

Synthesis and Characterization Study of New Dithiocarbamate Complexes with some of Transition Metals

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Abstract: This research includes preparation and identification of new ligand N-3- acetyl phenyl -N-5,5- dimethyl-3-oxocyclohex -1- enyl dithiocarbamate, and its metal (II) complexes were synthesized and characterized by spectral (UV-Vis,IR) studies, elemental analysis ,molar conductance, magnetic susceptibility and melting point .Three different new complexes have been prepared of some transition metals (Co(II),Ni(II) and Cu(II))

Key words: Dithiocarbamate, actophenon, ligand complexes.

Introduction

Dithiocarbamats are versatile ligands with a wide range of chemistry and numerous applications in different areas such as medicine [1], materials science and in industrial applications in the vulcanization of rubber [2] and in sensing [3]. Furthermore Dtc. derivatives are used as precursors for nanoparticles [4] and in the preparation of pesticides [5]. Dtc are often used for the synthesis of transition metal complexes [6-9] and are coordinat with transition metal asmono or bidentate chelate. The chelating property of Dt arises from the π - electrons flow from the nitrogen atom to the sulpher atom via a plane delocalized π - orbital system. The net effect of such an electron flow is strong donation to metal [10], resulting in a high electron density on the metal.

In this study, we present the synthesis and characterization of Co(II),Ni(II) and Cu(II) complexes of 3-(3- acetyl phenyl amino)-5,5- dimethylcyclohex -3- enone dithiocarbamate.

Experimental

Materials and Methods

All reagents and solvents were of analytical grade and used supplied from (Fluka , BDH or Merck) chemical companies.

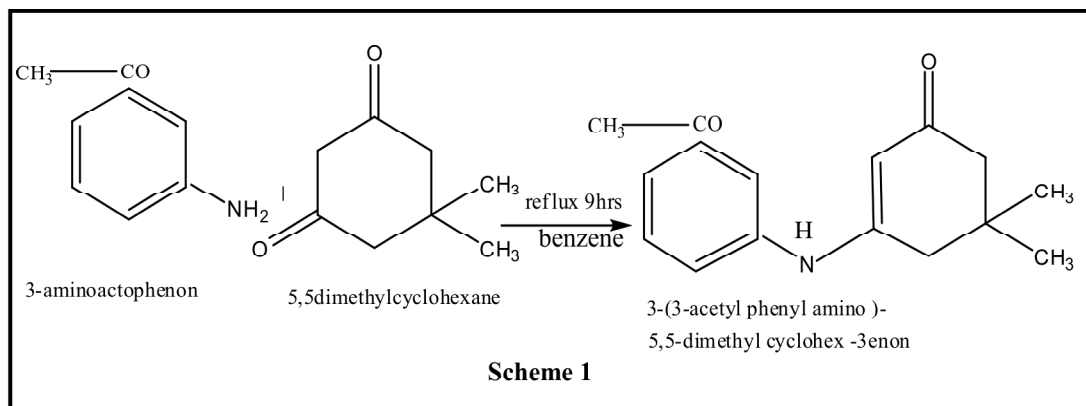
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Instrumentals

UV-Vis spectra were recorded on (Shimadzu UV-160 A) Ultra Violet –Visible spectrophotometer, IR-spectra were taken on a (Shimadzu, FTIR-8 400 S) Fourier Transform Infrared Spectrophotometer (4000-400) cm^{-1} with samples as discs. Elemental analysis (C, H, N) was (EURO3000 Singl)), Conductivities were measured for 10^{-3}M of complexes in DMSO at 25 C using (Digital conductivity meter WTW, 720), Metal contents complexes were determined by atomic absorption (A.A) technique using a Atomic Absorption spectrophotometer- 5000, Perkin-Elmer.

