Synthesis and characterization of new thiourea complexes

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Abstract

Four Complexes of thiourea derivative (4-methoxy- N-(phenylcarbamothioyl) benzamide) have been prepared by the reaction of 4-methoxybenzoyl isothiocyanate with aniline,then the ligand obtained reacted with (Mn^{II},Co^{II},Cu^{II},Ni^{II}) the resulting complexes were characterized by elemental analysis , FTIR , UV-Vis spectra and melting point. General formula that obtained is [L_2MCl_2] for all complexes with octahedral geometry, where(L)=(4-methoxy-N(phenylcarbamothioyl)benza-mide) and M= (Mn^{II},Co^{II},Cu^{II},Ni^{II}) .

Introduction

Compounds containing carbonyl and thiocarbonyl groups occupy an important position among organic reagents as potential donor ligands for transition metal ions [1-7]. Among these thiourea derivatives are potentially very versatile ligands, able to coordinate to a range of metal centers as neutral ligands, monoanions or dianions [1-12]. The oxygen, nitrogen and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities. Both the ligands and their metal complexes display a wide range of biological activity including antibacterial, antifungal, antitubercular, antithroid, antihelmintic, rodenticidal, insecticidal, herbicidal, and plant-growth regulator properties [13-17].

Thiourea, CSN2H4 is basically occurs in two tautomeric forms and has three functional groups which are very important for the structural modifications to synthesize new derivatives. Thiourea and its derivatives display a broad spectrum of applications in industries, chemistry, medicine and others. In these present years, a lot of thiourea derivatives have been synthesized and their antimicrobial properties were widely explored [1-5].

Industrial production and the use of Fe, Co, Cu, Ni, Zn, Cd, and Pb elements can cause environmental pollution. On the other hand, some of these metals are present in trace amounts as essential elements for biological systems and these metal ions also play an important role in bioinorganic chemistry. In order to understand the role of these metal ions in biological systems, structural studies of the biological compounds and their metal complexes are extremely important[17-24].

Experimental part

1- Materials

All chemical used were of reagent grade (supplied by Either Merck or Fluka) and used as supplied. The FTIR spectra in the range (4000–200) cm-1were recorded as cesium iodide disc on FTIR 8300 Shimadzu Spectrophotometer. The UV-Visible spectra were measured by using Shimadzu UV-Vis. 160 A spectrophotometer in the range (200 - 1000) nm. Elemental microanalysis was carried out using CHNOS elemental analyzer model 5500 Carlo-Erba instruments. Gallen Kamp M.F.B.600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds.

2- Synthesis of ligand

Solution of 4-methoxy benzoyl chloride (0.005 mole) in absolute ethanol (25 mL) was added dropwise to potassium thiocyanate (0.005 mole) in absolute ethanol (25 mL). The reaction mixture was heated (50 °C) under reflux for 1 h , and then cooled to room temperature then (0.005 mole) of aniline in 20ml absolute ethanol was added and the resulting mixture was stirred for 2 h. The solid product was washed with water and purified by washing with ethanol absolute [1,8].

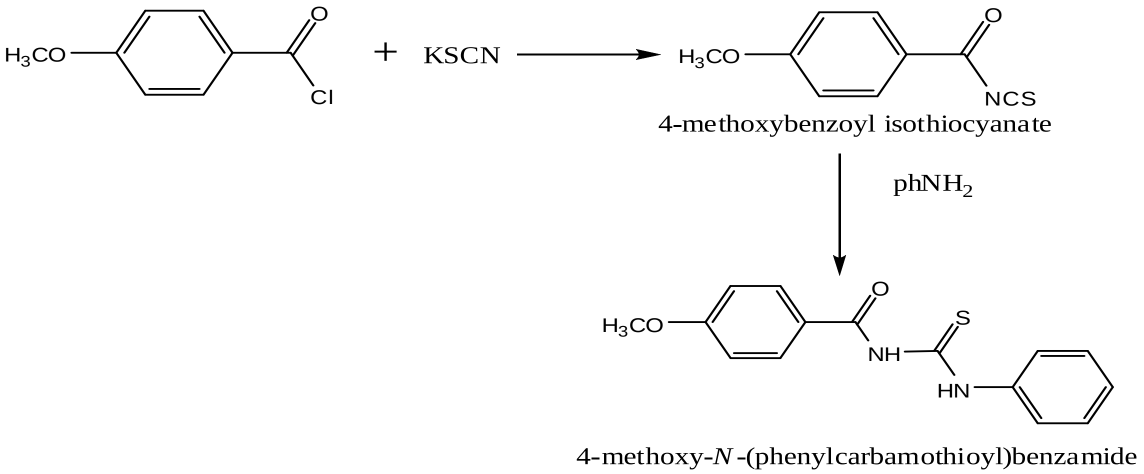
3- Synthesis of complexes

A solution of the metallic chlorides (0.01mole) in ethanol (30 mL) was added dropwise to a solution of the ligand in a 1:2 ratio for all metal with a small excess of ligand in ethanol (30 mL) at room temperature and the resulting mixture was refluxed for 2 hr. The solid complexes were filtered and washed with ethanol [1,8].

