

Synthesis and Characterization of Nickel(II) and Copper(II) Complexes of the Schiff Bases Derived from 4-/6-Methyl- Δ^3 -tetrahydrobenzaldehyde and Glycine

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Nickel(II) and copper(II) complexes with the Schiff bases derived from 4-methyl- Δ^3 -tetrahydrobenzaldehyde or 6-methyl- Δ^3 -tetrahydrobenzaldehyde and glycine were synthesized. These compounds have been characterized by elemental analysis, conductivity measurements and infrared spectroscopy. The Schiff base ligands and their complexes have been further characterized by ^1H NMR. The results suggest 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) and Cu(II) Complexes, Conductivity.

INTRODUCTION

Schiff base derivatives of 2-chlorobenzaldehyde and glycine and Δ^3 -tetrahydrobenzaldehyde or 2-methyl- Δ^3 -tetrahydrobenzaldehyde and glycine and their metal ligand complexes have been studied previously and their structures were characterized¹⁻³. In these works, the complex formation constants, the availability as carriers 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 usable as reference material for the identification of Schiff bases which may be obtained from the extraction of some lipids. In this paper we present the synthesis and characterization of the Schiff bases derived from 4-methyl- Δ^3 -tetrahydrobenzaldehyde or 6-methyl- Δ^3 -tetrahydrobenzaldehyde and glycine (Fig. 1) and their complexes with nickel(II) and copper(II).

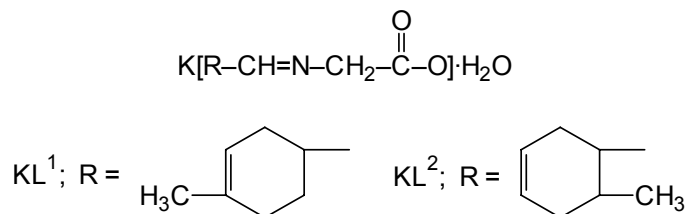


Fig. 1. Structure of the potassium salts of the ligands, $\text{KL}^1\cdot\text{H}_2\text{O}$ and $\text{KL}^2\cdot\text{H}_2\text{O}$

EXPERIMENTAL

All chemicals used in this work were of reagent grade. The metal chlorides and glycine were purchased from Sigma Chemical Company. 4-Methyl- Δ^3 -tetrahydrobenzaldehyde and 6-methyl- Δ^3 -tetrahydrobenzaldehyde were prepared according to published methods⁴.

Melting points were measured on a Gallenkamp melting point apparatus. Elemental analysis were performed by Tübitak Laboratory (Gebze, Kocaeli). ¹H NMR analysis were performed by M.E.T.U. Laboratory (Ankara, Turkey). Infrared spectra were recorded in KBr pellets and Perkin Elmer Model 1605 FTIR spectrometer in the range 4000-400 cm^{-1} . All conductivity measurement were performed in methanol using a Shanghai DDS-11A apparatus at 25 °C. The concentration of the solution was $1.0 \times 10^{-4} \text{ mol L}^{-1}$. The magnetic moments of the complexes were measured by to the Gouy method with a Newport Instruments type D-104 magnet power supply (293 K). The copper content was determined by iodometry⁵ and the nickel content as dimethylglyoximato-nickel⁶ by gravimetric analysis. H_2O analysis data were obtained using a TAS-100 thermoanalysis instrument.

Synthesis of the ligands

N-(4-Methyl)- Δ^3 -tetrahydrobenzylidenglycinatopotassium monohydrate salt ($\text{KL}^1\cdot\text{H}_2\text{O}$)^{1,2}: An ethanolic solution (60 mL) of glycine (1.50 g, 20 mmol) and potassium hydroxide (1.12 g, 20 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 (60 mL) of 4-methyl- Δ^3 -tetrahydrobenzaldehyde (2.48 g, 20 mmol). The mixture was stirred magnetically at room temperature for 1 h. A 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. Yield *ca.* 3.47 g (73 %).

