

# Transition Metal(II) Complexes of a Novel Symmetrical Benzothiazole-Based Ligand: Synthesis, Spectral/Structural Characterization and Fluorescence Properties

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Received: 7 August 2014 / Accepted: 4 September 2014 / Published online: 13 September 2014  
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**Abstract** 2,6-bis (benzothiazol-2-yl)-4-(*tert*-butyl) phenol ligand (HL) derived from *o*-aminothiophenol and 4-*tert*-butyl-2,6-diformylphenol was synthesized and characterized by using elemental analysis, FTIR, X-ray crystallographic analysis,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR and UV–vis spectra. Its complexes with Cu (II), Ni (II) and Co (II) were prepared and isolated as solid products and characterized by elemental analysis, spectral techniques as well as magnetic susceptibility. The FTIR spectra showed that the benzothiazole-based ligand under investigation behaves as a bidentate ligand. The UV–vis spectra and magnetic moment data suggested an octahedral geometry around Ni (II) and Co (II) complexes, and tetragonal geometry for Cu (II) complex. Moreover, the evaluation of absorption and emission properties of the ligand and its complexes were carried out in different solvents. The ligand and its complexes showed absorption maxima in the range of 275 – 432 nm, and emission maxima from 367 to 581 nm in toluene, tetrahydrofuran and ethyl acetate.

**Keywords** Benzothiazole · Metal complex · Fluorescence · X-ray structure

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## Introduction

The thiazole units are found in many naturally occurring compounds [1–3]. Vitamin B<sub>1</sub>, penicillin and coenzyme co-carboxylase contain the thiazole ring [4, 5]. Thiazoles are used as neuroprotectors [6, 7] and antioxidants [8, 9]. Thiazole derivatives are used in inorganic chemistry for building polydentate ligands [1, 10]. Benzothiazole are bicyclic ring system with multiple applications. It is an aromatic heterocyclic compound with the chemical formula C<sub>7</sub>H<sub>5</sub>NS [11]. Benzothiazoles consist of a 5-membered 1,3-thiazole ring fused to a benzene ring [11]. Benzothiazoles constitute an important class of compounds with profound interest to medicinal/industrial chemists as compounds bearing the benzothiazolyl moiety [12]. They exhibit diverse biological properties such as antitumour [13, 14], antimicrobial [15], cytotoxic [16], antiglutamate/antiparkinson [17], broad spectrum Ca<sup>2+</sup> channel antagonist [18], inhibition of enzymes [12]. Benzothiazole is an important class of N,S-containing heterocycles [15]. Metal complexes of N and S chelating ligands have attracted considerable attention because of their interesting physicochemical properties and pronounced biological and pharmacological activities. The N and S atoms play a key role in the coordination of metals at the active sites of various metallobiomolecules. Transition metal ions play a vital role in a vast number of widely different biological processes [15, 19, 20]. Moreover, the activity can be enhanced when the biologically active ligand is coordinated to a transition metal ion. Metal complexes of ligands derived from heterocyclic compounds containing nitrogen, sulfur and/or oxygen as ligand atoms are of interest as simple structural models of more complicated biological systems [19]. Recent years, many complexes of transition metal ions Cu (II) [15, 16, 21–26], Ni (II) [16, 23, 24, 27–29], Co (II) [23, 27–29] have been reported. Moreover, benzothiazole derivatives and their metal complexes have been studied because of their fluorescent and

luminescent properties [21, 30–33] and the possibility to give rise to supramolecular arrangements [34, 35].

In this work the benzothiazole-based ligand, HL, and its Cu (II), Ni (II) and Co (II) transition metal complexes were synthesized, characterized and their fluorescence features were determined in different solvents. The compounds were characterized by elemental analysis, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques. In addition, the structure of the ligand has been determined by X-ray crystallographic analysis.

## Experimental

### Reagents and Apparatus

All chemicals used in this study were of the purest grade and purchased from Aldrich and used without further purification. Solvents used for the reactions were purified and dried by conventional methods [36]. Elemental analyses (C, H, N and S) were performed on a Leco CHNS model 932 automatic elemental analyzer. Fourier transform infrared spectra were recorded on a Bio-Rad-Win-IR spectrophotometer applying KBr discs in the range of 4,000–400  $\text{cm}^{-1}$ . Electronic absorption spectra in the visible and ultraviolet regions were measured on a Shimadzu 1,601 PC spectrophotometer (Tokyo, Japan). The magnetic susceptibility was determined with a magnetic susceptibility balance 436 Devon Park Drive (USA) using Hg [Co (SCN)<sub>4</sub>] as a calibrant. Nuclear magnetic resonance spectra were carried out on a Bruker 300 MHz Ultrashield TM NMR instrument, using deuterated chloroform ( $\text{CDCl}_3$ ) as a solvent. All fluorescence measurements were undertaken by using Varian-Carry Eclipse spectrofluorimeter (Mulgrave, Australia). X-ray diffraction analysis was performed by a Bruker SMART BREEZE CCD diffractometer.

