

Synthesis and characterization of some Co(II), Ni(II) and Cu(II) complexes with 2,3-di(thiobutane) aniline

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Abstract

The new cobalt (II), nickel (II) and copper (II) complexes with 2,3-di(thiobutane) aniline in the coordination sphere were prepared. All the complexes were characterized by IR, UV-vis. Spectroscopy, conductivity and magnetic measurements and some of them by metal content. Conductivity data in DMSO showed that some complexes are 1:2 (M:L) electrolytes which assigning the formula $[M(L)_3]Cl_2$ while the other complexes are non-electrolyte which assigning the formulas $[M(L)Cl_2]$ and $[M(L)_2Cl_2]$. Electronic spectral data and magnetic measurements showed that some of the complexes have octahedral geometry while the other complexes have tetrahedral geometry.

Introduction

In recent years, there has been intensive activity involving the synthesis and evaluation of the biological activities of nitrogen and sulfur containing substituted mercapto compounds and their metal complexes [1-3]. The monosulfides ($n=1$) R_4tms , perhaps because they take the wide breadth of applications known for the disulfides in agriculture and experimental medicine have been much less extensively studied, and where such studies deal with the subject of interaction of monosulfides with metal species, the field remains virtually unexplored [4].

Buttrus *et al.* [5,6] reported the preparation of multinuclear complexes of general formula $[Se(Spy)_4(MCl_2)]$ and $[Se(Spy)_4(MCl_2)_4]$, where $Spy =$ pyridinthiolate, $M = Co(II), Ni(II), Cu(II), Pd(II)$ and $Pt(II)$ and their physico-chemical characterization.

Al-Ramadane [7] reported the preparation of mono-nuclear complexes of general formula $[M(L)Cl_2]$, $[M(L)_2Cl_2]$, $[M(L)_2(en)]Cl_2$ and $[M(L)_2(pph_3)_2]Cl_2$ were $L =$ bis (1,4-benzyl thio) butane, $M = Co(II), Ni(II)$ and $Cu(II)$, $en =$ ethylene diamine, $pph_3 =$ triphenyl phosphine and their physico-chemical characterization.

The aim of this work was the synthesis and physicochemical study of new cobalt (II), Nickel (II) and Copper (II) coordination complexes with 2,3-di (thiobutane) aniline.

Experimental

General

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ and the remaining reagents were products from Fluka and used as supplied. IR spectra were recorded on a Perkin-Elmer 580B spectra-photometer in the $4000-200\text{ cm}^{-1}$ rang using Nujol Mull or CsI discs. UV-vis spectra were recorded on a Shimadzu UV-vis spectrophotometer of type UV-160 for $10^{-3}M$ solution of the complexes in dimethyl sulfoxide (DMSO) at $25^\circ C$ using 1cm quartz cell.

The metal content of some of the complexes was estimated spectrophotometrically using Shimadzu AA670.

Conductivity measurements were made on $10^{-3}M$ solution of the complexes in (DMSO) solvent at $25^\circ C$ using conductivity natral model 4070 Jerway. The magnetic measurements were carried out at $25^\circ C$ on the solid state by Faradays method using Bruker BM6 instrument.

1. Preparation of the ligand 2,3-di(thio butane) aniline
Thiobutane (1.8g-0.02mol) and NaOH (0.8g-0.02mol) in ethanol (30ml) were mixed with 2,3-dichloro aniline

(3.2g-0.02mol) in ethanol (10ml). The mixture was boiled under reflux for 4h. After cooling to room temperature, NaCl was removed by filtration. The solution was reduced in volume *Ca* 15ml and on cooling to *Ca* $5^\circ C$, a precipitate was obtained the product can be recrystallized from ethanol.

2. Preparation of $[M(L)Cl_2]$, $[M(L)_2Cl_2]$ and $[M(L)_3]Cl_2$ complexes ($M = Co(II), Ni(II)$ and $Cu(II)$).

The complexes where prepared according to the following procedure. An alcoholic solution of metal salt (0.01mol) (10ml) was mixed with a solution of the ligand (0.01mol) or (0.02mol) or (0.03mol) dissolved in ethanol (10ml). The mixture was stirred with reflux for 2-3 h, to ensure completion of the reaction. The solid thus obtained was filtered off, washed with ethanol, diethyl ether and dried in vacuum for several hours.