N-(6-Methyl)- Δ^3 -tetrahydrobenzylidene-glycinatopotassium monohydrate salt ($\text{KL}^1 \cdot \text{H}_2\text{O}$)^{1,2}: An ethanolic solution (60 mL) of glycine (1.50 g, 20 mmol) and potassium hydroxide (1.12 g, 20 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 (60 mL) of 6-methyl- Δ^3 -tetrahydrobenzaldehyde (2.48 g, 20 mmol). The mixture was stirred magnetically at room temperature for 1 h. A 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. Yield *ca.* 3.35 g (70 %).

Preparation of metal complexes

$\text{NiL}^1_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuL}^1_2 \cdot 2\text{H}_2\text{O}$: An ethanolic solution (60 mL) of nickel(II) chloride (2.378 g, 10 mmol) or copper(II) chloride (1.706 g, 10 mmol) was mixed with KL^1 (4.74 g, 20 mmol) in 1:2 molar ratio. The mixture was stirred magnetically at room temperature for 2 h and then concentrated to about 10 mL at 65-70 °C in a water bath. Addition of 5 mL distilled water to the concentrated reaction mixture precipitated green or blue products, respectively. The precipitate was collected by filtration, washed with diethylether then 95 % ethanol and dried in a vacuum desiccator. The yields of the Ni and Cu complexes were 3.85 g (73 %) and 4.02 g (76 %), respectively.

$\text{NiL}^2_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuL}^2_2 \cdot 2\text{H}_2\text{O}$: 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 1.86 g (81 %) and 2.11 g (80 %), respectively. The yields of the Ni and Cu were 4.10 g (78 %) and 3.40 g (74 %), respectively.

RESULTS AND DISCUSSION

The elemental analysis (Table-1) are in agreement with the chemical formulas of the compounds. Molar conductivities in methanol (Table-1) indicate that the Schiff base potassium salts are 1:1 electrolytes, while all the complexes behave as non-electrolytes. 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 $\nu(\text{C}=\text{N})$ from 1640 to 1625 cm^{-1} .

This is in agreement with the results of Nakamoto *et al.*⁷. These authors showed that for selected metal complexes of glycine in the same physical state the asymmetrical carboxylate stretching frequency increased

TABLE-1
ANALYTICAL DATA AND SOME PHYSICAL
PROPERTIES OF COMPOUNDS

Compounds (m.f.)	Yield (%) / m.p. (°C)	μ_{eff} (BM) / (colour)	Found (calcd.) %				Cond. (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	M	
L ¹ KH ₂ O (C ₁₀ H ₁₆ NO ₃ K)	73 (>300)	– (White)	50.85 (50.63)	6.58 (6.75)	6.10 (5.90)	–	91.62
NiL ¹ ₂ 6H ₂ O (C ₂₀ H ₄₀ N ₂ O ₁₀ Ni)	73 (>300)	Diamagnetic (Green)	45.75 (45.57)	7.67 (7.59)	5.61 (5.32)	11.45 (11.15)	5.54
CuL ¹ ₂ 2H ₂ O (C ₂₀ H ₃₂ N ₂ O ₆ Cu)	76 (>300)	1.69 (Blue)	52.44 (52.23)	7.28 (6.96)	5.84 (6.09)	14.01 (13.82)	5.64
L ² KH ₂ O (C ₁₀ H ₁₆ NO ₃ K)	70 (>300)	– (White)	50.78 (50.63)	6.53 (6.75)	6.05 (5.90)	–	91.71
NiL ² ₂ 6H ₂ O (C ₂₀ H ₄₀ N ₂ O ₁₀ Ni)	78 (>300)	Diamag. (Green)	45.82 (45.57)	7.71 (7.59)	5.58 (5.32)	11.34 (11.15)	5.55
CuL ² ₂ 2H ₂ O (C ₂₀ H ₃₂ N ₂ O ₆ Cu)	74 (>300)	1.66 (Blue)	52.32 (52.23)	7.22 (6.96)	5.91 (6.09)	13.98 (13.82)	5.62

TABLE-2
INFRARED SPECTRAL DATA (cm⁻¹) OF THE COMPOUNDS

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{N})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$
L ¹ KH ₂ O	3320 m, br	1640 s	1595 s	1395 m
L ² KH ₂ O	3320 m, br	1640 s	1595 s	1395 m
CuL ¹ ₂ 2H ₂ O	3330 w, br	1625 s	1595 s	1380 s
NiL ¹ ₂ 6H ₂ O	3325 w, br	1620 s	1600 s, br	1385 m
CuL ² ₂ 2H ₂ O	3325 w, br	1625 s	1600 s	1385 s
NiL ² ₂ 6H ₂ O	3335 w, br	1625 s	1600 s, br	1380 m

while the symmetric one decreased in metal complexes. One may infer that the carboxylate oxygen takes part in coordination according to the changes of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of these complexes.

