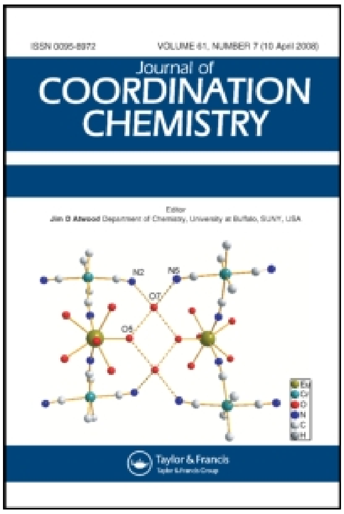

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A NEW CYCLOBUTANE SUBSTITUTED SCHIFF BASE LIGAND, SYNTHESIS OF ITS Cd(II), Co(II), Cu(II), Ni(II) AND Zn(II) COMPLEXES AND INVESTIGATION OF THEIR STRUCTURE

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A NEW CYCLOBUTANE SUBSTITUTED SCHIFF BASE LIGAND, SYNTHESIS OF ITS Cd(II), Co(II), Cu(II), Ni(II) AND Zn(II) COMPLEXES AND INVESTIGATION OF THEIR STRUCTURE

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A new, thiazole derivative ligand, 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(2-hydroxy-5-bromo benzylidenehydrazino) thiazole (LH), has been synthesized by the reaction of 2-hydroxy-5-bromobenzaldehyde, thiosemicarbazide and subsequently 1-phenyl-l-methyl-3-(2-chloro-1-oxoethyl) cyclobutane. Mononuclear complexes with a metal-ligand ratio of 1:2 have been prepared with Cd(II), Co(II), Cu(II), Ni(II) and Zn(II). The authenticity of the ligand and its complexes was established by elemental analyses, IR, ^{13}C and ^{1}H NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC).

Keywords: Cyclobutane; Thiazole; Schiff bases; Schiff base complexes

INTRODUCTION

Cyclobutanes, thiazoles and Schiff bases are of great importance for the preparation of various pharmaceuticals and used in many other fields of chemistry as starting materials. Three-Substituted cyclobutane carboxylic acid derivatives have anti-inflamatory and antidepressant activities [1,2], and liquid crystal properties [3], while various thiazole derivatives showed herbicidal [4], anti-inflamatory [5,6], antimicrobial [7] or antiparasitic

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activity [8]. However, the syntheses and chemical properties of 1,1,3-trisubstituted cyclobutane thiazoles and their Schiff base derivatives have not been reported so far. These compounds containing cyclobutane, thiazole and Schiff base functionality, seem to be suitable candidates for further chemical modifications and may be pharmacologically active.

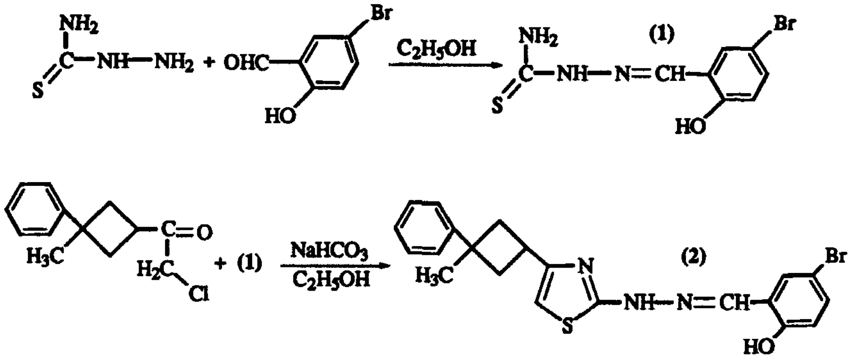
There have been a number of reports on Schiff bases and their transition metal complexes [9]. Thiazole and its derivatives have biological significance, *e.g.*, it is found in vitamin B_1 and in the coenzyme cocarboxylase. The penicillin molecule also contains a thiazolidine ring [10]. Two-Aminothiazoles are biologically-active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes. Substituted α-holaketones used in the production of our ligand are used for different purposes, especially in the synthesis of heterocyclic substances.

