

The Investigation of Synthesis, Spectroscopic and Thermal Characterization of Cu(II) Complexes of Some Tridentate Ligands

Özlen Altun, Murat Turkyilmaz, Ferhat Karabulut, and Yakup Baran

Abstract---The complexes of Cu(II) having tetra coordinate geometry around the metal ions with the general formula, [MLCl]Cl where L, azomethine have been isolated in the solid state. All the ligands were identified by spectroscopic methods and elemental analysis. The synthesized coordination compounds have been characterized by FTIR, magnetic measurements, elemental analysis, electrical conductance and thermal analysis. A square planer structures have been proposed for the Cu(II) complexes. Magnetic susceptibility measurements and electronic spectra of the complexes sustain the proposed square planer structures. The complexes thermally stable and this thermal stability discussed in terms of ligands donor atoms, geometry and central metal ions. Azomethine complexes have a similar thermal behavior for the selected metal ions. The TG analyses suggest high thermal stability for most complexes followed by thermal decomposition in different steps. The decomposition processes were observed as water elimination, chloride anion removal and degradation of the organic ligands.

Keywords---Azomethine, Copper(II), Thermal stability, Tridentate.

I. INTRODUCTION

AZOMETHINE have been playing an important role in the development of coordination chemistry because of the presence of hard nitrogen, oxygen and soft sulfur donor atoms in backbones of these ligands. Azomethine metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in many scientific areas. Azomethine complexes are of particular interest not only for their ability to form complexes, high thermodynamic stability and kinetic inertness but also for their ability to exhibit catalytic activity in a large number of homogeneous and heterogeneous reactions. Some dinuclear azomethine complexes of Cu(II) ions were used as an effective catalyst in hydroxylation of phenol, azomethines have been used in preparation of potentiometric sensors for determining cations and anions [1], [2].

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Azomethines mimic biological sites upon complexation with metal ions [3]-[5]. It has been reported that bis(salicylaldiminato) metal Schiff base complexes exhibit good second order NLO properties. Due to such a wide range of applications, new series of polydentate complexes of Pt (II), Cu (II) and Ni (II) are of particular interest. In our present struggle, we have chosen two tridentate azomethines, to prepare Cu (II) complexes. The thermal behavior of the complexes with azomethines have attracted attention in the last years [6], this attention being focused on the species that could have some practical applications. The details of synthetic, spectral, magnetic and thermal behaviors of these compounds are described.

II. EXPERIMENTAL

A. General synthesis of the ligands

10 mmol aldehyde and 10 mmol amine were mixed together in 60 mL dry argon saturated methanol and refluxed for 10 h. The colored solution was concentrated on a rotary evaporator and left for crystallization. A colored oily product was obtained. This oily product was loaded to alumina column for the purification. After purification colored (yellow-light brown) solids were obtained.

Synthesis of 2-((E)-[2-(1H-imidazol-4-yl)ethyl]imino)methyl)phenol, L¹

Yield: % 89, 1.92 g. Anal. calcd. for C₁₂H₁₃N₃O, (215.25 g/mol): C 66.96; H 6.09; N 19.52 %. Found: C 66.73; H 6.14; N 19.55%. FT-IR (KBr, cm⁻¹): 1634 ν(CH=N). ¹H NMR (δ, ppm, CDCl₃): 7.90 (CH=N, s), 7.60-6.75 (Ar-H), 5.28 (s, NH), 3.30 (t, CH₂-N), 2.71 (t, CH₂), ¹³C-NMR (δ, ppm, CDCl₃): 178.79 (CH=N), 156.48, 138.53, 135.78, 134.03, 128.64, 126.46, 118.85, 115.58 (aromatics), 54.63, 40.34 (aliphatics). GS MS (E⁺, m/z): 216.04 [M]⁺.

