

A New Mesitylenic Cyclobutane Substituted Schiff Base Ligand and its Co(II), Cu(II), Ni(II), and Zn(II) Complexes

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Received 22 June 2000; revised 25 September 2000

ABSTRACT: A new ligand, 4-(1-methyl-1-mesityl-3-cyclobutanyl)-2-(2-hydroxy-1-naphthylideneimino)thiazole (LH), has been synthesized starting from 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl)cyclobutane and thiourea and subsequently 2-hydroxy-1-naphthaldehyde. Mononuclear complexes with a metal-ligand ratio of 1:2 have been prepared with Co(II), Cu(II), Ni(II), and Zn(II) metals. The authenticity of the ligand and its complexes are proposed based on elemental analyses, IR, UV-vis, ^{13}C and ^1H NMR spectra, magnetic susceptibility measurements, thermogravimetric analyses, and differential scanning calorimetry. © 2001 John Wiley & Sons, Inc. *Heteroatom Chem* 12:42–46, 2001

INTRODUCTION

Schiff bases and their transition metal complexes have been extensively investigated because these types of molecules are important in chemistry. The Schiff bases derived from the condensation of salicylaldehyde with alkyl and arylamines, known as *N*-alkyl or *N*-arylsalicylaldimines, are considered to be suitable models for pyridoxal and, in general, B_6 vitamins [1]. Thiazole and its derivatives have biological significance, for example, it is found in the vita-

min B_1 molecule and in the coenzyme cocarboxylase [2]. The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes [3].

Substituted cyclobutanecarboxylic acid derivatives exhibit anti-inflammatory and antidepressant activities and liquid crystal properties [4]. Various thiazole derivatives have shown herbicidal, anti-inflammatory, antimicrobial, or antiparasitic activity [5]. However, the syntheses and physiochemical properties of 1,1,3-trisubstituted cyclobutane substituted thiazoles and their Schiff base derivatives have not been reported so far. These compounds, containing cyclobutane, thiazole, and Schiff base functions in their molecules seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful as ligands. The extensive synthetic possibilities of this heterocycle, due to the presence of several reaction sites, hold promise for the preparation of new and useful thiazole derivatives.

Since our ligand is not reported in the literature, this paper deals with the preparation and characterization of the complexes formed between the Schiff base ligand (see Figure 1) and cobalt(II), copper(II), nickel(II) and zinc(II) metal salts.

RESULTS AND DISCUSSION

The reaction steps for the synthesis of LH are given in Scheme 1. The first step is the synthesis of 1 by

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Contract Grant Sponsor: Firat University Research Fund.
Contract Grant Number: FÜNAF-300.
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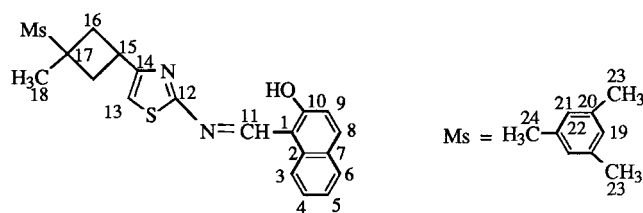


FIGURE 1 4-(1-Methyl-1-mesityl-3-cyclobutanyl)-2-(2-hydroxy-1-naphthylideneimino) thiazole; (LH).

the reaction of 1-phenyl-1-mesityl-3-(2-chloro-1-oxoethyl)cyclobutane with thiourea. In the second step, 2-hydroxy-1-naphthaldehyde and 4-(1-phenyl-1-mesitylcyclobutane-3-yl)-2-aminothiazole (**1**) were reacted to obtain 4-(1-phenyl-1-mesitylcyclobutane-3-yl)-2-(2-hydroxy-1-naphthylideneimino)thiazole (**2**) (LH); see Scheme 1.

IR, ^1H NMR, and ^{13}C NMR spectroscopy were used for the structural characterization of **1** and **2**, and the data obtained are given in the experimental section. Additional analytical data are tabulated in Tables 1 and 2.

In the IR spectrum of **1**, the most characteristic absorptions are at 3285 and 3310 cm^{-1} $\nu(-\text{NH}_2)$, 1604 cm^{-1} $\nu(\text{C}=\text{N})$ and 685 cm^{-1} $\nu(\text{C}-\text{S}-\text{C})$. Since there are no $\text{C}-\text{Cl}$ and $\text{C}=\text{O}$ bands in the IR spectra of the substance, these peaks imply that the formation of the compound is that expected from the formula given in Figure 1 and Scheme 1.