The ligand used in this work has three different and important properties of cyclobutane, thiazole and Schiff base characteristics. The extensive synthetic possibilities of this heterocycle due to the presence of several reaction sites hold promise for the preparation of new thiazole derivatives.

Since this ligand is not reported in the literature our paper deals with the preparation and characterization of the ligand as well as its complexes with cadmium(II), cobalt(II), copper(II), nickel(II), and zinc(II).

RESULTS AND DISCUSSION

The reaction steps for the synthesis of LH are given in Scheme 1. First is the synthesis of (1) from the reaction of thiosemicarbazide and 2-hydroxy-5-bromobenzaldehyde. In the second step, 2-hydroxy-5-bromobenzylide-



SCHEME 1

nethiosemicarbazone (1) and 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane were reacted to obtain (2) (abbreviated: LH), Scheme 1. Both reaction steps were carried out in ethanol. In every step, column chromatography was used to purify the compounds and analysis showed the substances sufficiently pure.

For the structural characterization of (1) and (2), IR, ^{1}H NMR and ^{13}C NMR were used and the data are given in the Experimental Section. Additional analytical data are given in Tables I–III.

In the IR spectrum of (1) the most characteristic absorptions are at 3285 and 3310 cm^{-1} v(—NH$_2$), 3182 cm^{-1} v(—NH—), 1625 cm^{-1} v(C=N azometine), 3131 cm^{-1} v(OH) and 1140 cm^{-1} v(C—O). Since there are no C=O absorptions in the IR spectrum of (1), these peaks indicate formation of the expected compound; the detailed ^{1}H NMR and ^{13}C NMR peaks are given in the Experimental Section. The IR, ^{1}H NMR and ^{13}C NMR spectra are consistent with the expected structure.

The characterization of the ligand (2) was also carried out by elemental analyses, IR, ^{13}C and ^{1}H NMR spectra and thermogravimetric analyses (TGA). In the IR spectrum of LH, characteristic bands appear at 3140 cm^{-1} v(O—H), 1600 cm^{-1} v(C=N in thiazole ring), 1625 cm^{-1} v(C=N azometine) and 1357 cm^{-1} v(C=O) as expected for the prepared substituted thiazole derivative. The TGA curve shows no residue of (2). ^{1}H NMR signal observed for the proton in C—OH on the ligand molecule disappeared upon addition of D$_2$O to the solution. Detailed ^{1}H NMR and ^{13}C NMR data are given in the Experimental Section. According to the elemental analyses, IR, ^{13}C and ^{1}H NMR results, the structure of the ligand is consistent with that shown in Figure 1.

The ligand LH, on interaction with metal salts yields complexes corresponding to the general formula M(L)$_2$. The analytical data for all prepared complexes are presented in Tables I–III.

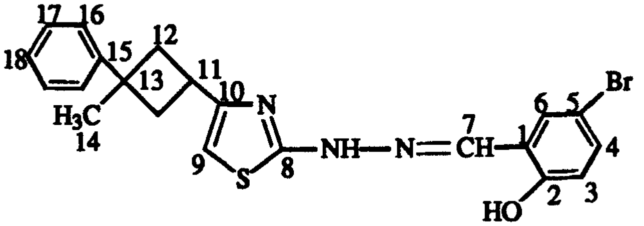


FIGURE 1 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidenehydrazino) thiazole.

