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Synthesis and Characterization of Nickel(II) and Copper(II) Complexes of The Schiff Bases Derived from 2,4,6-/3,5,6-Trimethyl-3-cyclohexene-1-carboxaldehyde and Glycine

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In this study, the synthesis of Schiff bases derived from 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde or 3,5,6-trimethyl-3-cyclohexene-1-carboxaldehyde and glycine and their complexes with nickel(II) and copper(II) were investigated. The synthesized compounds were characterized by elemental analyses, conductivity measurements, magnetic properties and FT-IR spectroscopy. The Schiff base ligands and their complexes have been further characterized by ^{1}H NMR. The results showed that the Schiff base acts as a bidentate ligand which bonds to the metal ions through the imino nitrogen and carboxylate oxygen. The potassium salts of the Schiff bases are 1:1 electrolytes, but all the complexes are non-electrolytes.

Key Words: Schiff bases, Glycine, Ni(II), Cu(II) complexes, Conductivity.

INTRODUCTION

The metal complexes of Schiff bases have been of interest in coordination chemistry for many years due to their facile synthesis and wide applications[1,2]. Nickel(II) and copper(II) complexes involving Schiff base ligands of different denticity were studied by some researchers[3-5]. Schiff base derivates of 2-chlorobenzaldehyde and glycine and Δ^3-tetra-hydrobenzaldehyde or 2-methyl-Δ^3-tetrahydrobenzaldehyde and glycine and their metal ligand complexes have been studied previously and their structures were characterized[6-8]. In these works, the complex formation constants, the availability as carries for ligand membrane transport and their reaction properties and mechanisms with epoxy compounds of the Schiff bases were investigated in detail. In addition, these Schiff bases may be use as reference material for the identification of Schiff bases which may be obtained from the extraction of some lipids. Some oximes can have many applications due to their importance from the point of psychologic or biological chararteristics. In this paper, the synthesis and characterization of the Schiff bases derived from 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde or 3,5,6-trimethyl-3-cyclohexene-1-carboxaldehyde and glycine (Fig. 1) and their complexes with nickel(II) and copper(II) (Fig. 2) are reported.

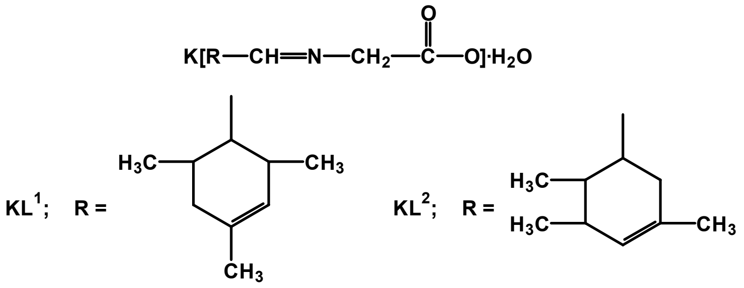

Fig. 1. Proposed structure of the potassium salts of the ligands, $KL^1 \cdot H_2O$ and $KL^2 \cdot H_2O$

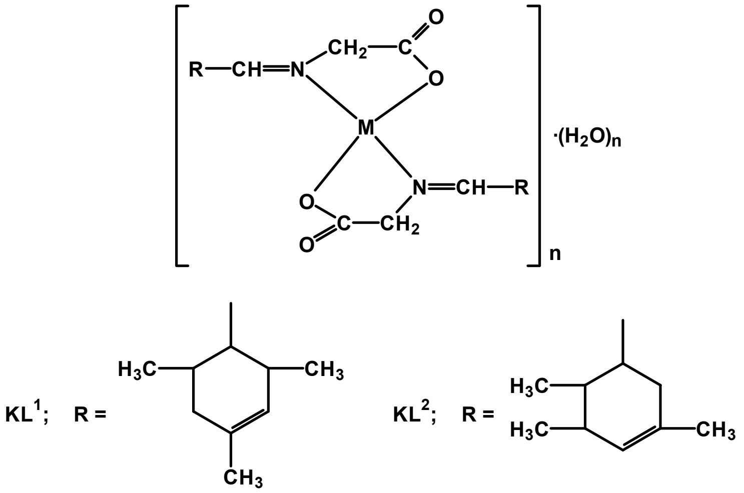

Fig. 2. Proposed structure of the Ni(II) and Cu(II) complexes of the ligands L^1 and L^2 (n = 6 for M = Ni and n = 2 for M = Cu)

EXPERIMENTAL

All chemicals used in this work were of reagent grade. The metal chlorides, glycine, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde and 3,5,6-trimethyl-3-cyclohexene-1-carboxaldehyde were purchased from Sigma Chemical Company.