In the IR spectra of **2**, the most characteristic absorptions are at 1606 cm^{-1} $\nu(\text{C}=\text{N}$ in thiazole ring), 1625 cm^{-1} $\nu(\text{C}=\text{N}$ azomethine) and 657 cm^{-1} $\nu(\text{C}-\text{S}-\text{C}$ thiazole). The Schiff base (**2**) shows intramolecular hydrogen bonding ($\text{O}\cdots\text{H}-\text{N}$) by virtue of a broad absorption band within the $3150\text{--}3060\text{ cm}^{-1}$ range [6]. Detailed characteristic ^1H NMR and ^{13}C NMR resonances are given in the experimental section. The data obtained from elemental analyses, IR, and ^1H and ^{13}C NMR spectra of **1** and **2** are consistent with data expected from the formula shown in Scheme 1 and Figure 1.

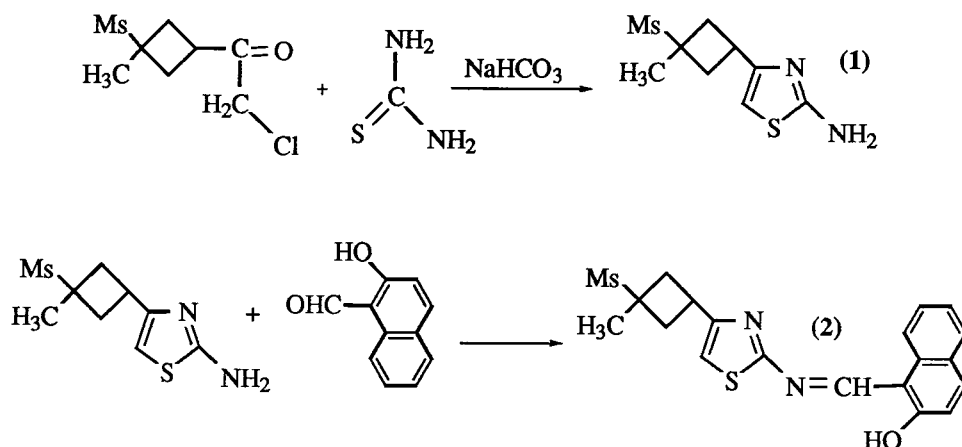
The ligand LH (see Figure 2 for structure), on reaction with Co(II), Cu(II), Ni(II), and Zn(II) salts, yielded complexes corresponding to the general formula $\text{M}(\text{L})_2$, and some of them contain water of hydration. The IR spectra of the prepared complexes have broad absorptions with a maximum in the ranges of $3470\text{--}3360\text{ cm}^{-1}$ for the Ni(II) complex and $3430\text{--}3350\text{ cm}^{-1}$ for the Zn(II) complex, confirming the presence water of hydration. This observation also agrees with the TGA results of the complexes mentioned. The analytical data for all these complexes are presented in the experimental section and in Tables 1 and 2.

The metal to ligand ratio of the Co(II), Cu(II), Ni(II), and Zn(II) complexes was found to be 1:2. The band observed as a broad band in the $3150\text{--}3060\text{ cm}^{-1}$ range and assigned to $\nu(\text{OH})$, disappeared upon formation of the complex compounds. The infrared band observed at 1625 cm^{-1} which is assigned to the $\nu(\text{C}=\text{N}$ azomethine) frequency in the free ligand is shifted to lower frequencies after complexation. The shift of the $\text{C}=\text{N}$ vibration to lower frequency ($1618\text{--}1615\text{ cm}^{-1}$) is due to N-metal coordination [7]. At the same time, the band observed at 1176 cm^{-1} in the free ligand that is assigned to the $\nu(\text{C}-\text{O})$ frequency is shifted to higher frequencies ($1190\text{--}1195\text{ cm}^{-1}$) after complexation. On the other hand, the band not seen in the ligand (**2**) but present in the complexes was assigned to $\nu(\text{M}-\text{C}=\text{N})$ [8], observed at 854 cm^{-1} for Co(II), 866 cm^{-1} for Cu(II), 862 cm^{-1} for Ni(II), and 858 cm^{-1} for Zn(II) complexes. These indicate that the $\text{C}-\text{OH}$ and $-\text{N}=\text{CH}-$ groups of the ligand are involved in the complexation. Despite their presence in the ligand and the possibility of complexation by the $\text{C}=\text{N}$ and sulphur atoms in the thiazole ring, the unchanged band positions for these groups in the IR spectra of the complexes indicate that the thiazole ring does not complex to the metal.