TABLE I The colors, formulas, formula weights, melting points, yields and elemental analyses results of the ligand and the complexes

	F.W		*M.p*	*Yield*	*Elemental analyses % Calculated (found)*			
Compound	*g/mole*	*Color*	*°C*	*%*	*C*	*H*	*N*	*S*
(1)	274.15	Pale Yellow	241	94	35.05 (34.95)	2.94 (2.86)	15.33 (15.47)	11.70 (12.05)
Ligand **(2)** $C_{21}H_{20}N_3OSBr$	442.38	Yellow	201	62	57.02 (56.69)	4.56 (4.41)	9.50 (9.67)	7.25 (7.44)
$Cd(L)_2$ $C_{42}H_{38}N_6O_2S_2Br_2Cd$	995.16	Yellow	291	91	50.69 (50.17)	3.85 (3.59)	8.45 (8.39)	6.44 (6.34)
$Co(L)_2$ $C_{42}H_{38}N_6O_2S_2Br_2Co$	941.69	Light Brown	304 (dec.)	83	53.57 (53.00)	4.07 (3.81)	8.93 (8.77)	6.81 (7.19)
$Cu(L)_2$ $C_{42}H_{38}N_6O_2S_2Br_2Cu$	946.30	Dark Brown	261 (dec.)	86	53.31 (52.42)	4.05 (3.68)	8.88 (8.64)	6.78 (7.20)
$Ni(L)_2$ $C_{42}H_{38}N_6O_2S_2Br_2Ni$	941.46	Yellow	308 (dec.)	88	53.58 (53.15)	4.07 (3.90)	8.93 (8.73)	6.81 (6.42)
$Zn(L)_2$ $C_{42}H_{38}N_6O_2S_2Br_2Zn$	948.15	Yellow	292	92	53.21 (52.63)	4.04 (3.71)	8.86 (8.67)	6.76 (7.27)

TABLE II Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets

Compound	*O—H*	*C—O*	*C═N thiazole*	*C═N azometine*	*—NH$_2$*	*C—S—C thiazole*	*μ_{eff} (B.M.)*
(1)	3131	1140	–	1625	3285 and 3310	–	–
Ligand, LH (2)	3131	1140	1600	1625	3182 (NH)	655	–
Cd(L)$_2$	–	–	1600	1610	3182 (NH)	655	dia
Co(L)$_2$	–	–	1600	1604	3182 (NH)	655	4.13
Cu(L)$_2$	–	–	1600	1608	3182 (NH)	655	1.69
Ni(L)$_2$	–	–	1600	1594	3182 (NH)	655	2.92
Zn(L)$_2$	–	–	1600	1615	3182 (NH)	655	dia

TABLE III ^{1}H NMR spectra of the ligand and some complexes in DMSO-d$_6$ and in CDCl$_3$ in δ(ppm)

Substance	*—OH*	*—NH—*	*Aromatics*	*N═CH*
Ligand	12.4 (s, 1H) [b]	6.91 (s, 1H)	7.02–7.35 (m, 8H)	8.0 (s, 1H)
Cd(II)	–	6.88 (s, 2H)	7.10–7.35 (m, 16H)	8.35 (s, 2H)
Zn(II)	–	6.87 (s, 2H)	7.12–7.27 (m, 16H)	8.46 (s, 2H)

[b] Broad.

The metal to ligand ratio of all the complexes synthesized was found to be 1:2. The infrared band observed at 1625 cm^{-1} which is assigned to the v(C═N) frequency in the free ligand is shifted to lower frequency after complexation. The shift of the C═N vibration to lower frequencies (1615–1594 cm^{-1}) is due to N-metal coordination [11]. On the other hand, the band observed at 1140 cm^{-1} in the free ligand which is assigned to the v(C—O) frequency disappeared after complexation. At the same time, the band seen at 3131 cm^{-1} in (2), assigned to v(—OH) does not exist in the IR spectra of the complexes as expected for the complex formula in Figure 2. This indicates that the OH group of the ligand takes part in complexation. The band not seen in the ligand but present in the complexes was assigned to v(M—C═N), [12] observed at 864 cm^{-1} for Cd(II), 875 cm^{-1} for Co(II), 890 cm^{-1} for Cu(II), 876 cm^{-1} for Ni(II) and 873 cm^{-1} for Zn(II) complexes. This indicates that the —N═CH— group of the ligand is involved in complexation. The unchanged band positions of the C═N, —NH— and C—S—C groups in the IR spectra of the complexes indicate that these groups do not take part in complexation.