Elemental analyses were performed by Tübitak Laboratory (Gebze, Kocaeli). ^1H NMR analyses were performed by M.E.T.U. Laboratory (Ankara, Turkey). Infrared (IR) spectra were recorded in KBr pellets (Perkin Elmer

Model 1605 FT-IR spectrometer) in the range 4000-400 cm^{-1}. The conductivity measurement were performed in methanol using a Shanghai DDS-11A apparatus at 25 ºC; the concentration of the solution was 1.0×10^{-4} mol L^{-1}. The magnetic moments of the complexes were measured by the Gouy method with a Newport Instruments type D-104 magnet power supply (293 K). H_2O analysis data were obtained using a TAS-100 thermoanalysis instrument. The metal contens of each complex were determined on a Varian, Vista AXCCD Simultaneous model ICP-AES spectrophotometer.

Synthesis of the ligands

N-(2,3,6-Trimethyl)-3-cyclohexene-1-carboxylideneglycinatopotassium monohydrate salt ($KL^1 \cdot H_2O$)[5,6]: An ethanolic solution (80 mL) of glycine (2.25 g, 30 mmol) and potassium hydroxide (1.68 g, 30 mmol) was stirred magnetically at room temperature for 1 h and then filtered. The colourless solution of potassium glycinate was added dropwise to an ethanolic solution (80 mL) of 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde (4.57 g, 30 mmol). The mixture was stirred magnetically at room temperature for 1 h. After a while white solid particles appeared in the solution and precipitation was gradually increased by stirring. The resulting white solid product was filtered, washed with 95 % ethanol and dried in a vacuum desiccator; the yield was 5.56 g (70%).

N-(3,5,6-Dimethyl)-3-cyclohexene-1-carboxylideneglycinatopotassium monohydrate salt ($KL^1 \cdot H_2O$)[5,6]: An ethanolic solution (80 mL) of glycine (2.25 g, 30 mmol) and potassium hydroxide (1.68 g, 30 mmol) was stirred magnetically at room temperature for 1 h and then filtered. The colourless solution of potassium glycinate was added dropwise to an ethanolic solution (80 mL) of 6-methyl-Δ^3-tetrahydrobenzaldehyde (4.57 g, 30 mmol). The mixture was stirred magnetically at room temperature for 1 h. After a while white solid particles appeared in the solution and precipitation was gradually increased by stirring. The resulting white solid product was filtered, washed with 95 % ethanol and dried in a vacuum desiccator; the yield was 5.56 g (70 %).

Preparation of metal complexes

$NiL^1_2 \cdot 6H_2O$ and $CuL^1_2 \cdot 2H_2O$: An ethanolic solution (60 mL) of nickel chloride (2.378 g, 10 mmol) or copper chloride (1.706 g, 10 mmol) was mixed with KL^1 (5.30 g, 20 mmol) in 1:2 molar ratio. The mixture was stirred magnetically at room temperature for 2 h and then concetrated to *ca.* 10 mL at 65-70 ºC in a water bath. Addition of 7 mL distilled water to the concentrated reaction mixture precipitated green or blue products, respectively. The precipitate was collected by filtration, washed with diethyl ether then 95 % ethanol and dried in a vacuum desiccator; the yields of the Ni and Cu complexes were 4.19 g (72 %) and 3.66 g (71 %), respectively.

$NiL^2_2·6H_2O$ and $CuL^2_2·2H_2O$: The reactions were performed in a analogous manner as the preparation of the complexes of L^1; the yields of the Ni and Cu were 4.31 g (74 %) and 3.71 g (72 %), respectively.

RESULTS AND DISCUSSION

The elemental analyses (Table-1) are in agreement with the chemical composition of the compounds. Molar conductivities in methanol (Table-1) indicate that the Schiff base potassium salts are 1:1 electrolytes, but all the complexes behave as non-electrolytes.

TABLE-1
ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF COMPOUNDS

Compound (formula)	Color / Yield (%) / m.p. (ºC)	μ_{eff}	Elemental analysis %: Found (Calcd.)				Conductivity (Ohm^{-1} cm^2 mol^{-1})
			C	H	N	M	
$L^1K·H_2O$ ($C_{12}H_{20}NO_3K$) 265.1	White 70 >300	–	53.85 (54.32)	7.58 (7.54)	5.10 (5.28)	–	91.50
$NiL^1_2·6H_2O$ ($C_{24}H_{48}N_2O_{10}Ni$) 582.8	Green 72 >300	Diamg.	48.75 (49.42)	8.67 (8.24)	4.61 (4.80)	10.45 (10.09)	5.54
$CuL^1_2·2H_2O$ ($C_{24}H_{40}N_2O_6Cu$) 515.5	Blue 71 >300	1.66	54.44 (55.87)	7.32 (7.76)	5.64 (5.43)	12.01 (12.32)	5.51
$L^2K·H_2O$ ($C_{12}H_{20}NO_3K$) 265.1	White 70 >300	–	54.01 (54.32)	6.95 (7.54)	5.70 (5.28)	–	91.68
$NiL^2_2·6H_2O$ ($C_{24}H_{48}N_2O_{10}Ni$) 582.8	Green 74 >300	Diamg.	47.65 (49.42)	8.07 (8.24)	4.92 (4.80)	11.02 (10.09)	5.53
$CuL^2_2·2H_2O$ ($C_{24}H_{40}N_2O_6Cu$) 515.5	Blue 72 >300	1.66	55.25 (55.87)	6.98 (7.76)	4.84 (5.43)	11.63 (12.32)	5.53