The Co(II), Cu(II), and Ni(II) complexes are paramagnetic, while the Zn(II) complex is diamagnetic, and their magnetic susceptibility values are 4.37 B.M., 1.82 B.M., and 3.29 B.M., respectively. Since the Co(II), Cu(II), and Ni(II) complexes are paramagnetic, their ^1H NMR spectra could not be obtained. ^1H NMR spectral data of the Zn(II) complex are given in the experimental section. As can be seen in the ^1H NMR spectra of the Zn(II) complex, there is no OH peak, as expected. This observation supports our IR interpretation.

The metal contents were determined by FAAS, and the TGA curves were studied in the temperature range $20\text{--}900^\circ\text{C}$. The weight losses in TGA and metal contents in the FAAS of the complexes have been found to be approximately the same as the percentages estimated stoichiometrically from their chemical formulas given in Table 1. All these complexes undergo complete decomposition to the corresponding metal oxides, CuO, Co_3O_4 , NiO, or ZnO.

The UV spectral data of the ligand and its complexes were obtained in two different solvents, ethanol and chloroform, and are compiled in Table 3. It is interesting that the data of both ligand and complexes obtained in ethanol solvent are closely similar to each other. In the visible region, expected $d \rightarrow d$ transitions were not observed. Absorptions in the UV region and at 420 nm may be the result of a coincidence of intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.



SCHEME 1

TABLE 1 The Colors, Formulas, Formula Weights, Melting Points, Yields, and Elemental Analyses Results of the Ligand and the Complexes

Compound	f.w. (g/mol)	Color	m.p. (°C)	Yield (%)	Elemental Analyses % Calculated (Found)			
					C	H	N	S
Ligand (2)	440.61	Yellow	199	76	76.33 (75.94)	6.41 (6.28)	6.36 (6.12)	7.28 (7.38)
C ₂₈ H ₂₈ N ₂ O ₂ S								
Co(L) ₂	938.14	Black	236	84	71.70 (71.59)	5.80 (6.02)	5.97 (5.80)	6.84 (7.03)
C ₅₆ H ₅₄ N ₄ O ₂ S ₂ Co								
Cu(L) ₂	942.75	Brown	262	91	71.35 (71.44)	5.77 (5.57)	5.94 (5.82)	6.80 (6.71)
C ₅₆ H ₅₄ N ₄ O ₂ S ₂ Cu								
Ni(L) ₂ · H ₂ O	955.93	Claret	258	87	70.36 (70.57)	5.91 (6.07)	5.86 (5.68)	6.71 (6.89)
C ₅₆ H ₅₆ N ₄ O ₃ S ₂ Ni								
Zn(L) ₂ · 1.5H ₂ O	971.63	Orange	269	90	69.23 (70.04)	5.91 (5.79)	5.77 (5.92)	6.60 (6.81)
C ₅₆ H ₅₇ N ₄ O _{3.5} S ₂ Zn								

TABLE 2 Characteristic IR Bands (cm⁻¹) of the Ligand and Complexes as KBr Pellets

Compound	O-H	H ₂ O	C-O	CH ₃ /CH ₂	C=N Thiazole	C=N Azometine	C-S-C Thiazole	μ _{eff} (B.M.)
Ligand, LH (2)	3107	—	1176	2978–2928	1606	1625	657	—
Co(L) ₂	—	—	1195	2978–2928	1608	1618	660	4.37
Cu(L) ₂	—	—	1195	2978–2928	1610	1615	658	1.82
Ni(L) ₂ · H ₂ O	—	3421	1190	2978–2928	1610	1615	658	3.29
Zn(L) ₂ · 1.5H ₂ O	—	3473	1195	2978–2928	1608	1616	660	dia

However, the spectral data obtained in chloroform of Co(II) and Ni(II) complexes showed bands at 530, 894, 928 and 520, 860, 920 and 1063 nm, respectively. For the Co(II) complex, the bands obtained at 530 nm and at 894 and 928 nm may be due to $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1(P)$ transitions in each tetrahedral field, respectively [9].

The low intensity bands at 860 and 920 nm, and 1063 nm for the Ni(II) complex, may originate from the $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{2g}$ transitions in the octahedral field [10].

