Preparation, Characterization and Structural Studies of Some Phenyl Isothiocynate Metal Complexes

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Abstract

Phenyl isothiocynate complexes of Cu (I), Cu(II), Mn(II), Fe(II), Fe (III), Cr(III) and Ce(III) have been prepared and analyzed spectroscopicaly by Elemental analyses and atomic absorption technique; the magnetic susceptibility and the conductivity have also been measured and molar ratio of Ligand: Matale with mole ratio method and Job Method. From these measurement it is concluded that Cu(I), Fe(III) and Mn(II) form tetrahedral complexes, while Cu (II) Forms square planner complexes, and Cr (III) and Ce(III) forms octahedral complexes.

Keywords: complexes of metal ions, Phenyl isothiocynate

تحضير وتشخيص ودراسة تركيبية لبعض المعقدات الفلزية لفنيل أيزوثيوسيانات

الخلاصة

لقد حضرت معقدات النحاس(I) والنحاس(II) والمنغنيز(II) والحديد(II) والحديد(III) والكروم(III) والسيريوم(III) مع ايزوثايوسيانات الفنيل. وحللت كميا باستخدام تقانة الامتصاص الذري بالنسبة للايونات الفلزية وتحليل العناصر الدقيق لعناصر الكاربون والهيدروجين والنتروجين والكبريت ودرست اطياف الاشعة التحت الحمراء والفوق البنفسجية والمرئية لها كذلك درست التوصيلية الكهربائية لمحاليل 10^{-3} مولاري في مذيب الـ DMF وحسبت قيم العزوم المغناطيسية، وعينت النسبة المئوية للكلوريد بطريقة مور وكذلك حسبت النسبة المولية لليكاند مقابل الفلز بطريقة المول ريشيو وطريقة جوب.ولقد تبين من هذه القياسات ان اشكال المعقدات هي: رباعية السطوح بالنسبة لأيونات النحاس(I) والحديد(II) والمنغنز(II)، وأنها مربعة مستوية بالنسبة لأيونات النحاس(II) بينما كانت ثمانية السطوح بالنسبة لأيونات الكروم(III) والسيريم(III)

Introduction

Al though the compound was known for a long period of time, but little is known about its coordination ability with metal ions. this compound may be considered as a ligand with tow possible basic sites for coordination , one of which (sulpher atom) could be considered as pearsons soft site while the other (nitrogen atom) could be considered as pearsons hard site (1-3). For a particular ligand, the overall tendency for coordination with metal ions (acid centers) is governed basically by the nature of metal ions , In this work, the intention is drawn to verify bonding and structure of metal complexes according to Hard-Soft interaction concept, and for that reason soft metal ions like (Cu^{+1}, Fe^{+2} and Cu^{+2}) and hard metal ions like (Cr^{+3},Fe^{+3}, Ce^{+3} and Mn^{+2}) were used for complexation with this ligand A

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search through literature reveals that there is no work has been done on the transition metal complexes of the Phenyl isothiocyanate 4,5.

Experimental:

All reagents were used from Fluka and Redial –deHaen Chemical elemental analysis for carbon, hydrogen, nitrogen and sulfur elements were carried out at the micro-analytical center Cairo University, Giza, Egypt. Fourier Transfer Infrared Rays (FTIR) the spectra were recorded in range (200-4000) cm^{-1} on a Shimadzu 3800, FTIR spectrophotometer, using CsI Pellets. Electronic absorption spectra were recorded in the range (200-1100) nm on a Shimadzu 160

Spectrophotometer, in freshly prepared 10^{-3} M solutions in (DMF) at room temperature using quartz cell (1.000) cm. the metal contents of the complexes were determined using a Shimadzu A.A680G atomic absorption Spectrophotometer.

Molar conductivity measurements of the complexes at 25°C in freshly prepared 10^{-3} M solutions in DMF were determined using a PW 9526 Digital Conductivity meter. The melting points of the prepared complexes were measured using Gallen Kamp apparatus. The chlorine content was determined gravimetricall6.

Preparation of the ligand (L) 7:

Preparation of the Complex [CuL2 $(H_2O)_2]SO_4$:

A solution of the ligand (L) (0.199g, 1.48 mM) in DMF (5ml) was added to a stirred solution of $CuSO_4.5H_2O$ (0.184g, 0.74 mM) in (5ml) of DMF, The resulted mixture was heated under reflux for one hour, and then the mixture was filtered. The precipitate washed with an excess of DMF and dried. A deep yellow brown solid, which decomposes at (220 ^oC), was obtained .Yield (85%)

Preparation of complexes:

The complexes of Cu(I), Mn(II), Fe(II) and Fe(III) were also precipitated by a similar procedure in DMF medium of the ligand L (6 mM) and the metal ions (2 mM) in 3:1 ratio.The Ce(II) and Cr(III) complexes was also precipitated by a similar procedure in DMF medium of the ligand L (8 mM) and the metal ions (2mM) in 4:1 ratio (L:M).