Synthesis of 1-(3-[(1E)-(3-methyl-2-thienyl)methylene]amino)propyl)pyrrolidin-2-one, L²

Yield: % 76, 1.90 g. Anal. calcd. for C₁₃H₁₈N₂OS, (250.36 g/mol): C 62.37; H 7.25; N 11.19 %. Found: C 62.44; H 7.12; N 11.30%. FT-IR (KBr, cm⁻¹): 1627 ν(CH=N). ¹H NMR (δ, ppm, CDCl₃): 8.46 (CH=N, s), 7.30-6.86 (Ar-H), 3.63 (t, CH₂), 3.36 (t, CH₂), 2.41 (t), 2.26 (t), 1.92 (d m, CH₂), ¹³C-NMR (δ, ppm, CDCl₃): 175.20 (CH=N), 153.99, 140.54, 135.81, 130.95, 128.04 (aromatics), 59.42, 47.30, 40.98, 31.30, 28.47, 18.09, 14.05 (aliphatics). MS (m/z, E⁺): 250.07.

Synthesis of 2-((E)-{[2-(1H-imidazol-4-yl)ethyl]imino}methyl)phenol, L3

Yield: % 81, 1.89 g. Anal.calcd. for C₁₂H₁₅N₃S (233.33): C 61.77; H 6.48; N 18.01 %. Found: C 61.65; H 6.54; N 18.17 %. FT-IR (KBr, cm⁻¹): 1627 ν(CH=N). ¹H-NMR (δ, ppm, CDCl₃): 7.49 (CH=N, s), 7.32-6.86 (Ar-H), 4.08 (t, CH₂-N=), 3.53 (t, CH₂-N), 2.39, (s, CH₃), 2.17 (m, -CH₂). ¹³C-NMR (δ, ppm, CDCl₃): 170.90 (CH=N), 154.33, 140.77, 137.41, 131.05, 129.62, 128.49, 119.08 (aromatics), 57.65, 44.79, 32.13, 14.11 (aliphatics). MS (ED, m/z): 233.03 [M]⁺

B. General synthesis of the complexes

All the complexes of azomethines with Cu(II) were prepared by following general method. The metal salt (10 mmol) was dissolved in 40 mL argon saturated methanol and the solution was added to a stirred solution of azomethine (11 mmol) in 30 mL argon saturated methanol solution at room temperature. On addition of metal to ligand solution immediate color change was observed according to the metal ions. Then the solution was warmed up to 50°C and stirred for 10 hours and then solution was concentrated on rotary

evaporator. Solutions were left for crystallization but amorphous powders were obtained. The solid substance dissolved in acetonitrile and loaded to a alumina column for the purification. The volume of the solution was reduced by rotary evaporation and left for the crystallization. The resulting precipitates were filtered by suction and then dried at vacuum oven at room temperature for 24 hours. The elemental analysis data are given in TABLE 1. The proposed ligands are given in Fig. 1.

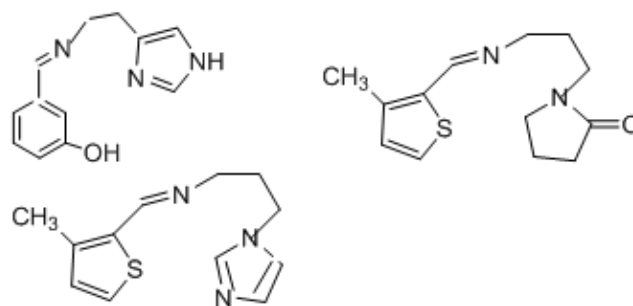


Fig.1 Structures of the ligands(L1, L2 and L3)

TABLE I
ANALYTICAL DATA OF THE AZOMETHIN CU (II) COMPLEXES

Compounds	Fw	C	H	N	M	μ_{eff}
[CuL ¹ Cl]Cl.1.5H ₂ O	367.71	39.12/39.20	4.23/4.11	11.52/11.43	17.12/17.26	1.64
[CuL ² Cl]Cl.2H ₂ O	420.86	37.27/37.10	5.18/5.27	6.58/6.66	14.21/14.35	1.57
[CuL ³ Cl]Cl.5H ₂ O	385.58	37.25/37.36	4.42/4.44	10.77/10.89	16.43/16.47	1.66