Results and discussion

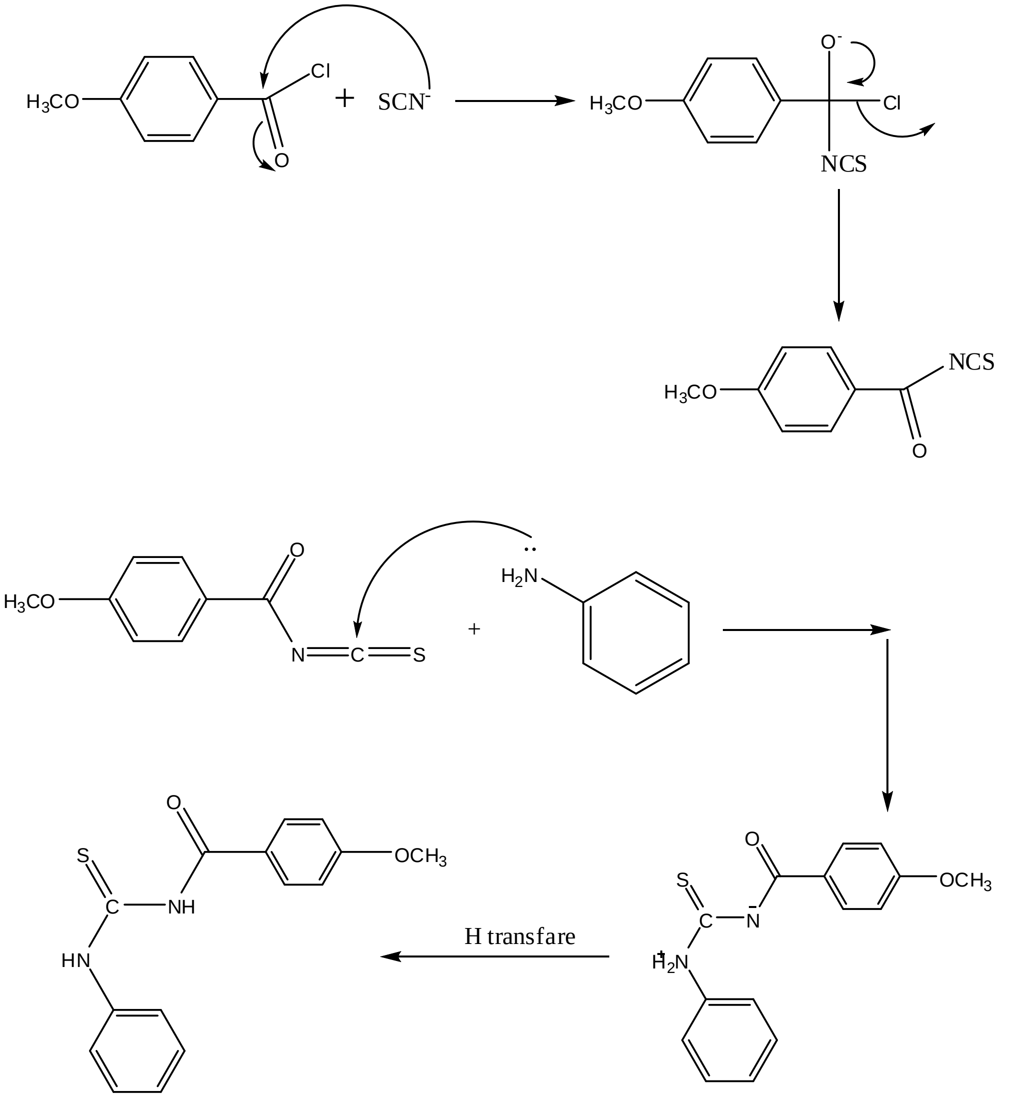
1- Synthesis of ligand (L)

The syntheses (Scheme 1) involve the reaction of a 4-methoxybenzoyl chloride with potassium thiocyanate in absolute thanol, followed by condensation of the resulting 4-methoxybenzoyl isothiocyanate with aniline The ligands were purified by washing with absolute ethanol .



Scheme 1

The steps of synthesis could be predicted in the following mechanisms



2. **Synthesis of complexes**

The complexes were synthesized by the reaction of the ligand with the metal ions in 1:2 molar ratios in ethanolic medium. The ligand behaves as bidentate coordinate through oxygen and sulpher donor atoms.

The analytical data of these complexes are presented in Table 1. All the complexes are stable and can be stored at room temperature.