¹H NMR Spectra of the Schiff base ligands and complexes: The ¹H NMR spectra of the synthesized ligand and metal complexes are given in Table-3. When the ¹H NMR spectra of KL¹ and KL² 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 CH₂ groups. Moreover, the peaks for the CH₃ group of ligands were observed at 0.95 ppm.

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

Compd.	Chemical shift (δ ppm)
$\text{L}^1\text{KH}_2\text{O}$	8.25 (CH=N, 1H, s); 4.15 (CH ₂ , 2H, s); 0.95 (CH ₃ , 3H, s)
$\text{L}^2\text{KH}_2\text{O}$	8.25 (CH=N, 1H, s); 4.10 (CH ₂ , 2H, s); 0.95 (CH ₃ , 3H, d, $J=5.5$ Hz)
$\text{NiL}_2^1 \cdot 6\text{H}_2\text{O}$	8.70 (CH=N, 2H, s); 4.85 (CH ₂ , 4H, s); 1.00 (CH ₃ , 6H, s)
$\text{NiL}_2^2 \cdot 6\text{H}_2\text{O}$	8.75 (CH=N, 2H, s); 4.80 (CH ₂ , 4H, s); 0.95 (CH ₃ , 6H, d, $J=6.0$ Hz)

When the ^1H 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 CH₂COO⁻ protons. This was expected, because there has been charge transfer from these groups to the metal. When the ^1H NMR spectra of the complexes of Ni(II) with KL^2 were compared, the CH=N and CH₂COO⁻ protons were shifted by 0.45 and 0.50 ppm, respectively.

The mononuclear complexes of Ni(II) are diamagnetic as expected for a d^8 metal in a square-planar field⁸⁻¹¹. The magnetic moments of the mononuclear complexes of Cu(II) are about 1.65-1.68 BM, which is comparable with values reported for slightly distorted square-planar copper(II) complexes¹².

The obtained results are in agreement with our previous work¹ and Zhang's study². Therefore, the data in the literature are strongly supportive of the obtained results.

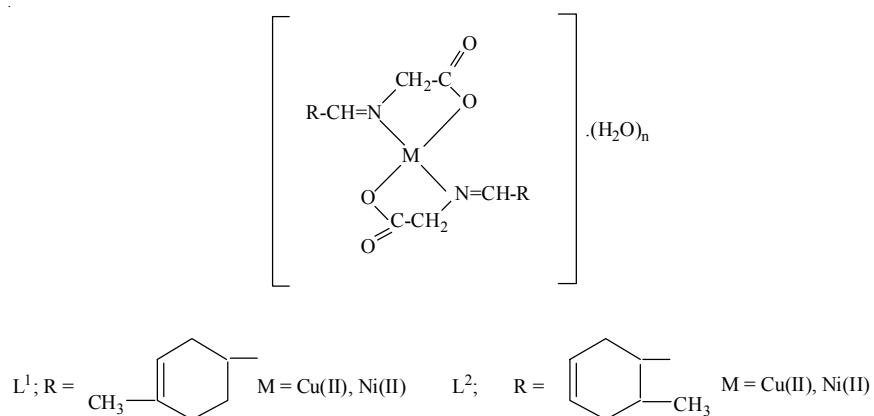


Fig. 2. Structure of the Ni(II) and Cu(II) complexes of the ligands L^1 and L^2 ($n = 6$ for $\text{M} = \text{Ni}$ and $n = 2$ for $\text{M} = \text{Cu}$)

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 modes⁸ are shown in Fig. 2. The water molecules are identified by broad O–H absorptions around 3335–3325 cm⁻¹ in the IR spectra of the complexes and the bands disappeared on heating at 110 °C for 6 h. Thus, the water molecules are not directly coordinated to the central metal atom but held in the crystal lattice of the complexes¹³.

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