

Synthesis and Characterization of a New Thiazole Schiff Base 5-Bromo-2-hydroxybenzylidene-2-aminobenzothiazole and Its Complexes with Co(II), Cu(II) and Ni(II)

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A new ligand 5-bromo-2-hydroxybenzylidene-2-aminobenzothiazole has been synthesized from 2-aminobenzothiazole and 5-bromosalicylaldehyde by condensation in ethanol. Metal complexes of the ligand were prepared from chloride salts of Co(II), Cu(II), and Ni(II) in ethanol. Characterization of the ligand and its complexes were carried out by microanalyses, magnetic susceptibility measurements, FT-IR, ^{13}C , ^1H NMR, and UV-Visible spectroscopy. It was suggested that two ligands with two water molecules coordinate to each metal atom by hydroxy oxygen and imino nitrogen to form high spin distorted octahedral complexes with Co(II), Ni(II) and Cu(II).

Key words: 2-aminothiazole, thiazole, 5-bromosalicylaldehyde, Co(II), Ni(II), Cu(II) complex, synthesis

Numerous Schiff bases [1,2,3] and their transition metal complexes [4,5,6], have been investigated by various techniques [7]. Thiazole and its derivatives has been found to be of biological significance, for example vitamine-B1 and coenzyme cocarboxylase contain the thiazole ring [8]. It is known that 2-aminothiazole is a biologically active compound with a broad range of activity and also it is an intermediate in the synthesis of antibiotics and dyes.

Metal complexes of sulphur-nitrogen chelating ligands have attracted considerable attention because of their interesting physicochemical properties, pronounced biological activities [9,10,11] and as models of the metalloenzyme active sites. It is well known that nitrogen and sulphur atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [12]. Thiazoles are known to possess antitubercular [13,14] antibacterial [15,16], fungicidal [17] hypotensive and hypothermic [18] activities. Therefore, it has been found interesting to study of a complex containing the thiazole moiety.

In our best knowledge, transition metal complexes of the 5-bromo-2-hydroxybenzylidene-2-aminobenzothiazole (LH) have not been synthesized. Therefore, we synthesized the complexes of Co(II), Ni(II) and Cu(II) of the LH (Figure 1).

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EXPERIMENTAL

5-Bromo-2-hydroxybenzaldehyde and 2-aminobenzothiazole were purchased from Merck and used without further purification. The ligand synthesized was crystallized from ethanol and its purity checked by IR, NMR and elemental analysis. The elemental analysis were made by LECO-CHNS 932 micro-analysis apparatus. IR spectra were taken using Mattson 1000 FT-IR spectrophotometer as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on Jeol FX-90Q spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance model MK1 at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_2]$ as calibrant. Diamagnetic correction was calculated from Pascal's constant. Melting points were determined on a Gallenkamp melting point apparatus. Electronic spectra were recorded on a Cecil 1000 UV-Vis Spectrophotometer in the quartz cell path length of 1 cm. Metal content of the complexes were determined by an Ati Unicam atomic absorption spectrophotometer model 929 in a solution prepared by decomposing the complexes in concentrated HCl and subsequent dilution with distilled water.

Synthesis of the ligand (LH): To a hot solution of 20 mmol (3.0040 g) 2-aminobenzothiazole in 30 ml absolute ethanol, 10 mmol (4.0020 g) of 5-bromo-2-hydroxybenzaldehyde dissolved in 30 ml hot ethanol was added dropwise with a continuous stirring. The mixture was further stirred and refluxed for two hours and left overnight. The precipitate was filtered, washed with cold ethanol several times and dried at 100°C to a constant weight. Yield, colour, melting point elemental analysis results and characteristic IR bands (KBr pellets, cm^{-1}) are given in Tables 1 and 2. The compound found to be soluble in CHCl_3 , THF, methanol, ethanol, DMSO, DMF, acetone and insoluble in diethylether, and water. Characteristic ^1H peaks are (CCl_4 TMS, δ ppm), 8.16 (s, $-\text{CH}=\text{N}$), 9.42 (s, $-\text{OH}$), 7.07 (s, $=\text{CH}-$ in thiazole ring). Aromatic protons appeared at about 7.4–7.9 as multiplets. C–OH signal at 9.42 ppm, disappeared upon addition of D_2O to the solution, indicating that it is an acidic proton. The characteristic ^{13}C NMR peaks are: (CCl_4 TMS, δ ppm), 112.3 (C_1), 160.6 (C_2), 136.6 (C_3), 118.4 (C_4), 131.9 (C_5), 132.5 (C_6), 162.4 (C_7), 166.3 (C_8), 152.4 (C_{14}). Anal. cal. for $\text{C}_{14}\text{H}_9\text{N}_2\text{SO}$ (333.21): C 50.47, H 2.72, N 8.41, S 9.62; found: C 50.59, H 2.70, N 8.36, S 9.31.