Mole Ratio Method 8:-

The absorption spectra were measured for many mixed solutions containing (1ml) of the metal ion salt, in the optimum concentration, and variable volumes of the ligand solution in the same concentration. M: L ratio was obtained by plotting the relation between the mole ratio in the X-axis and absorbance in the Y-axis .The intercept of the two straight lines represent the M: L ratio.

Job Method 8:-

In this method, variable volumes of solutions containing same molar concentration of ligand and metal ion salt were mixed together. The total volume was kept constant. The absorbance of each solution was measured and the relation between the mole fraction of the volume (Vm/Vm+VL) on the X-axis (where Vm and Vl represent the volume of the metal and ligand respectively) was plotted against the absorbance on the Y-axis. The intercept of the two straight lines represent the M: L mole ratio.

Results and Discussion

The composition and analytical results are summarized in table (2).

The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases the results reveals (1:2) for Cu(II) complex and (1:3) for Mn(II),Fe(II),Fe(III) and Cu(I) complexes and (1:4) for Cr(III) and Ce(III) complexes (metal: ligand) ratio.

Infrared Spectra:

The important infrared spectral bands for the synthesis complexes and ligand are given in table (3).The band at υ =1408 cm-1 symmetric and 1435 cm-1 asymmetric are characteristic of the sulfur of thioketo group (C=S) was shifted to lower wave numbers (8-72 cm^{-1}) in all complexes ,which indicates the involvement of thioketo sulfur in coordination 4,9.

The IR spectra of complexes show new bands at 370-390 cm^{-1} assigned to υ (M-S) (10), the Cu (I), Fe (III) and Cr (III) complexes showed a new band at 350-351 cm-1, due to υ (M-Cl).

The Cu(II),Cr(III) and Mn(II) complexes showed a new band at 440-480 cm-1, due to υ(M-O).the presence of a broad band at 3348-3512 cm-1 in the spectra of all metal complexes are associated with coordination and / or Lattice water molecules supported from thermal analysis 9,11.

The coordinated –NO3 group in Ce complex showed two bands at 1005 cm-1 and 1302 cm-1,which may be assigned to the asymmetric and symmetric stretches υ1 and υ2 of the nitrate group . We can conclude that the NO3 group is coordinated in a unidentate manner 12.

Electronic spectra for the ligand and metal complexes:

Solution of the ligand in D.M.F as solvent gave a distinct absorption peaks in the (U.V) region (215nm) and (260nm) with a molar extinction coefficients (1920) and (2050) were assigned to the ligand filed and charge transfer ,similar results were obtained with $[CuL_3Cl]$ complex which were attributed to ligand field and charge transfer transition[13]

The electronic spectrum of $[CrL_4Cl_2]Cl$ complex exhibited the absorption peaks at (305nm) (32786 cm^{-1}) (ε_{max}=301), which were assigned to $^4A_{2g}\rightarrow{}^4T_{1g}p$ transition ,and the peaks in the visible region at (452nm) (22123 cm^{-1})(ε_{max}=323) and at (631nm) (15847 cm^{-1}) (ε_{max}=318) were attributed to the d─d transition of the type $^4A_{2g}\rightarrow{}^4T_{1g}F$ and $^4A_{2g}\rightarrow{}^4T_{2g}F$ respectively indicating an octahedral structure about Cr^{+3}.This result is in agreement with that reported previously about the electronic spectra of six coordinated chromium(III) complexes [13].

The complex $[MnL_3(H_2O)]Cl_2$ showed two distinct peaks at (301nm) (33222cm^{-1}) (ε_{max}=745) and at (760nm)(13157 cm^{-1}) (ε_{max}=52) the first peak was attributed to ligand filed transition of the type ($\pi\rightarrow\pi^*$) while the second peak was attribute to the (d─d) transition of the type ($^6A_1\rightarrow{}^4A_1$).

The complex $[CuL_2(H_2O)]SO_4$ showed peaks at (300nm) (33333 cm^{-1}) (ε_{max}=537)and at (706nm) (14164 cm^{-1})(ε_{max}=28).The first peak was attributed to ligand field transition ($\pi \rightarrow \pi^*$) while the second peak was attribute to the($^2B_{1g} \leftarrow {}^2A_{1g}$) and ($^1B_{1g} \leftarrow {}^2E_g$) transition [14]. $[FeL_3Cl]2Cl$ and $[FeL_3Cl]$ Cl complexes ,The showed complexes of Fe(II) and Fe(III) two bands at (363 nm,27548Cm^{-1}, ε_{max}=2484) and (363 nm ,27548 cm^{-1}, ε_{max}=2484) which belongs to charge transfer and another bands at (455 nm ,21978 cm^{-1}, ε_{max}=178) and (580 nm ,17241 cm^{-1}, ε_{max}=785) respectively which are caused by the electronic transition $^6A_1g \rightarrow {}^4T_1g$ (G) and $^5E(D) \rightarrow {}^5T_2(D)$ respectively [13] .the cerium (III) complex show a new absorption band at (363 nm ,27548 cm^{-1}, ε_{max}=2484) which may be related to metal ligand charge transfer excitations.