Synthesis of 3-(3-acetyl phenyl amino)-5, 5-dimethyl cyclohex -3-enone [HL]

The synthesized according to the literature method [11]. Dimedone (7.13 mmol) was grinded together with 3- amino acetophenone (7.10mmol), then adding (25ml) of dry benzene and continuous stirring. To the solution a few drops of glacial acetic acid was added, then resulting was refluxed for (9) hrs, the reaction mixture was allowed to cool temperature, a light yellow product was isolated by filtration and washed several times with benzene and dried to give a yellow precipitate (Scheme 1) . Yield 1.38(80%), M. P. (178-180C). Anal. Cal for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ (257): C, 74.68, H, 7.44, N, 5.44%, Found: C, 72.828, H, 6.558, N, 5.67%



Synthesis of potassium salt of dithiocarbamate ligand:

(HL) (0.05 mol) was dissolved in 10ml of absolute alcohol and potassium hydroxide (0.05) were mixed stirred vigorously in ice bath. Carbon disulfide (0.05mol) was added in drop wise. Stirring continued for one hour in an ice bath and another three hours at (30 C), resulting in the formation of solid mass which was filtered and washed with diethyl ether. yield (Scheme 2) : 1.42 g (78%) with M.p of 207 C. Anal. Calc for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{S}_2^+$ (333.47): C, 61.23; H, 5.74; N, 4.20; S, 19.23%. Found C, 62.29; H, 4.23; N, 3.07; S, 21.23%.

Synthesis of Metal Complexes

Ethanol solution $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.001mol) was added drop wise to ethanol solution of potassium dithiocarbamate ligand (0.002). The mixture was

refluxed for 3h with constant stirring, on cooling the contents. The product precipitate was filtered off, washed with water. Then with diethylether and dried under vacuum.

Result and Discussion

Micro Elemental analysis Table (1) reveals that complexes are good purity and the reaction of the ligand with their respective metal salts in 2:1 mole ratio. The molar conductance values of the complexes measured in DMOS and suggesting their non electrolytic nature of the complexes. All complexes are soluble in dimethyl form amide (DMF) and dimethyl sulfoxid (DMSO) solvent.

Table 1
Micro Element Analysis of Complexes

No	Complex, Mol,Formula. Mol.Wt.	Color Yield (%)	Found(calculated)%			Molar conductance,(cm ² mol)	μ_{eff} (B.M)
			C	H	M		
1	CoC ₃₄ H ₃₆ N ₂ O ₄ S ₄ 723.85	Green 56%	56.42 (54.32)	5.01 (4.76)	8.14 (7.10)	21.7	4.10
2	Ni C ₃₄ H ₃₆ N ₂ O ₄ S ₄ 723.61	Green 60%	56.43 (54.20)	5.01 (4.61)	8.11 (6.96)	18.5	3.20
3	C ₁₁ C ₃₄ H ₃₆ N ₂ O ₄ S ₄ 728.47	Yellow 64%	56.06 (54.55)	4.98 (3.90)	8.72 (6.88)	9.6	2,83

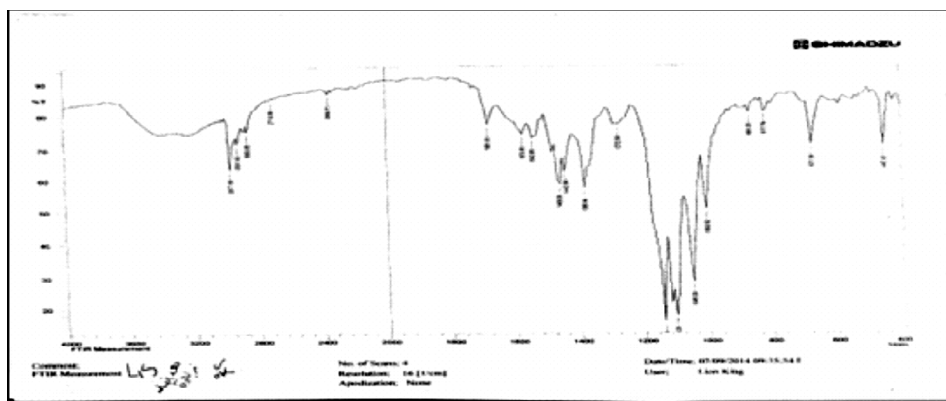
Infrared Spectra

The IR bands of the spectra of ligand and their complexes are listed in Table (2), shown in Fig (1). The dithiocarbamate complexes three main regions of IR. First, the 1550-1450 cm⁻¹ region. This was primarily associated with the stretching vibrations of C-N group [4]

