diphenyl-α-hydroxy thiourea) Scheme.1.

Experimental

The ligand L_1 has been synthesized according to the following procedure[(10)].

A hot ethanolic solution (20ml) of benzilic acid (1.40g,0.05 mol) was mixed slowly with stirring with a hot ethanolic solution (20 ml) of thiourea (3.80 g, 0.05 mol). The mixture has been refluxed at ~ 80°C for 7hrs. in presence of 2ml of concentrated hydrochloric acid, on cooling a pale yellow precipitate was formed which has been filtered off, washed with cold EtOH and dried under vacuum (Scheme.1). Some of it's physical properties were listed in table 1.



$$Ph-C(OH)(Ph)-C(=O)-OH + NH_2-C(=S)-NH_2 \xrightarrow[HCl]{Reflux} Ph-C(OH)(Ph)-C(=O)-NH-C(=S)-NH_2 + H_2O$$

Scheme1 : Preparation and structure of the ligand α,α-Diphenyl-α-hydroxy thiourea

A. Preparation of the metal complexes :

A hot ethanolic solution of the ligand L_1 (0.002 mol/20 ml) and ethanolic solution of the corresponding metal salt (0.001 mol/20 ml have been mixed together with stirring. The mixture was refluxed for 5 hrs. at ~90°C , on cooling a colored precipitate of the complexes were formed , filtered off, washed with cold EtOH and dried under vacuum.

B. Physical measurements :

Metal contents were determined using standard method (gravimetric analysis), Infrared spectra of the ligand and it's complexes ($4000-400 cm^{-1}$)were recorded on a Perkin-Elmer 580B spectrophotometer , as KBr discs. Electronic spectra of the ligand and it's complexes have been recorded with Shimadzu UV / vis ,recording UV/160 spectrophotometer at room temperature. using 10^{-3} M in DMSO. Magnetic measurements were carried out at 25°C by Faraday method using a Bruker BM6 instrument. Conductivities were measured using a conductivity meter mode. PCM3-Jeuway, for 10^{-3} M using DMSO at 25°C.

Result and Discussion

All the complexes were air stable solids and the molar conductance values in DMSO, indicated non electrolytic nature(2.56-8.26) $cm^2\ ohm^{-1}\ mol^{-1}$. of all the complexes table (1) The data of metal analysis were listed in table (1).

The most important infrared spectral bands of the ligand and it's complexes are listed in the table (2) .The IR spectra of ligand showed bands at 3256 cm^{-1} assigned to [ν(N-H)] this band shifted to lower frequency on complexation also there is four band appear in the spectrum of the ligand assigned to amid I [ν(C-O)] , amid II [ν(C-N)+ δ (N-H)] and III [δ(N-H)] attributed to the amine of the thiourea , the band II and III shifted to the lower side suggest and that the coordination through the nitrogen of NH group further supported by the appearance of a medium band intensity in the range of 429-455 cm^{-1},which was attributed to [ν(M-N)].

IR spectra of nitrate complex showed bands in the range 1420-1434 , 1300-1332 and 1006-1029 cm^{-1} attributed to asymmetric , symmetric stretching and N-O bending respectivlly suggesting that the two nitrate groups have been coordinated to the metal (17) Scheme (2) Table (2).

The ν C= S and ν C=O for ligand appear at 989 cm $^{-1}$ and 1710 cm $^{-1}$ respectively and did not change on complexation .This will be further support that it happens on the nitrogen only Scheme (2).

The shifting to lower frequency of (ν NH) as well as no change in (νOH) (νC=O) and (νC=S) bands on complexation assist the proposed stricture shown in Scheme(2)

Manganese(II) complexes :

The magnetic moment measurement at room temperature 5.94 BM of manganese(II) complexes which have been in according with those having octahedral high spin structure (11,12). The electronic spectra exhibit band at 37037-43201 cm^{-1}, which may be due to the charge transfer .

Iron(II) complexes :

The magnetic moment values at room temperature 4.60-4.64 BM of Fe (II) complexes were well according with those having octahedral structure(16) .

The electronic spectra for the two Iron complexes showed a band at 13803, 14925 cm^{-1}, which attributed to the ($^{5}T_{2}g \rightarrow {}^{5}Eg$) transition and could be assigned to a distorted octahedral structure. The conductivity values of those two complexes were in according with their tentative structure(16,17) .