### Synthetic Procedure

#### Synthesis of Ligand (HL)

The benzothiazole-based ligand (HL) was prepared by 2:1 condensation reaction between *o*-aminothiophenol and 4-*tert*-butyl-2, 6-diformylphenol. A hot anhydrous ethanolic solution of *o*-aminothiophenol (1 mmol; 0.11 mL) and 4-*tert*-butyl-2, 6-diformylphenol (0.5 mmol; 103 mg) was refluxed for *ca.* 24 h. Then the solvent was reduced to one third of its volume and the resulting solution was cooled to room temperature. The orange solid product formed (Scheme 1) was removed by filtration and recrystallised from butanol. Orange, yield was 160 mg (77 %), Mp 245 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_5\text{S}_2$  (416,56 g/mol): C, 69.20; H, 4.84; N, 6.72; S, 15.40. Found: C, 68.98; H, 4.84; N, 6.69; S, 15.40 %. Selected IR data (KBr,  $\nu\text{ cm}^{-1}$ ):  $\sim$ 3,450  $\nu$  (OH), 3,054  $\nu$  (C-H<sub>aromatic</sub>),

2,941  $\nu$  (C-H<sub>aliphatic</sub>), 1,621  $\nu$  (C=N<sub>thiazole</sub>), 1,495  $\nu$  (C=C), 1,103  $\nu$  (C-O<sub>phenolic</sub>), 752  $\nu$  (C-S-C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ =14.01 (bs, 1H, OH), 8.31 (bs, 2H, Ar-H), 8.12 (d, J=7.9 Hz 2H, Ar-H), 7.99 (d, J=7.0 Hz, 2H, Ar-H), 7.56 (dt, J=7.0 Hz, 2H, Ar-H), 7.45 (dt, J=7.9 Hz, 2H Ar-H), 1.50 (s, 9H, *tert*-but) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  =154.0, 151.6, 142.3, 134.4, 128.6, 126.2, 125.2, 122.5, 121.5, 119.4, 34.6, 31.5 ppm.

### Synthesis of Transition Metal Complexes

Cu (II), Ni (II) and Co (II) complexes were prepared by mixing a hot butanolic solution (20 mL) of the ligand (0,5 mmol, 208 mg) with metal salts (0,5 mmol), namely,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (85 mg),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (119 mg) and  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  (83 mg) in 10 mL butanol. The mixture was stirred and heated to reflux *ca.* 20 h. The solution was concentrated. The resultant products were collected by filtration, washed with hot butanol and diethylether. The obtained solid was dried under vacuum at 80 °C overnight (Scheme 2).

#### [CuHLCl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O

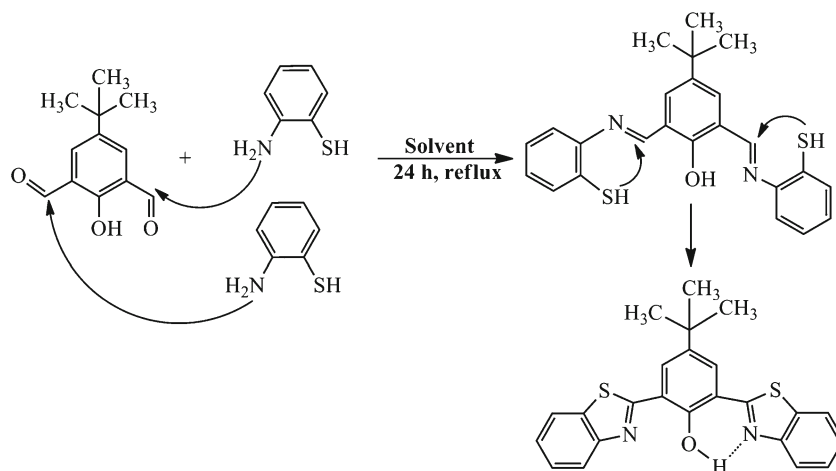
The dark brown product is soluble in dimethylsulfoxide, *N,N'*-dimethylformamide. Yield 180 mg (58 %); Mp: >300 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{CuN}_2\text{O}_5\text{S}_2$  (623,07 g/mol): C, 46.26; H, 4.53; N, 4.50; S, 10.29. Found: C, 46.26; H, 4.39; N, 4.52; S, 10.34 %. Selected IR data (KBr,  $\nu\text{ cm}^{-1}$ ): 3,449  $\nu$  (OH/H<sub>2</sub>O), 3,054  $\nu$  (C-H<sub>aromatic</sub>), 2,957  $\nu$  (C-H<sub>aliphatic</sub>), 1,604  $\nu$  (C=N<sub>thiazole</sub>), 1,491  $\nu$  (C=C), 1,130  $\nu$  (C-O<sub>phenolic</sub>), 752  $\nu$  (C-S-C), 521  $\nu$  (M-O), 428  $\nu$  (M-N); UV-Vis [ $\lambda$  (nm)]: 684, 424, 284, 212;  $\mu_{\text{eff}}$ , 1.88 BM,  $\Lambda_o$  ( $\text{S cm}^2\text{ mol}^{-1}$ ) 6.10 (Scheme 2).