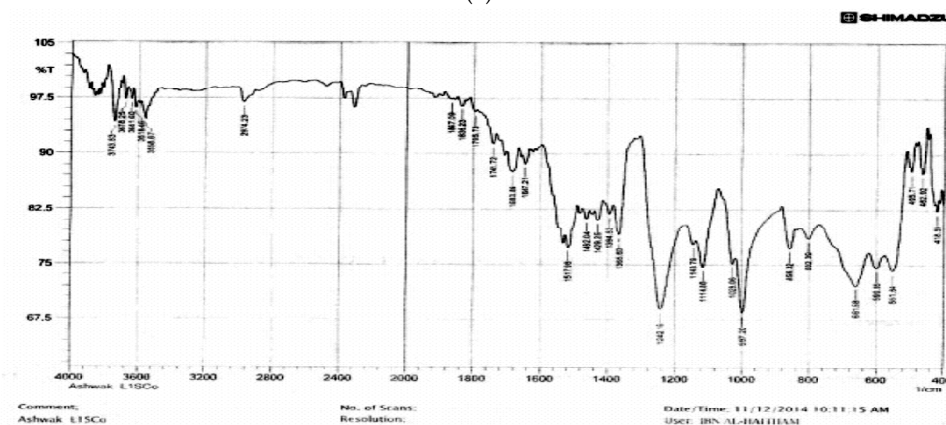
Table 2
FTIR spectral data (wave number) cm⁻¹ of complexes

Comp	$\nu_{\text{ar}}(\text{C-H})$	$\nu_{\text{al}}(\text{C-H})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N-CS}_2)$	$(\text{CS}_2)\nu$	$\nu(\text{M-S})$
HL	3059	2977	1469	1458	1002	-
Co(II)	3070	2974	1460	1440	1035,1028,997	418
Ni(II)	3039	2998	1462	1429	1042,1014, 995	414
Cu(II)	3028	2974	1462	1429	1017,1001 1035	403

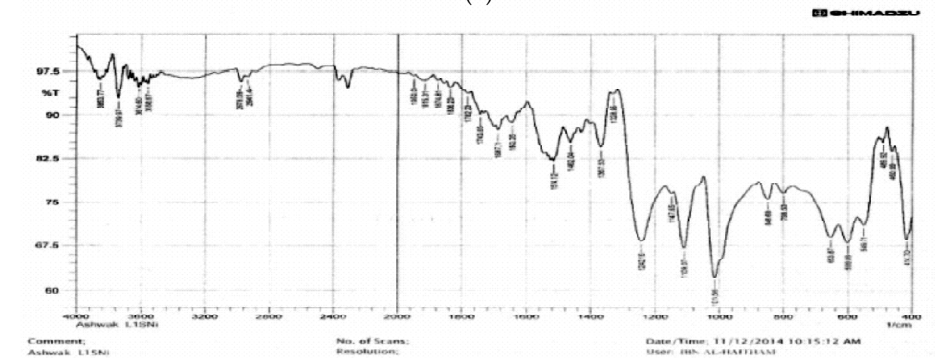
of N-CSS- moiety. The second region of ν CS₂ was observed in the 997-1035 cm⁻¹ [12] the a positive shift of (33)cm⁻¹ in comparison to the corresponding band in the free ligand indicates that the dithiocarbamate ligand coordinates with the metal through sulfur atoms. IR spectra showed a new band at 403-418 cm⁻¹ which is the evidence for the coordination of metal sulfur ν M-S [13].