Since the Co(II), Cu(II) and Ni(II) complexes of the ligand are paramagnetic (4.13 B.M., 1.69 B.M. and 2.92 B.M., respectively), their ^{1}H NMR spectra could not be obtained. The Cd(II) and Zn(II) complexes are diamagnetic. Their ^{1}H NMR absorptions are given in Table III. The most notable trend in the data of Table III is the pronounced upfield shift of the azometine proton resonance in the complexes as compared with

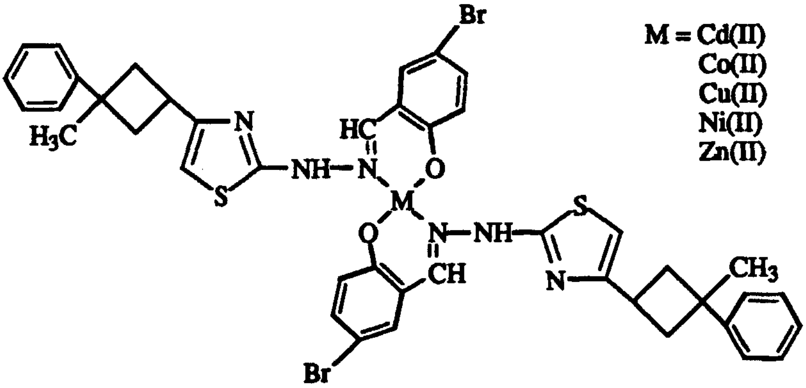


FIGURE 2 Suggested structure of the square-planar and tetrahedral complexes of the ligand LH.

the —C=N— resonance of the ligand. The —NH— resonances of the complexes are very slightly different than those of free ligand, indicating that the —NH— group of the ligand is not involved in complexation. The resonance due to the *ortho* hydroxy group (12.4 ppm) of the ligand disappears in the complexes indicating that substitution has taken place through the —OH of the Schiff base supporting our infrared interpretation. In the visible region, the Cu(II) complex exhibits a high intensity shoulder at ~460 nm and a weak broad shoulder at ~700 nm assignable to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ in a tetragonal field, respectively. Because the complexes were isolated as fine powders rather than single crystal, no structural determination using X-ray crystallography was carried out. However, the spectroscopic and magnetic data enable us to predict the possible structure for the metal complexes as shown in Figure 2. At higher temperatures, thermal studies of all the complexes show that these complexes decompose to the related metal oxides by loss of organic ligands.

According to the above results, a square-planar geometry for the Cu(II) and Ni(II), and a tetrahedral geometry for the Cd(II), Co(II) and Zn(II) complexes are proposed. The suggested structure of the complexes is shown in Figure 2.

EXPERIMENTAL

2-Hydroxy-5-bromosalicylaldehyde and thiosemicarbazide were purchased from Merck (Pure) and used without further purification. 1-phenyl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane was synthesized by the method described in the literature [13] and purified through column chromatograpy prior to use.

The elemental analyses were determined on a LECO CHINSO-932 elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets, ^{13}C and ^{1}H NMR spectra were recorded on a JEOL FX-90Q Spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature (20°C) using $Hg[Co(SCN)_2]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp melting point apparatus and checked by differential scanning calorimetry (DSC) and uncorrected. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance. Metal contents of the complexes were determined by an Ati Unicam (Model 929) atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in concentrated HCl and subsequent dilution with 0.01 M HCl.