III. RESULT AND DISCUSSION

A. Electronic spectra

Electronic spectra of the complexes show high intensity intra-ligand (π - π^*) transitions in between at 270–300 nm. Another high intensity band, d- π^* Metal-Ligand Charge Transfer (MLCT) transitions were observed in the region 305-350 nm. The third expected low-energy ligand field bands, observed in between 408–448 nm range and are assigned as d-d transitions. Cu (II) complexes shows d-d transitions in the region 400-550 nm which can be assigned to the combination of ²B_{1g}→²E_g transitions in a distorted square-planar [7], [8]. The appearance of two/three bands in the present complexes suggests them to process square planar structures.

B. 1H and 13C NMR spectra

The ¹H and ¹³C NMR spectra of the azomethines were carried out at room temperature in CDCl₃. The data are summarized in the synthesis of ligands. All the ligands show characteristic singlets at 7.90(L¹) and 7.49(L²) ppm for -CH=N-protons and ¹³C peaks at 178.79, 175.20, 178.79, and 170.90 ppm are observed for -CH=N- respectively. Aromatic protons appear in between 7.60-6.75 ppm and ¹³C peaks are observed in between 156.48-115.58 ppm.

C. Molar conductance

The azomethine complexes of Cu (II) was dissolved in nitromethane and the molar conductivities of 10⁻³ M of their solutions at 25 ± 2 °C were measured. It is concluded from the results that all the complexes are considered 1:1 electrolytes with the molar conductance values in between 68-82 Ω⁻¹mol⁻¹cm² indicating the ionic nature of these complexes.

D. Infrared spectra

Ligands show absorption bands at 1634, 1627 and 1627 cm⁻¹ which are attributed to the ν(C=N) vibration for the ligands L¹, L² and L³ respectively. This is regarded as a satisfactory criterion of the formation of Schiff base. The frequency 3340 cm⁻¹ are due to ν OH of ligand L¹. The frequencies 1280 cm⁻¹ is due to ν C-O of L¹. Cu (II) complexes show that most of the absorption bands are shifted infrequency. The medium intensity band appeared around 1627–1634 cm⁻¹ due to ν(C=N) in azomethine shifted to 1610-1634 cm⁻¹ in the complexes. The low and high frequency shift from ligands indicate that the azomethine group of the ligands has coordinated to the metal ion through nitrogen. In addition, the Cu (II) complexes exhibit a broad bands at ca. 3400 cm⁻¹; which were attributed to the -OH stretching frequencies of coordinated water molecules [9]. The sharp IR ligand bands at 724-728 cm⁻¹ which are attributed to, ν(C-S-C) of thiophene for the L² ligand, shifted to 746-751 cm⁻¹ in

complexes. The important features of the infrared spectra of the complexes are the appearance of two weak bands at 536–554 cm^{-1} region which are assignable $\nu(\text{M-O})$ and those in the region 462–499 cm^{-1} to $\nu(\text{M-N})$ vibrations, respectively. Thus, the IR spectral analyses results provide strong evidence for the complexation of the potentially tridentate azomethines.

E. Thermal analysis

TG-DTA analyses (Fig.1) were made in between 25 and 1200 $^{\circ}\text{C}$ in the static atmosphere of dry air to examine thermal stabilities of complexes. Thermal analysis data of the complexes are summarized in TABLE 2. The TG curves show mainly three stages in the decomposition process. The first stage decomposition is endothermic in the range of 25 and $\sim 204^{\circ}\text{C}$, with a mass loss of water. The second stage of decomposition was also endothermic in the 197 and $\sim 581^{\circ}\text{C}$, range with the mass loss of L^1 , L^2 , L^3 and Cl_2 , the third stage decomposition was endothermic which was observed in between 423 and $\sim 677^{\circ}\text{C}$, The final product is the CuO . These results are in good agreement with the

suggested structures of the complexes. It is confirmed that most of the complexes contain water in the structure. As a result of the thermal study, qualitative conclusion can be done for the stability of the complexes.