The infrared spectra of the potassium salts of the Schiff base ligands and their complexes (Table-2) provide insight into the mode of bonding of the ligands to the metal ions. The strong and broad absorption in the region 3350-3300 cm^{-1} of all the compounds substantiates the presence of water. The coordination of the imino nitrogen to the metal ion may be inferred from the shift of ν(C=N) from 1645 to 1620 cm^{-1}. This is in agreement with the results of Nakamoto *et al.*[9]. These authors showed that for selected metal complexes of glycine in the same physical state the asymmetrical carboxylate stretching frequency increased while the symmetric one decreased form Cu and Ni. One may infer that the carboxylate oxygen takes part in coordination according to the changes of ν_{as}(COO) and ν_s(COO) of these complexes.

TABLE-2
INFRARED SPECTRAL DATA OF THE COMPOUNDS (cm^{-1})

Compounds	$\nu(H_2O)$	ν(C=N)	ν_{as}(COO)	ν_s(COO)
$L^1K{\cdot}H_2O$	3320 m,br	1640 s	1595 s	1390 m
$L^2K{\cdot}H_2O$	3325 m,br	1645 s	1595 s	1390 m
$CuL^1_2{\cdot}2H_2O$	3330 w,br	1635 s	1605 s	1385 s
$NiL^1_2{\cdot}6H_2O$	3335 w,br	1620 s	1600 s,br	1380 m
$CuL^2_2{\cdot}2H_2O$	3335 w,br	1635 s	1600 s	1380 s
$NiL^2_2{\cdot}6H_2O$	3330 w,br	1630 s	1605 s,br	1385 m

^{1}H NMR Spectra of the Schiff base ligands and complexes: The ^{1}H NMR spectra of the synthesized ligand and metal complexes are given in Table-3. When the ^{1}H NMR spectra of KL^1 and KL^2 are compared, the spectra are quite similar to each other. The peak seen at 8.25 ppm belongs to the protons in the CH=N groups and those at 4.15 ppm belong to the CH_2 groups. Morever, the peaks for the CH_3 group of ligands were observed at 0.95 ppm.

TABLE-3
^{1}H NMR SOME SELECTED CHEMICAL SHIFT SIGNAL DATA (DMSO)

Compounds	Chemical shift (δ, ppm)
$L^1K{\cdot}H_2O$	8.30 (CH = N, 1H, s); 4.15 (CH_2, 2H, s); 0.95 (CH_3, 9H, s)
$L^2K{\cdot}H_2O$	8.25 (CH = N, 1H, s); 4.15 (CH_2, 2H, s); 0.95 (CH_3, 9H, d, *J* = 6.0 Hz)
$NiL^1_2{\cdot}6H_2O$	8.70 (CH = N, 2H, s); 4.75 (CH_2, 4H, s); 1.00 (CH_3, 18H, s)
$NiL^2_2{\cdot}6H_2O$	8.75 (CH = N, 2H, s); 4.80 (CH_2, 4H, s); 1.00 (CH_3, 18H, d, *J* = 6.5Hz)

When the ^{1}H NMR spectra of the complexes are compared with those of the ligands, the observed peaks for the ligands, generally, were shifted to lower field. This shift indicates that the complex formation take place. However, the largest shifts were observed for the CH=N and CH_2COO^- protons. This was expected, because there has been charge transfer from these groups to the metal. When the ^{1}H NMR spectra of the complexes of Ni(II) with L^2K were compared, the CH=N and CH_2COO^- protons were shifted by 0.40 and 0.50 ppm, respectively.

Magnetic susceptibility measurements provided sufficient data to characterize the structure (Table-1). The mononuclear complexes of Ni(II) are diamagnetic as expected for a d^8 metal in a square-planar field[10-13]. The magnetic moments of the mononuclear complexes of Cu(II) are about 1.66 BM, which is comparable with values reported for slightly distorted square-planar copper(II) complexes[14]. The results are in agreement with our previous work[6] and Zhang's work[7].

Structure of the metal complexes: From the above discussion, it is seen that the metal ions in the complexes are bonded to the ligands through the imino nitrogen and carboxylate oxygen atoms. As the complexes are presumed to be tetra-coordinate, the proposed coordination structures[8] are shown in Fig. 2. The water molecules are identified by broad O-H absorptions around 3335-3330 cm^{-1} in the IR spectra of the complexes and the bands disappeared *via* heating at 110 ºC for 6 h. Thus, the water molecules are not directly coordinated to the central metal atom but held in the crystal lattice of the complexes[15].

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