Synthesis of 2-hydroxy-5-bromobenzylidenethiosemicarbazone (1)

To a solution of 0.91 g (10 mmole) of thiosemicarbazide in 50 mL of absolute ethanol, a solution of 2.01 g of 5-bromosalicylaldehyde in 20 mL of absolute ethanol was added dropwise at 60–70°C with continuous stirring. The solid product was filtered off, washed with water several times, dried in air and crystallized from aqueous ethanol (1 : 3). The compound was soluble in methanol, ethanol, $CHCl_3$, acetone, THF, DMSO or DMF. Characteristic ^{1}H NMR peaks ($CDCl_3$, TMS, δ ppm): 6.94 (s, 2H, $-NH_2$), 7.34 (s, 1H, —NH—), 8.17 (m, 3H, aromatic), 8.41 (s, 1H, —N=CH— in thiazole ring). Characteristic ^{13}C NMR peaks ($CDCl_3$, TMS, δ ppm): 122.81 (C_1), 155.76 (C_2), 118.65 (C_3), 133.64 (C_4), 111.36 (C_5), 128.84 (C_6), 139.11 (C_7), 178.29 (C_8).

Synthesis of the 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidenehydrazino)thiazole Ligand. LH (2)

To a suspension of 2.74 g (10 mmole) of (1) in 30 mL of absolute ethanol, a solution of 2.225 g (10 mmole) of 1-phenyl-l-methyl-3-(2-chloro-1-oxoethyl)-cyclobutane in 20 mL absolute ethanol was added dropwise with continuous stirring. The temperature was raised to around 60°C. Using IR for the C=O and C—Cl absorptions the reaction was run to completion. After completion the solution was made alkaline with an aqueous solution of NH_3 (5%) to separate the pale yellow solid, 4-(1-phenyl-l-methylcyclobutane-3-yl)-2-(2-hydroxy-5-bromobenzylidenethiosemicarbazone)thiazole (**2**). The precipitate was filtered, 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 I and II.The compound was very soluble in $CHCl_3$, and slightly soluble in common solvents such as methanol,ethanol, acetone, THF, DMSO or DMF. Characteristic ^1H NMR peaks ($CDCl_3$, TMS, δ ppm): 1.50 (s, 3H, CH_3), 2.41 – 2.62 (m, 4H, —CH_2— in cyclobutane ring), 3.54 (quint, 1H, > CH— in cyclobutane), 6.05 (s, 1H,=CH— in thiazole ring), 6.91 – 7.27 (m, 8H aromatic), 8.0 (s, 1H, N=CH—), 12.4 (s, 1H, —OH on salicylaldehyde ring)). Characteristic ^{13}C NMR peaks ($CDCl_3$, TMS, δ ppm): 119.87 (C_1), 155.13 (C_2), 117.32 (C_3), 130.33 (C_4), 109.87 (C_5), 127.06 (C_6), 131.41 (C_7), 167.10 (C_8), 99.12 (C_9), 152.70 (C_{10}), 37.55 (C_{11}), 38.02 (C_{12}), 39.00 (C_{13}), 29.18 (C_{14}), 142.20 (C_{15}), 123.63 (C_{16}), 124.17 (C_{17}), 123.80 (C_{18}).

Synthesis of the Complexes

A quantity of 0.442 g (1.0 mmole) of the ligand was dissolved in 30 – 40 mL of absolute methanol. A solution of 0.5 mmole of the metal salt [$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.134 g), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.1245 g), $Cu(CH_3COO)_2 \cdot H_2O$ (0.0998 g), $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.1245 g) or $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.092 g)] in 20 mL of methanol was added dropwise under continuous stirring. In the preparation of the Co(II) complex, nitrogen gas was bubbled through the solution. Every mixture was refluxed for 1 hour and left to stand overnight. In every case, the complexes were microcrystalline. The complexes were filtered, washed with cold ethanol and water several times and dried *in vacuo* at 60°C. All complexes were found to be soluble in DMSO, DMF, THF and $CHCl_3$. Yields, colors, melting points, elemental analyses and characteristic IR bands (NaCl cell, cm^{-1}) are given in Tables I and II.

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