Results and Discussion

The reaction of the ligand 2,3-di(thiobutane) aniline with metal chloride in (1:1), (2:1) and (3:1) ligand to metal molar ratio afforded the complexes of the general formula $[M(L)Cl_2]$, $[M(L)_2Cl_2]$ and $[M(L)_3]Cl_2$.

The physical properties of the complexes are tabulated in Table (1). The complexes are quite stable in air and decompose above $240^\circ C$, and they are insoluble in most organic solvent but soluble in DMSO.

The most important IR assignment of the complexes are listed in Table (2). The most important band which appeared at 710 cm^{-1} due to $\square(C-S)$ stretching in the free ligand is shifted to the lower field in the prepared complexes. This is usually indicates that the C-S groups of the ligands are involves in coordination with metal through sulphur atom [8]. Further support for the formation of the complexes is provided by the appearance of a new band within $329-421\text{ cm}^{-1}$ range characteristic of bidentate from the ligand and tentatively attributed to $\square(M-S)$ [9] $M = Co, Ni$ and Cu . Furthermore, the IR spectra of the complexes showed another band within $280-350\text{ cm}^{-1}$ range which may be due to $\square(M-Cl)$ [10].

The values of magnetic moment of Co(II) complex (No. 1) is (4.02)B.M. The electronic spectrum (Table 2) of Co(II) complex shows bands at 11601 and 13550 cm^{-1} due to $^4A_2 \rightarrow ^4T_1P (\square_3)$ transition, due to spinorbit coupling similar to those report for $[CoCl_4]^{2-}$ and $[CoI_4]^{2-}$ suggesting a tetrahedral geometry of Co(II) complex [10].

Besides the structural formula of the prepared complexes have been supported by sodium fusion test which indicated the presence of sulphur atoms.

The Ni(II) complex (No.2) show a magnetic moment of (3.32)B.M. which agree well with high-spin configuration and indicates the presence of tetrahedral environment [11]. The electronic spectra of the complex show bands at 12285-12594cm⁻¹ which correspond to the transition $^3T_1(F) \rightarrow ^3T_1(P)$ (\square_3) in tetrahedral environment.

The Cu(II) complex (No. 3) show a magnetic moment (2.11)B.M. the electronic spectrum showed a band at 13182cm⁻¹ which correspond to the transition $^2B_{1g} \rightarrow ^2A_{1g}$ or $^2B_{1g} \rightarrow ^2E_g$ and another band at 28896cm⁻¹ corresponds to charge transfer. This shows that the Cu(II) complex has tetrahedral geometry [11]. The electronic spectra of the complexes (4-9) in DMSO are listed in Table (2). The Co(II) complexes (4,7) show the presence of three bands in the region 10460 - 10612, 13121 - 15090 and 26176 - 27988 cm⁻¹ which assigned to $^4T_{1g} \rightarrow ^4T_{2g}(F)$, $^4T_{1g}(F) (\square_1) \rightarrow ^4A_{2g}(F) (\square_2)$ and $^4T_{1g}(F)$ transitions respectively. This shows that the positions

of the electronic spectral bands have change from tetrahedral to octahedral environment.

The Ni(II) complexes (5,8) show the presence of three bands in the region 10550-12498, 12116-13172 and 27021-28609 cm⁻¹ which are assigned to $^2A_{1g} \rightarrow ^2A_{2g}(P) (\square_1)$, $^2A_{21g} \rightarrow T_{1g}(F) (\square_2)$, and $^2A_{2g} \rightarrow ^3T_{2g}(F) (\square_1)$ transitions respectively. This shows that the Ni(II) complexes have an octahedral geometry.

The Cu(II) complexes (6,9) shows the presence of a bands at 11575 - 11626, 12089 - 15338 and 27027-28601cm⁻¹ which may assigned to $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2E_g$ transitions. This shows that the Cu(II) complexes have distorted octahedral geometry. The molar conductivities of 10⁻³M solution of the complexes (1-6) are non electrolyte in DMSO while the complexes (7-9) are 1:2 electrolyte in DMSO [13].

According to the above measurements, it may be suggested that the following structures of the complexes as in Fig. 1.