According to the aforementioned results, an octahedral geometry for the Ni(II) complex and a tetrahedral geometry for the Co(II), Cu(II), and Zn(II) complexes are proposed [11].

EXPERIMENTAL

2-Hydroxy-1-naphthaldehyde and thiourea were purchased from Merck (Darmstadt) (pure) and used without further purification. 1-Phenyl-1-mesityl-3-(2-chloro-1-oxoethyl)cyclobutane was synthesized by the method described in the literature [12] and

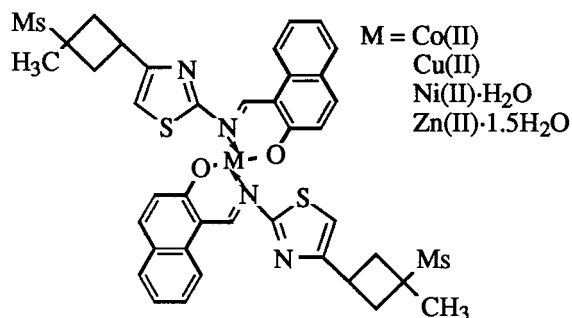


FIGURE 2 Suggested Structure of the Tetrahedral and Octahedral Complexes of the Ligand LH.

purified by the column chromatographic method prior to use.

The elemental analyses were determined on a LECO CHNSO-932 elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q Spectrometer. Electronic spectra were obtained on a CECIL CE 5502 UV-vis spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using $\text{Hg}[\text{Co}(\text{SCN})_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. Metal contents were determined by an Ati Unicam Model 929 Atomic Absorption Spectrophotometer (FAAS). Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance.

Synthesis of 4-(1-Phenyl-1-mesitylcyclobutane-3-yl)-2-aminothiazole (1)

To a solution of 0.76 g (10 mmol) of thiourea in 50 mL of absolute ethanol, a solution of 2.645 g (10 mmol) of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane in 20 mL of absolute ethanol was added dropwise at $60\text{--}70^\circ\text{C}$ with continuous stirring and with monitoring of the course of the reaction by the IR technique. Since monitoring of the carbonyl group of 1-phenyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane is easy, it is also easy to determine the reaction time. After the reaction was finished, the solution was made alkaline with an aqueous solution of NH_3 (5%) to cause the silky pale yellow solid substance 4-(1-methyl-1-mesitylcyclobutane-3-yl)-2-aminothiazole (1) to precipitate. The precipitate was filtered off, washed with aqueous ammonia solution and water several times, dried in air, and recrystallized from aqueous ethanol (1:3). The compound was found to be slightly soluble in methanol and ethanol, and soluble in common solvents such as CHCl_3 ,

acetone, THF, DMSO, or DMF. Characteristic ^1H NMR peaks (CDCl_3 , TMS, δ ppm): 1.49 (s, 3H, CH_3), 2.14 (s, 6H, CH_3), 2.21 (s, 3H, CH_3), 2.55 (d, 4H, $-\text{CH}_2-$ cyclobutane), 3.31 (quint, 1H, $>\text{CH}-$ in cyclobutane ring), 5.44 (s, 2H, $-\text{NH}_2$), 5.96 (s, 1H, $=\text{CH}-$ in thiazole ring), 6.70 (s, 2H, aromatics, in mesitylene). Characteristic ^{13}C NMR peaks (CDCl_3 , TMS, δ ppm): 170.53 (C_1), 102.56 (C_2), 157.86 (C_3), 32.73 (C_4), 40.62 (C_5), 42.43 (C_6), 32.24 (C_7), 130.30 (C_8), 127.41 (C_9), 126.96 (C_{10}), 126.98 (C_{11}), 23.38 (C_{12}), 26.45 (C_{13}).

Synthesis of 4-(1-Phenyl-1-mesitylcyclobutane-3-yl)-2-(2-hydroxy-1-naphthylideneimino)thiazole, (2)