Synthesis of the complexes: 2 mmol of the ligand was dissolved in 30–40 ml of absolute ethanol, a solution of 1 mmol of the metal salt in 10 ml of ethanol was added dropwise to the ligand solution with continuous stirring and the mixture left to refluxed overnight. The pH of the solutions were adjusted to about pH 5–6 by adding the solution of Na_2CO_3 in ethanol. Then the volumes of the solutions were reduced to about 10 ml and complexes were precipitated in dry diethylether (1/10). The precipitate was filtered, washed with water and cold ethanol and then dried at room temperature. After that the precipitate was dissolved in 15 ml of CHCl_3 and precipitated from diethylether (1/10) and washed with ether several times, and then dried *in vacuo* at 60°C . The complexes are soluble in CHCl_3 , DMSO, DMF, acetone and slightly soluble in THF, methanol, ethanol and insoluble in water and diethylether. The yield, color, melting point, and characteristic IR bands as KBr pellets, are given in Tables 1 and 2. Anal. cal. for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4\text{Co}$ (759.38): C 44.29, H 2.26, N 7.38, S 8.45; found: C 44.23, H 2.55, N 7.70, S 8.25, for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4\text{Ni}$: (723.12): C 44.30, H 2.66, N 7.38, S 8.45; found: C 46.21, H 2.53, N 7.73, S 8.34; and for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{S}_2\text{O}_4\text{Cu}$: (727.95): C 44.02, H 2.64, N 7.33, S 8.39; found: C 44.22, H 2.43, N 7.56, S 8.87.

RESULTS AND DISCUSSION

The synthesis reaction of the ligand is given in Figure 1. In the first step the ligand was obtained by condensation of 2-aminobenzothiazole with 5-bromo-2-hydroxybenzaldehyde and was crystallized from cold ethanol. Then its purity was checked by FT-IR, ^1H and ^{13}C NMR and elemental analysis. In the second step coordination compounds were synthesized in dry ethanol by the reaction of metals halides with the ligand.

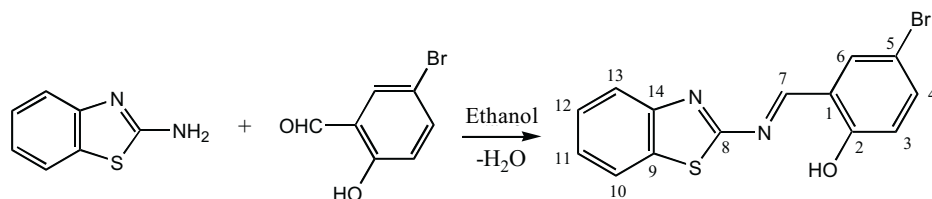


Figure 1. Scheme for the synthesis of the ligand, (LH).

IR spectra: Table 1 lists the major bands of the ligand and its complexes. Absence of C=O and NH₂ peaks in the spectra of the ligand point that the expected imino compound was formed by condensation from the 2-aminobenzothiazole and 5-bromo-2-hydroxybenzaldehyde and there was no residual starting material left in the ligand compound as well. In the IR spectra of the ligand's (LH) the most characteristic bands appeared at 3460 cm⁻¹ ν (O-H), 1612 cm⁻¹ ν (C=N thiazole ring), 1562 cm⁻¹ ν (C=N azomethine), and 1157 cm⁻¹ ν (C-O), 723 cm⁻¹ ν (C-S-C) and 631 cm⁻¹ ν (C-Br).

Table 1. Characteristic IR bands of the ligand and its complexes as KBr pellets (in cm⁻¹).

	Ligand (LH)	CoL ₂ ·2H ₂ O	NiL ₂ ·2H ₂ O	CuL ₂ ·2H ₂ O
ν (O-H)	3460 br	3450 br	3450 br	3450 br
ν (C=N) azomethine	1562 m	1515 m	1520 m	1516 s
ν (C=N) (thiazole ring)	1612 s	1635 s	1602 s	1635 s
ν (C-O)	1157 m	1138 m	1138 m	1138 m
ν (C-S-C)	723 w	716 w	724 w	716 w
ν (M-N)	–	550 w	535 w	571 w
ν (M-O)	–	529 w	521 w	521 w
ν (C-Br)	631 w	638 w	640 w	638 w

s (strong), m (medium), br (broad), w (weak).