Co(II) complexes :

The magnetic moment values of the two cobalt(II) complexes were 4.83, 4.86 BM corresponding to three unpaired electrons Table 3.

The electronic spectra of the complexes showed an absorption in the (1)10141,10676, (2) 16235,18181, and (3)23696, 23809 cm^{-1} respectively .These bands may be assigned to the transition $^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(F)(\nu_1)$,$^{4}T_{1}g \rightarrow {}^{4}A_{2}g\ (\nu_2)$ and $^{4}T_{1}g(F) \rightarrow {}^{4}T_{1}g(P)(\nu_3)$, respectively(17). The fourth band may be due to charge transfer. The position of electronic spectral bands indicated that these complexes have octahedral geometry (10,11,13) The ligand field parameter B and the ligand field splitting energy (10Dq)in case of Co(II) complexes have been calculated , the values of(B, β,ν_2/ν_1) suggested octahedral geometry for all the complexes (15) Scheme.(2).

Nickel(II) complexes :

The Ni(II) complexes showed a magnetic moments of 2.93, 3.0 BM at room temperature, indicating a high-spin configuration and showed the presence of an octahedral environment around Ni(II) ion in the complexes(10).

The electronic spectrum of the complexes showed three bands at(1)9960,10080,(2) 14925, 15015, and (3) 25641, 27855 cm^{-1} correspond to $^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)(\nu_1)$,$^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)(\nu_2)$ and $^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)(\nu_3)$ respectively, indicating that the complexes had octahedral geometry The ligand field parameter B and the ligand field splitting energy (10Dq) have been calculated which indicat the distance of the electronic cloud form the metal ion in the complexes , the type of the ligand affect directly this value , the values of (B, β,ν_2 /ν_1)

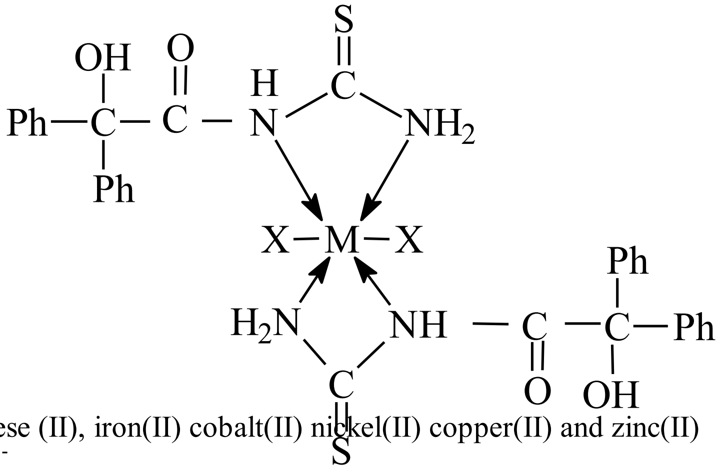
suggested octahedral geometry for all the complexes (15) Scheme.(2).

Copper(II) complexes :

The magnetic moment of the two Cu(II) complexes at room temperature 1.88, 1.91 BM corresponding to one unpaired electron.

Electronic spectra of copper(II) complexes (1) 10183,11709(2) (14877,14925) assigned to the $^2E_{2}g \rightarrow {}^2T_{2}g$ transitions in distorted octahedral structure around the Cu(II) ion(11) Scheme.(2).

On the basis of the above results the following structures of metal(II) complexes have been suggested as in Scheme.(2)



M = Manganese (II), iron(II) cobalt(II) nickel(II) copper(II) and zinc(II)
X = Cl^- , NO_3^-

Scheme2 : structure of the complexes

Scheme (2) showed the suggested structure of all the complexes , the coordination through the nitrogen in according with complexes coordinated in the same way (18)