#### [NiHLCl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O

The green product is soluble in dimethylsulfoxide, *N,N'*-dimethylformamide. Yield 190 mg (63 %); Mp: >300 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{25}\text{Cl}_2\text{NiN}_2\text{O}_4\text{S}_2$  (600,2 g/mol): C, 48.03; H, 4.37; N, 4.67; S, 10.68. Found: C, 48.09; H, 4.18; N, 4.66; S, 10.64 %. Selected IR data (KBr,  $\nu\text{ cm}^{-1}$ ):  $\sim$ 3,500  $\nu$  (OH/H<sub>2</sub>O), 3,057  $\nu$  (C-H<sub>aromatic</sub>), 2,957  $\nu$  (C-H<sub>aliphatic</sub>), 1,607  $\nu$  (C=N<sub>thiazole</sub>), 1,499  $\nu$  (C=C), 1,125  $\nu$  (C-O<sub>phenolic</sub>), 753  $\nu$  (C-S-C), 508  $\nu$  (M-O), 422  $\nu$  (M-N); UV-Vis [ $\lambda$  (nm)]: 448, 282, 262, 220;  $\mu_{\text{eff}}$ , 3.01 BM,  $\Lambda_o$  ( $\text{S cm}^2\text{ mol}^{-1}$ ) 4.71 (Scheme 2).

#### [CoHLCl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O

The dark green product is soluble in dimethylsulfoxide, *N,N'*-dimethylformamide. Yield 175 mg (57 %); Mp: >300 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{CoN}_2\text{O}_5\text{S}_2$  (618,46 g/mol): C, 46.61; H, 4.56; N, 4.53; S, 10.37. Found: C, 46.65; H, 4.47;

**Scheme 1** Synthetic route of the ligand (HL)

N, 4.58; S, 10.35 %. Selected IR data (KBr,  $\nu$   $\text{cm}^{-1}$ ):  $\sim 3,500$   $\nu$  (OH/H<sub>2</sub>O), 3,063  $\nu$  (C-H<sub>aromatic</sub>), 2,950  $\nu$  (C-H<sub>aliphatic</sub>), 1,609  $\nu$  (C=N<sub>thiazole</sub>), 1,492  $\nu$  (C=C), 1,118  $\nu$  (C-O<sub>phenolic</sub>), 752  $\nu$  (C-S-C), 502  $\nu$  (M-O), 433  $\nu$  (M-N); UV-Vis [ $\lambda$  (nm)]: 674, 434, 376, 286, 214;  $\mu_{\text{eff}}$ , 3.99 BM,  $\Lambda_o$  ( $\text{Scm}^2\text{mol}^{-1}$ ) 23.6 (Scheme 2).