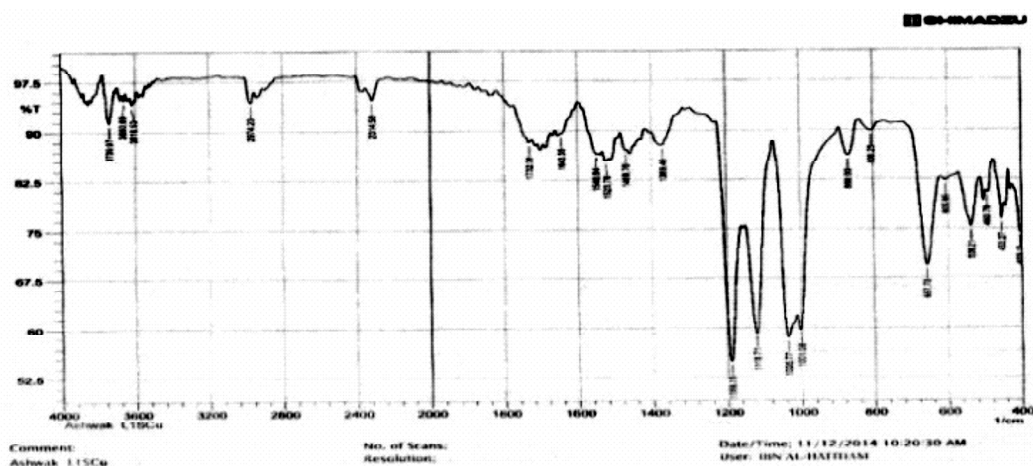
(a)



(b)



(c)



(d)

Figure 1: FTIR spectra of the ligand (a) Co(II) (b), Ni(II) (c) and Cu(II) (d) complexes

Electronic Spectra

The solution electronic spectra of the ligand and the complexes were recorded in DMSO as solvent in the UV-Visible region. The electronic transition data was given in the Table (3). Bands at 280 nm 312nm related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of N-C-S group and electronic transition involving Ion pair of electrons located on the sulfur atom. On complexation these bands were shifted to lower wavelength. In the complexes, band below 300nm are attributed to the intraligand transition. The Co(II) complex exhibited an absorption band at 19607 cm^{-1} and 16286.6 cm^{-1} region, which was assigned ${}^4A_2(F) \rightarrow {}^4T_2(F)$ and ${}^4A_2(F) \rightarrow$

Table 3
UV-Vis spectral of complexes in DMSO solution

No.	Compound	Wave number		Assignment	Suggested structure	
		nm	Cm^{-1}			
1	Co(L) ₂	278	35971	L.F	Td	
		368	27173	L.F		
		510614	196072	${}^4A_2(F) \rightarrow {}^4T_2(F)$		
			16286	${}^4A_2(F) \rightarrow {}^4T_1(F)$		
2	Ni(L) ₂	280	35714	L.F	Td	
		301	33222			
		385	25974			C.T
		420	23809			${}^3T_1 \rightarrow {}^3T_1(F)$
3	Cu(L) ₂	757	13210	${}^3T_1(F) \rightarrow {}^3A_2(F)$	Td	
		297	33670	L.F		
		301	33222	C.T		
		345	28985	C.T		
		405	24691	C.T		
	676	14792	${}^3T_2 \rightarrow {}^3E$			

$^4T_1(F)$, characteristic for tetrahedral geometry around Co atom [14]. The Ni(II) complex shows two absorption bands at (23809, 13210 cm^{-1}) which was assigned to $^3T_1(F) \rightarrow ^3T_1(P)$ and $^3T_1(F) \rightarrow ^3A_2(F)$ transition in tetrahedral geometry [15]. The Cu(II) complex gives an absorption at (14792 cm^{-1}) which corresponds to ($^2E \rightarrow ^2T_2$) transition in tetrahedral geometry [16].

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