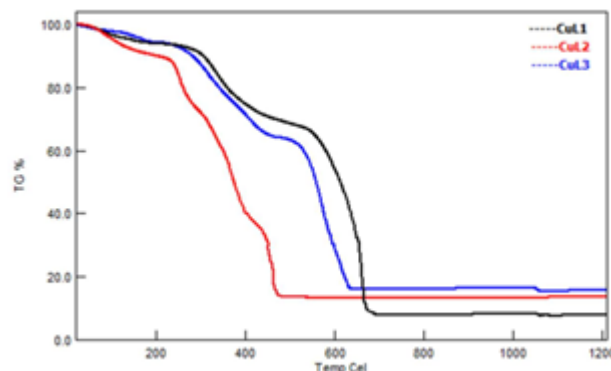


Fig. 2 The TG curves of the Cu(II) complexes

TABLE II
THERMAL ANALYSIS DATA OF THE COMPLEXES

Comp	Step	One	End	Leaving group	Mass Loss		Residue
					Exp./	Cal	
[CuL ¹ Cl]Cl.1.5H ₂ O	1	25	199	H ₂ O	5.8/	4.9	
	2	199	581				
	3	581	677	L ¹ + Cl ₂	76.3/	77.8	CuO/17.7
[CuL ² Cl]Cl.2H ₂ O	1	25	197	H ₂ O	8.5/	9.9	
	2	197	336				
	3	336	423	L ² +			
	4	423	478		73.8/	75.6	CuO/16.3
[CuL ³ Cl]Cl.5H ₂ O	1	25	204	H ₂ O	5.6/	4.7	
	2	204	441				
	3	441	630	L ² +	78/	7	CuO

F. Magnetic Susceptibility

The measurement of the magnetic moment of a coordination compound containing unpaired electron spins is useful in the establishment of the valency of the metal atom, and in many cases also helps to determine the geometrical structure of the complex. The magnetic susceptibilities of the solid-state complexes under discussion were measured by the Gouy balance method. The magnetic moment of copper complexes is in the range 1.57–1.66 BM. The electronic spectra of the Cu(II) complexes exhibited bands in the region 400–448 nm, which showed that these complexes are distorted square planar structure.

IV. CONCLUSION

In this article, we present Cu(II) complexes of three tridentate azomethine ligands. The copper center is four coordinated with distorted square planar geometry, which was also confirmed through UV-Vis spectral studies in solution. All the complexes are mono metallic. The structure of

the complex is well sustained by the other spectral, magnetic, thermal, and conductometric studies. The higher decomposition temperature under the linear heating rate indicates that Cu(II) complexes are much stable with the hard base donor atoms. The proposed structures of the complexes are given in Fig.3.

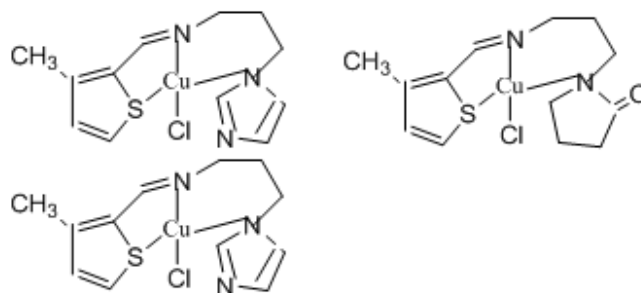


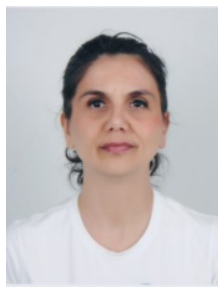
Fig.3 Proposed structures of the complexes. Counter ions and waters are omitted

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