The assignment of characteristic bands of ligand and metal complexes are summarized in table (4).

Molar conductivity

The conductances of solutions of the complexes in DMF (10^{-3} mol dm^{-3}) are shown in Table 4. Complexes Fe (II), Cr (III) and Ce (III) are 1:1 electrolytes and Complexes Fe (III) and Mn (II) are 1:2 electrolytes [15], [16], while the other complexes are nonelectrolytes.

Magnetic moment measurements

Magnetic moment has been determined in the solid state by Faradays, method. The magnetic properties of these complexes should provide a testing ground for the oxidation state of the complexes, therefore provide a way of counting the number of unpaired electrons which help in predicting the bonding model and electronic structure17.The effective magnetic moments in Born Magnetos were calculate and were given in Table (4).

Conclusions:

From data of conductivity, UV─Visible and Magnetic moments measurements in table (4). The structures of Phenyl isothiocyanate complexes with Cu(I), Fe(III) and Mn(II) Form tetrahedral complexes, but Cu (II)Forms square planner complexes, and Cr (III) and Ce(III) forms octahedral complexes respectively. More over FT-IR measurements indicate bonding of metal ions with the ligand through sulpher atom, this situation needs to be more clarified by performing X─ ray diffraction studies in order to find the actual sites of bonding to the metal ions in these complexes.

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Table (1) some physical properties of the complexes and their reactants quantities

Empirical Formula	colour	m.p °C	Yield %
L			
$[CuL_2(H_2O)_2]SO_4$	Gray	220	85
$[CuL_3Cl]$	Leaden	320	80
$[FeL_3Cl]Cl_2$	Orange	183	70
$[FeL_3Cl]Cl$	Dark green	245(d*)	78
$[MnL_3(H_2O)]Cl_2$	Gray	210	82
$[CrL_4Cl_2]Cl$	Green	288(d*)	81
$[CeL_4(NO_3)_2]NO_3$	Brown	295(d*)	69

Table (2) Results of elemental analyses

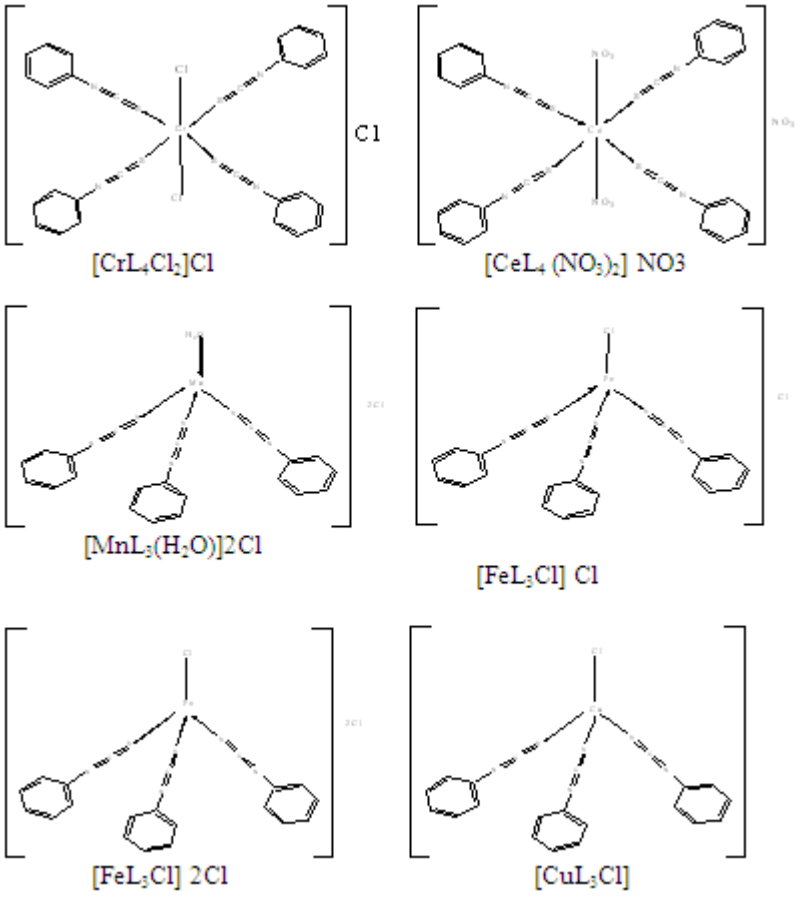
Mol. Formula Mol. Weight	M% Calcd M% Expt	C% Calcd C% Expt	H% Calcd H% Expt	N% Calcd N% Expt	S% Calcd S% Expt	Cl% Calcd Cl% Expt
(C_7H_5NS) L=135	-	62.22	3.7	10.37	23.27	-
	-	61.01	4.21	10.12	22.7	-
$[CuL_2(H_2O)_2]SO_4$ =465.54	13.64	36.08	3.0	6.01	20.62	-
	14.21	35.53	3.78	7.95	21.95	-
$[CuL_3Cl]$ =504.04	12.6	49.99	2.97	8.33	19.04	7.04
	13.26	50.52	3.65	9.65	19.38	7.62
$[FeL_3Cl]2Cl$ =566.34	9.85	44.49	2.64	7.41	16.63	18.62
	9.75	43.79	3.48	7.84	15.95	17.48
$[FeL_3Cl]$ Cl =530.84	10.51	47.47	2.82	7.91	18.08	13.18
	10.37	47.41	3.82	8.78	17.62	13.69
$[MnL_3(H_2O)]2Cl$ =547.93	10.02	45.99	3.1	7.66	17.52	12.77
	11.63	46.81	4.06	7.08	18.59	13.83
$[CrL_4Cl_2]Cl$ =697.49	7.45	48.17	2.86	8.02	18.35	15.12
	8.74	49.63	3.09	7.84	17.06	15.54
$[CeL_4(NO_3)_2]NO_3$ =770.11	18.19	43.63	2.59	12.72	16.62	-
	19.74	44.29	2.08	11.37	15.73	-