To a hot ($60\text{--}70^\circ\text{C}$) solution of 1.43 g (10 mmol) of (1) in 30 mL of absolute ethanol, a hot ($60\text{--}70^\circ\text{C}$) solution of 0.86 g (10 mmol) of 2-hydroxy-1-naphthaldehyde in 20 mL of absolute ethanol was added dropwise with continuous stirring. The mixture was stirred for 1 hour more and left to stand overnight. The precipitate was filtered off, washed several times with cold ethanol, and dried at 110°C to constant weight. Yield, color, melting point, elemental analysis results, and characteristic IR bands (NaCl cell, cm^{-1}) are tabulated in Tables 1 and 2. The compound was found to be very soluble in DMF, THF, and CHCl_3 , moderately soluble in acetone and DMSO, and slightly soluble in ethanol and methanol. Characteristic ^1H NMR peaks (CDCl_3 , TMS, δ ppm): 1.53 (s, 3H, CH_3), 2.13 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 2.60 (d, 4H, $-\text{CH}_2-$ in cyclobutane ring), 3.94 (q, 1H, $>\text{CH}-$ in cyclobutane ring), 5.95 (s, 1H, $=\text{CH}-\text{S}$ in thiazole ring), 6.70 (s, 2H, aromatics, in mesitylene), 7.16–7.55 (m, 6H, aromatics), 8.02 (s, 1H, $-\text{N}=\text{CH}-$), 13.63 (s, 1H, OH). Characteristic ^{13}C NMR peaks (CDCl_3 , TMS, δ ppm): (161.06, 135.13, 130.27, 127.40, 127.00, 130.82, 131.31, 126.82, 129.75, 161.39, naphthalene ring carbons), 167.01 (C_{11}), 171.06 (C_{12}), 102.39 (C_{13}), 157.81 (C_{14}), 32.64 (C_{15}), 40.67 (C_{16}), 42.39 (C_{17}), 32.20 (C_{18}), 130.33 (C_{19}), 127.42 (C_{20}), 126.90 (C_{21}), 16.98 (C_{22}), 22.42 (C_{23}), 26.45 (C_{24}).

Synthesis of the Complexes

A quantity of 0.220 g (0.50 mmol) of the ligand was dissolved in 30–40 mL of absolute methanol. A solution of 0.25 mmol of the metal salt [$\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.063 g), $\text{Cu}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.050 g), $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.063 g), $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.046 g)] in 20 mL of methanol was added dropwise under continuous stirring. Every mixture was refluxed for

TABLE 3 Characteristic UV-vis Bands of The Ligand and Complexes

Compound	Solvent	$\lambda_{\max}$ $L \cdot mol^{-1} \cdot cm^{-1}$ (nm) ($\epsilon \times 10^4$)
HL (2)	EtOH	204 (9.0), 224 (5.4), 260, ^a 355 (1.1), 414 (2.5)
Co(L) ₂	EtOH	204 (1.2), 222, ^a 250, ^a 341 (1.5)
	CHCl ₃	300, 530, 894, 928
Cu(L) ₂	EtOH	204 (8.4), 220 (5.7), 240, ^a 333 (1.5), 423 (1.5)
	CHCl ₃	204 (1.8), 220 (1.3), 352 (2.0), 426 (3.1)
Ni(L) ₂ · H ₂ O	EtOH	204 (8.4), 220 (5.7), 240, ^a 333 (1.5), 423 (1.5)
Zn(L) ₂ · 1.5H ₂ O	EtOH	204 (1.8), 220 (1.3), 352 (2.0), 426 (3.1)

^aShoulder.

1 hour and left to stand overnight. The complexes precipitated as microcrystals and were filtered off and washed with cold ethanol and water several times, then dried in vacuo at 60°C. The cobalt complex is very soluble in acetone, CHCl₃, DMF, DMSO, and THF, and sparingly soluble in methanol and ethanol. The copper complex is very soluble in acetone, DMF, DMSO, THF, and CHCl₃, and sparingly soluble in methanol and ethanol. The nickel complex is very soluble in THF, CHCl₃, and DMF, and sparingly soluble in ethanol, methanol, and DMSO; the zinc complex is very soluble in CHCl₃ and DMSO, soluble in ethanol, and slightly soluble in methanol. Yield, color, melting point, elemental analysis results and characteristic IR bands (NaCl cell, cm⁻¹) are given in Tables 1 and 2.

Characteristic ¹H NMR peaks for the Zn(II) complex (CDCl₃, TMS, δ ppm): 1.49 (s, 6H, CH₃), 2.10 (s, 12H, CH₃), 2.21 (s, 6H, CH₃), 2.62 (d, 8H, -CH₂- in cyclobutane ring), 3.86 (q, 2H, >CH- in cyclobutane ring), 5.90 (s, 2H, =CH-S in thiazole ring), 6.72 (s, 4H, aromatics, in mesitylene), 7.12–7.52 (m, 12H, aromatics), 8.22 (s, 2H, azometine).

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