The azomethine vibration of the ligand at 1562 cm⁻¹ was shifted to lower frequency after complexation, which is 1515, 1520, 1516 cm⁻¹ for Co(II), Ni(II) and Cu(II) complexes respectively. At the same time ν (C-O) band at 1157 cm⁻¹ in the free ligand was moved to lower frequency for about 10 cm⁻¹ after complexation, which means that the shifts are due to coordination of ligand to metal atom by azomethine nitrogen [19] and oxygen of hydroxyl groups. A broad band at 3450 cm⁻¹ was observed in the spectra of the complexes, due to the coordinated water molecule to the metal atoms in the complexes. The shift of ν (C-O) band at 1157 cm⁻¹ to lower energy suggests the weakening of ν (C-O) and formation of a more stronger bond between O-M. Practically unchanged ν (C=N) at 1612 and ν (C-S-C) 723 cm⁻¹ of the thiazole ring indicate that the thiazole group itself does not coordinate to metal atom by neither nitrogen nor sulphur atom. A weak band around 550 cm⁻¹ in the complexes is absent in the ligand spectrum assigned to ν (M-N) vibration. Another weak band, which appeared

in the spectra of the complexes at about 520 cm^{-1} was attributed to $\nu(\text{M}-\text{O})$ vibration. From these observations it is suggested that both the azomethine nitrogen and hydroxy oxygen are involved in the complexation reaction as donor atoms.

UV-Vis spectra and magnetic moments: The electronic spectrum of the Schiff base LH and its complexes were taken in acetone. Two very strong bands at 390 nm and 336 nm were observed in the spectra of the ligand, which is attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the aromatic ring and $\text{C}=\text{N}$ chromophore [20]. Cobalt complex has two bands the one at 490 as shoulder, and the other at 680 nm. Nickel complex also exhibits two absorption bands at 400 and 475 nm. On the other hand, the copper complex has one broad band at 450 nm. The magnetic moments 4.63 and 3.31 B.M. are observed for the Co(II) and Ni(II) complexes respectively. On the other hand, 1.67 B.M. is observed for the Cu(II) complex. Cu(II) complexes take a wide range of geometries, often with a low symmetry and in most geometries the electronic spectra exhibit a very broad band with maximum, which contains all the expected transitions [21]. Thus, electronic spectrum of the Cu(II) is of little value in structure assignment. However, the UV-visible spectra of the Cu(II) complex has a broad band at 450 nm, which is tailing into the visible region of the spectrum (up to 800 nm), assigned to charge-transfer band of distorted octahedral Cu(II) complex [22]. This tailing suggests that d-d transitions of the complex is mixed with the charge transfer band. Therefore, electronic spectrum of the Cu(II) complex is not informative for structure assignment. However, the structure of the complex was tentatively assigned to octahedrally distorted geometry from the elemental analysis results. The magnetic moment of the Co(II) and Ni(II) complexes at room temperature falls in the range of 4 to 5 B.M and 2.9 to 3.3 B.M. (Table 2), which is characteristic for mononuclear high spin octahedral complexes [23,24] (Figure 2).

The UV-visible spectra of the Co(II) complex show two bands, at 490 and 680 nm, which may be assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{1g}(\text{P})$ transitions in octahedral complexes. The electronic spectra of the Ni(II) complex presents two bands: one at 400 and the other at 475 nm, which might be assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ transitions respectively. From these transitions of

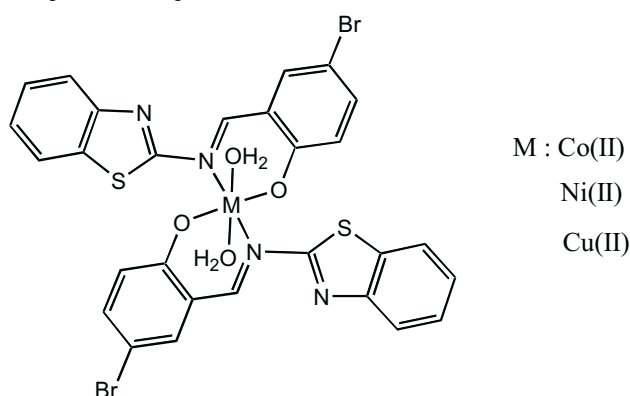


Figure 2. Suggested structure of the Co(II), Ni(II) and Cu(II) complexes.

the Ni(II) complex and the magnetic moment measurements the structure of the Ni(II) complex can be assigned to distorted octahedral geometry with two moles of water on the z axes of the cartesian coordinate.

Table 2. Formulas, formula weights, colors, melting points (Ni(II) and Co(II) complexes decompose over 230°C), yields, metal contents of the ligand and its complexes with transition metals of Co(II), Ni(II) and Cu(II).

Compounds	FW g/mole	Color	M.p. (°C)	Yield %	% Metal Calc. (found)
LH					–
C ₁₄ H ₉ N ₂ SO	333.21	Orange	183.4	76	–
CoL ₂ ·2H ₂ O					7.76
C ₂₈ H ₂₀ N ₄ S ₂ O ₄ Co	759.38	Orange	Dec >330	65	(8.05)
NiL ₂ ·2H ₂ O					7.73
C ₂₈ H ₂₀ N ₄ S ₂ O ₄ Ni	723.12	Orange	Dec >330	58	(7.93)
CuL ₂ ·2H ₂ O					8.32
C ₂₈ H ₂₀ N ₄ S ₂ O ₄ Cu	727.95	Orange-green	291.1	70	(8.53)

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