Table (3) F.T.I.R for the ligand and metal complexes

Mol Formula Mol. Weight	υ C=S sym and asym	υ C=N	υ M-S	υ M-O	υ M-Cl	Other bands
(C_7H_5NS) L=135	1408 1435	1658	-	-	-	
$[CuL_2(H_2O)_2]SO_4$ =465.54	1384	1651	390	440	-	3348-3512(H_2O)
$[CuL_3Cl]$ =504.04	1384	1620	380	-	350	
$[FeL_3Cl]2Cl$ =566.34	1400	1620	383	-	351	
$[FeL_3Cl]$ Cl =530.84	1401	1623	373	-	355	
$[MnL_3(H_2O)]2Cl$ =547.93	1404	1616	370	442	-	3348-3512 (H_2O)
$[CrL_4Cl_2]Cl$ =697.49	1337	1643	391	-	350	
$[CeL_4(NO_3)_2]NO_3$ =770.11	1355	1655	390	453	-	1005 – 1302 NO_3

Table (4) UV–Vsible spectra, Molar conductivity in 10^{-3} DMF and Magnetic moments of ligand and metal complexes

Compound	λ_{max}	υ cm^{-1}	ABS	ε= $mole^{-1}$ cm^{-1}	Bands Assignments	Λm (Ω^{-1} cm^2 mol^{-1})	M (B.M)	Sugg Strucur e
C_6H_5NCS= (L)	215 260	46511 38461	1.92 2.05	1920 2050	n →π* charge transfer	-	-	-
$[CuL_2$ $(H_2O)_2]$ SO_4	300 706	33333 14164	0.537 0.028	537 28	π→π* $^2B_1g \rightarrow {}^2A_1g$, $^1B_1g \rightarrow {}^2Eg$	76	1.70	Sq.pl
$[CuL_3Cl]$	217 220	46082 15454	1.443 1.422	1443 1422	n →π* charge transfer	21	Dia	T.h
$[FeL_3Cl]$ 2Cl	363 580	27548 17241	2.484 0.785	2484 785	Charge transfer $^6A_1g \rightarrow {}^4T_1g$ (G)	145	5.40	T.h
$[FeL_3Cl]$ Cl	363 455	27548 21978	2.484 0.178	2484 178	Charge transfer $^5E(D) \rightarrow {}^5T_2(D$	78	5.40	T.h
$[MnL_3$ $(H_2O)]$ 2Cl	301 760	33222 13157	0.745 0.052	745 52	π→π* $^6A_1 \rightarrow {}^4A_1$	158	5.57	T.h
$[CrL_4Cl_2]$ Cl	305 452 631	32786 22123 15847	0.301 0.323 0.318	301 323 318	$^4A_2g \rightarrow {}^4T_1g$ (P) $^4A_2g \rightarrow {}^4T_1g$ (F) $^4A_2g \rightarrow {}^4T_2g$ (F)	77	3.9	O. h
$[CeL_4$ $(NO_3)_2]$ NO_3	300 363	33333 27548	1.443 2.484	1433 2484	n →π* Charge transfer	83	2.34	O. h



Suggested Structures Of The Ligand Complexes