Table 1. Physical data of complexes.

No.	**Complexes**	**Color**	**M.P. °C**	**Yield (%)**	**M:L**
1	CoL_2Cl_2	Dark brown	154	82	1:2
2	NiL_2Cl_2	Green	132	74	1:2
3	CuL_2Cl_2	Green	250dec.	65	1:2
4	MnL_2Cl_2	Light yellow	260dec.	68	1:2

Infrared spectra of ligand [25]

The infrared of the ligand show the appearance of 3140 cm $^{-1}$ of N-H and disappearance of NH_2 double band of the primary amine and show disappear of C=N at 1600cm^{-1} of the isothiocyanate derivative and shifting of C=O band from 1650 cm^{-1} to 1610cm^{-1} because of formation of amide group (NH-C=O) . The ligand also showed shifting of C=S from 1320cm^{-1} to 1230cm^{-1} because of formation of thiourea derivative (NH-C=S) . and showed S-H band from the totumaresim of thiourea (NH-C=S N=C-SH) ⟷

S-H shown at 2644cm-1 C=N show at 1553cm-1 .

Infrared spectra of complexes [25]

Complexes spectra showed distinct deference comparing with the spectrum of the ligand. They showed shifting of C=S from 1230 cm-1 to 1124cm-1 because of the coordination bond formed between S and metal (S-M) and shifting of C=O from 1610 to 1580 cm^{-1} because of the formation of coordination bond between O and metal (O-M) .

the presence of M-S & M-O where confirmed the IR by the presence these bands between(546-522) cm^{-1} and (462-410) cm^{-1} respectively

Table 2. Infrared date of the ligand and complexes

		N-H	C=N	C=S	C=O	S-H	M-S	M-O
1	Ligand	3140	1553	1230	1610	2644		
2	CuL_2Cl_2	3090	---	1129	1605	---	426	529
3	$Mn\ L_2Cl_2$	3110	---	1197	1598	---	446	522
4	$Ni\ L_2Cl_2$	3125	---	1218	1586	---	410	537
5	$Co\ L_2Cl_2$	3108	---	1145	1580	---	426	546

CHN analysis of ligand

The C, H, N and M contents (both theoretically calculated values and actual values) are in accordance with the formula ML_2Cl_2 indicating that the ligand is neutral. This can be explained by the absence of any deprotonating agent during the synthesis. The complexes are generally soluble in common organic solvents.

Table 3. Chemical analysis data of the complexes.

		Elemental analysis							
No.	**Complexes**	**Theoretically calculated values**				**Actual calculated values**			
		C%	H%	N%	M%	C%	H%	N%	M%
1	Ligand	62.92	4.93	9.78		62.52	4.08	9.43	
2	CuL_2Cl_2	51.10	3.72	7.95	9.01	50.12	3.00	7.52	8.99
3	Mn L_2Cl_2	51.73	3.76	8.04	7.89	50.92	2.98	8.00	7.92
4	Ni L_2Cl_2	51.45	3.74	8.00	8.38	50.33	3.42	7.83	8.22
5	Co L_2Cl_2	51.44	3.74	8.00	8.41	51.01	3.60	7.74	8.02

Electronic spectra of ligand

the ligand exhibited absorption band in UV region at wave number (32245)cm^{-1} which maybe attributed to($\pi \rightarrow \pi^{*}$) transition another band of low intensity appears at (27723) cm-1 maybe refer to ($n \rightarrow \pi^{*}$) [26].

Electronic spectra of complexes

The ultraviolet spectrum of the synthesized cupper complex showed two absorption bands, the position of the first band at 312 nm(31644cm^{-1})which represents the charge transfer while the position of the second band appeared at 608nm (17173cm^{-1}) which represents the ($^{2}Eg \rightarrow {}^{2}T_{2g}$) transition.

The spectrum of synthesized Mn(II) complex showed an absorption band at 310nm(31644cm^{-1}) related to the charge transfer and anther absorption band was observed in the visible region 830nm(12165cm^{-1}) which was assigned to ($^{6}A_{1g} \rightarrow {}^{4}T_{2g}$).

The Co(II) complex exhibits three electronic transitions (328nm (33056cm^{-1}), 668nm(14660cm^{-1}),796nm(12916cm^{-1})) which represents the charge transfer and ($^{4}T_{1g} \rightarrow A_{2g}$) and ($^{4}T_{1g} \rightarrow {}^{4}T_{2g}$)respectively[26]. In the case of Ni(II) complex, the three observed absorptions (316nm(32462cm^{-1}), 462nm(19241cm^{-1}), 810nm(13143cm^{-1})) can be attributed to the transitions, charge transfer and $^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ and $^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ respectively[26], table 4. All evidence from electronic spectra refer to octahedral geometry and suggested structural formula of the complexes in Fig1.