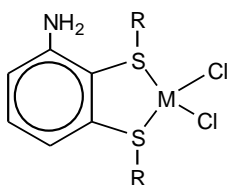
Table 1: Physical properties of the complexes

Seq.	Compounds	Colour	m.p.* °C	Cond. \square_M ohm ⁻¹ .cm ² .mol ⁻¹	\square_{eff} B.M.	%M
1.	[C ₁₄ H ₂₃ S ₂ N]CoCl ₂	Blue	240	18.2	4.02	(14.78) 14.48
2.	[C ₁₄ H ₂₃ S ₂ N]NiCl ₂	Green	261	9.5	3.32	-
3.	[C ₁₄ H ₂₃ S ₂ N]CuCl ₂	Brown	256	12.1	2.11	-
4.	[C ₁₄ H ₂₃ S ₂ N] ₂ CoCl ₂	Pale blue	249	17.5	4.96	-
5.	[C ₁₄ H ₂₃ S ₂ N] ₂ NiCl ₂	Pale green	272	21.4	2.90	(8.83) 8.5
6.	[C ₁₄ H ₂₃ S ₂ N] ₂ CuCl ₂	Pale brown	264	20.1	1.80	
7.	[C ₁₄ H ₂₃ S ₂ N] ₃ Co]Cl ₂	Gray	270	67	5.1	
8.	[C ₁₄ H ₂₃ S ₂ N] ₃ Ni]Cl ₂	Yellowish green	280	59.2	3.0	
9.	[C ₁₄ H ₂₃ S ₂ N] ₃ Cu]Cl ₂	Green	289	63.3	1.68	(6.74) 6.43

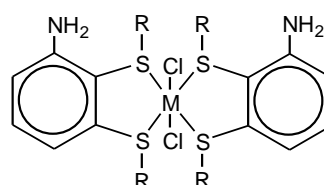
* Decomposition

Table 2: IR spectra (cm⁻¹) and electronic spectra of the ligand and their metal compounds

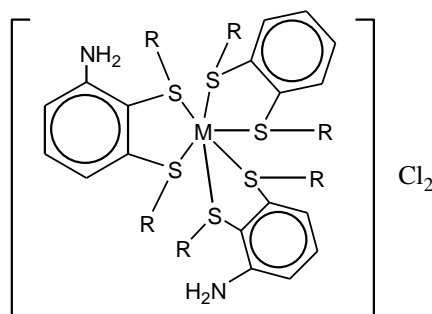
Compounds	\square (C-S)	\square (M-S)	\square (M-Cl)	M _{max} (U.V.)
C ₁₄ H ₂₃ S ₂ N	710(m)	-	-	-
1	655(m)	406(w)	350(w)	11601, 13550
2	653(m)	329(w)	280(m)	12285, 12594
3	661(w)	356(m)	339(m)	13182, 28896
4	668(w)	410(m)	298(m)	10460, 15090, 27088
5	654(w)	373(w)	310(m)	10550, 11467, 13172, 27027
6	651(w)	392(w)	290(m)	11629, 12089, 27027
7	684(w)	421(s)	-	10612, 13121, 12019, 26176
8	686(m)	361(m)	-	12116, 12498, 28609
9	701(w)	335(m)	-	11575, 14460, 15338, 28601



Complexes [1-3]



Complexes [4-6]



Complexes [7-9]

R = CH₂CH₂CH₂CH₃
M = Co(II), Ni(II), Cu(II)

Fig. 1: Suggested structures for complexes

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تحضير وتشخيص بعض معقدات الكوبلت والنيكل والنحاس مع ٢،٣-ثنائي ثايوبيوتان انيلين

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الملخص

يتضمن البحث تحضير معقدات Co(II) و Ni(II) و Cu(II) جديدة مع ٢،٣-ثنائي (ثايو بيوتان) انيلين. تم تشخيص جميع المعقدات بواسطة طيف الاشعة تحت الحمراء وفوق البنفسجية وكذلك القياسات الموصلية والمغناطيسية كذلك تم تحليل المحتوى الفلزي لبعض المعقدات. بينت دراسات الموصلية الكهربائية في مذيب ثنائي مثيل سلفوكسايد ان بعض المعقدات ذات توصيلية الكتروليتيكية بنسبة ١:٢ (M:L) واتخذت الصيغة [M(L)₃]Cl₂ واخرى غير موصلة واتخذت الصيغ [M(L)Cl₂] و [M(L)₂Cl₂] وقد بينت القياسات المغناطيسية واطياف الاشعة فوق البنفسجية بان بعض المعقدات تمتلك بنية ثماني السطوح بينما المعقدات الاخرى تمتلك بنية رباعي السطوح.