Table 1 : Some physical properties and metal contents of the complexes

No.	Compound	Colour	M.weight	M.P (^{o}C)	Yield %	Molar conductance cm^{2}ohm^{-1}mol^{-1}	Salts	weight	Metal analysis found (calculated) %
1	Ligand	Pale yellow	302	166-168	65	---	----	0.604	------
2	$Mn(L)_2Cl_2$	Dark Yellow	729.9	170-174	60	5	$MnCl_2$. $4H_2O$	0.198	7.67 (7.86)
3	$Fe(L)_2Cl_2$	Black	730.8	198-200	55	6	$FeCl_2$. $6H_2O$	0.234	7.79 (7.98)
4	$Co(L)_2Cl_2$	Gray	733.9	225-227	65	8	$CoCl_2$. $6H_2O$	0.238	8.21 (8.39)
5	$Ni(L)_2Cl_2$	Pale green	733.7	298	42	12	$NiCl_2$. $6H_2O$	0.237	8.25 (8.36)
6	$Cu(L)_2Cl_2$	Brown	738.5	215-217	64	14	$CuCl_2$. $2H_2O$	0.170	9.01 (8.98)
7	$Zn(L)_2Cl_2$	yellow	740.3	198-200	38	5	$ZnCl_2$. $6H_2O$	0.244	8.99 (9.21)
8	$Fe(L)_2(NO_3)_2$	Dark gray	783.8	297*	52	7	$Fe(NO_3)_3$. H_2O	0.259	7.31 (7.42)
9	$Co(L)_2(NO_3)_2$	Brown	786.9	212-214	70	15	$Co(NO_3)_2$. $6H_2O$	0.291	7.69 (7.80)
10	$Ni(L)_2(NO_3)_2$	Gray	786.7	297*	46	13	$Ni(NO_3)_2$. $6H_2O$	0.290	7.65 (7.77)
11	$Cu(L)_2(NO_3)_2$	Brown	791.5	183-185	60	9	$Cu(NO_3)_2$. $6H_2O$	0.295	8.17 (8.36)
12	$Zn(L)_2(NO_3)_2$	White	793.3	186-188	29	10	$Zn(NO_3)_2$. $4H_2O$	0.297	8.51 (8.57)

* decomposition temperature

Table 2 : Selected I.R. bands and their assignment in cm^{-1}

No.	Compound	Amid II	Amid III	νN-H	M-N	NO_3		
						ν_a	ν_s	ν_{NO}
1	Ligand	1448	1252	3256	------			
2	$Mn(L)_2Cl_2$	1398	1168	------	439			
3	$Fe(L)_2Cl_2$	1363	1167	2924	436			
4	$Co(L)_2Cl_2$	1395	1148	3144	450			
5	$Ni(L)_2Cl_2$	1383	1165	3157	435			
6	$Cu(L)_2Cl_2$	1371	1184	3248	429			
7	$Zn(L)_2Cl_2$	------	------	------	------			
8	$Fe(L)_2(NO_3)_2$	1410	1206	------	450	1424	1312	1029
9	$Co(L)_2(NO_3)_2$	1395	1149	3164	455	1422	1304	1019
10	$Ni(L)_2(NO_3)_2$	1383	1235	3150	434	1434	1323	1015
11	$Cu(L)_2(NO_3)_2$	1371	1184	3150	429	1431	1332	1006
12	$Zn(L)_2(NO_3)_2$	1384	1202	3172	455	1420	1300	1025

ν_a : asymmetric stretching
ν_s : symmetric stretching
ν_{NO} : N-O group bending

Table 3 : Magnetic moment and electronic spectral data of the complexes

No.	Compound	μeff BM 25 °C	λ max cm^{-1}	10Dq cm^{-1}	ν_2/ν_1	B cm^{-1}	$\beta = \frac{B}{B^0}$	C.F.S.E cm^{-1}
1	Ligand		24271,34246					
2	$Mn(L)_2Cl_2$	5.94	37037-43201					
3	$Fe(L)_2Cl_2$	4.64	14925,26200, 31550					
4	$Co(L)_2Cl_2$	4.86	10141,16235, 23809 , 30864	10141	1.79	771	0.79	8112.8
5	$Ni(L)_2Cl_2$	3.0	9960 , 15015 , 25641, 34013	9960	1.5	964.99	0.9	11952
6	$Cu(L)_2Cl_2$	1.91	10183,14877, 35971					
7	$Zn(L)_2Cl_2$	------	-------------					
8	$Fe(L)_2(NO_3)_2$	4.60	13803 , 25641 , 31446					
9	$Co(L)_2(NO_3)_2$	4.83	10674,18181 , 23696 , 31055	8555	2.13	972	1.0	6844
10	$Ni(L)_2(NO_3)_2$	2.93	10080 , 14925, 27855, 36764	10080	1.64	1008	0.97	12096
11	$Cu(L)_2(NO_3)_2$	1.88	11709 , 14925, 35714					
12	$Zn(L)_2(NO_3)_2$	------	----------------					

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