Table 4.Electronic spectra of the ligand and its complexes

Complexes	λ nm	Wave number cm^{-1}	Transition type
Ligand	322 385	32245 27723	$\pi \rightarrow \pi^{*}$ $n \rightarrow \pi^{*}$
CuL_2Cl_2	312 608	31644 17173	C.T $^{2}Eg \rightarrow {}^{2}T_{2g}$

Mn L_2Cl_2	310 830	33543 12165	C.T $^6A_{1g} \longrightarrow {}^4T_{2g}$
Ni L_2Cl_2	316 462 810	32462 19241 13143	C.T $^3A_{2g} \longrightarrow {}^3T_{1g}$ $^3A_{2g} \longrightarrow {}^3T_{2g}$
Co L_2Cl_2	328 668 796	33056 14660 12916	C.T $^4T_{1g} \longrightarrow A_{2g}$ $^4T_{1g} \longrightarrow {}^4T_{2g}$

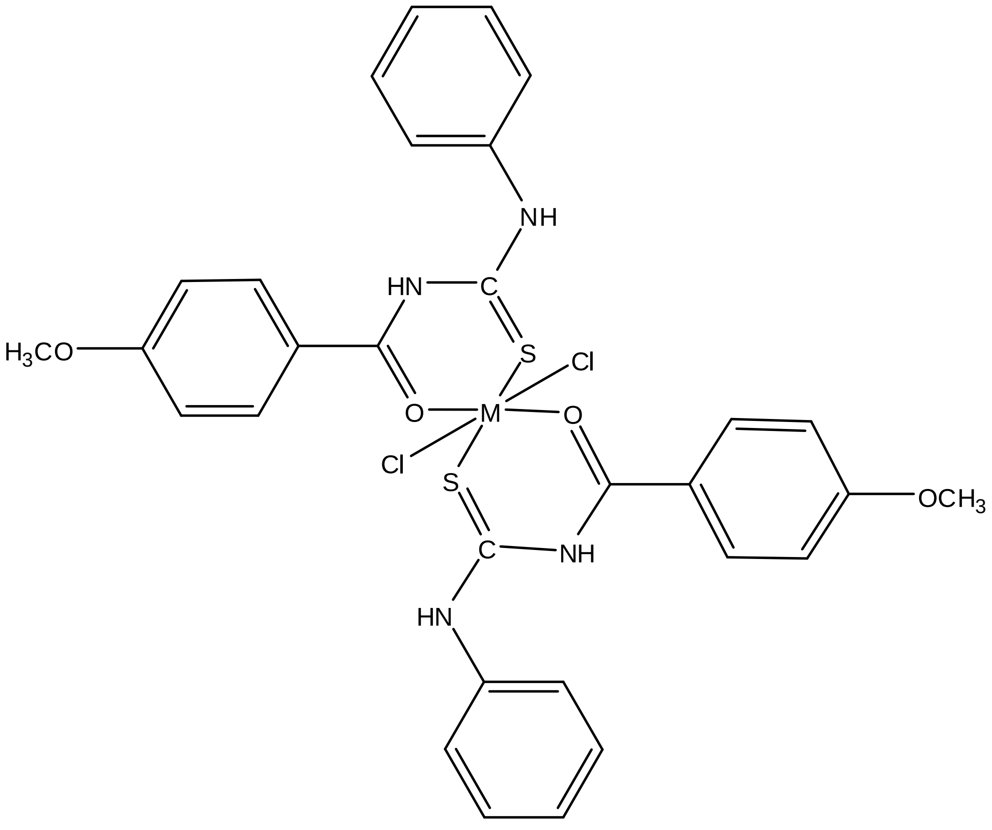


Figure 1. Proposed structure for the complexes

Conclusions

it may be concluded that ligand coordinate through one of the sulfer atom and oxygen. In the present investigations, all the complexes are found to be mononuclear, based on the FT-IR spectral data. The coordination number six is attained by coordination with the two bidentate ligand molecules and to two chloride atoms. Based on the physicochemical and the spectral studies the tentative structures proposed for the complexes are shown in Figure 1.

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الخلاصة

من تفاعل (4-methoxy-N- (phenylcarbamothioyl)benzamide) تم تحضير الليكند ثم تفاعل الليكند المحضر مع الايونات 4-methoxybenzoyl isothiocyanate مع aniline لينتج أربعة معقدات ، شخصت هذه المعقدات (Mn^{II},Co^{II},Cu^{II},Ni^{II}) المحضرة باستخدام مطيافية الاشعه تحت الحمراء ومطيافية الاشعة فوق البنفسجية والمرئية وتحليل العناصر ودرجة الانصهار.وتبين ان هذه المعقدات تأخذ الصيغة وذات شكل ثماني السطوح .