#### X-Ray Structure Determination

For the crystal structure determination, the single-crystal of the ligand (HL) was used for data collection on a Bruker SMART BREEZE CCD diffractometer. The graphite-monochromatized MoK $\alpha$  radiation ( $\lambda=0.71073$  Å) and oscillation scans technique with  $\Delta\omega=5^\circ$  for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with  $F^2 > 2\sigma(F^2)$ . Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using Bruker SAINT (Bruker AXS Inc, 2012) software [37]. The structures were solved by direct methods using

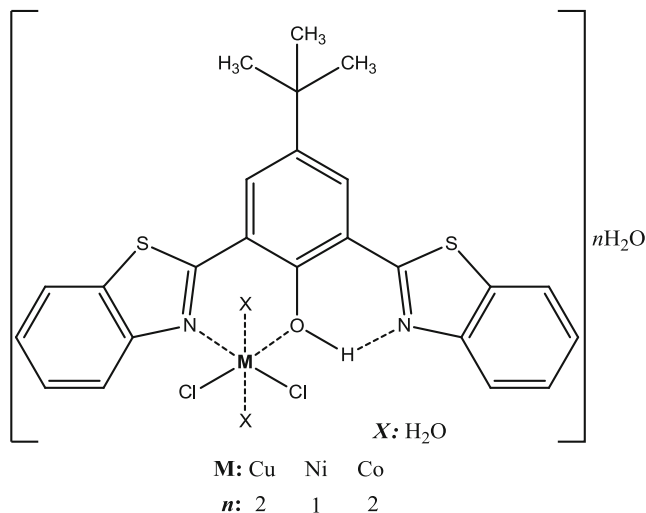
SHELXS-97 [38] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [38]. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. *Crystal data for ligand (HL)*: C<sub>24</sub>H<sub>20</sub>ON<sub>2</sub>S<sub>2</sub>; crystal system, space group: monoclinic,  $P2_1/n$ ; (no:14); unit cell dimensions:  $a=13.6400$  (6),  $b=7.8969$  (4),  $c=19.1847$  (9) Å,  $\alpha=90$ ,  $\beta=92.721$  (2),  $\gamma=90^\circ$ ; volume: 2064.13 (4) Å<sup>3</sup>;  $Z=4$ ; calculated density: 1.34 g cm<sup>-3</sup>; absorption coefficient: 0.276 mm<sup>-1</sup>;  $F(000)$ : 872;  $\theta$  range for data collection 1.8–26.4°; refinement method: full-matrix least-square on  $F^2$ ; data/parameters: 3271/267; goodness-of-fit on  $F^2$ : 1.040; final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1=0.046$ ,  $wR_2=0.111$ ;  $R$  indices (all data):  $R_1=0.064$ ,  $wR_2=0.122$ ; largest diff. peak and hole: 299 and -0.240 e Å<sup>-3</sup>. An ORTEP plot of the ligand is shown in Fig. 1.

#### Results and Discussion

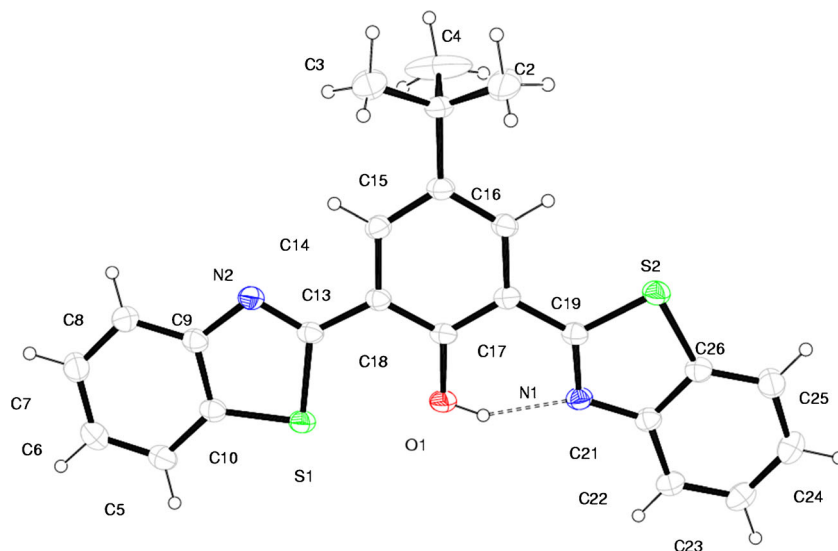
The ligand and its metal complexes are stable at room temperature. The ligand is soluble in common organic solvents such as 1-propanol, n-butanol and chloroform, but its metal (II) complexes are sparingly soluble in common organic solvents but soluble in DMF and DMSO. The analytical, physical properties and molar conductance data of the complexes are given in “Experimental Section”. Elemental analysis indicates that the found and calculated values were within acceptable limits ( $\pm 0.5$ ).

#### Molar Conductance

The molar conductance data of the metal (II) complexes measured in DMF for 0.001 M solutions are given in “Experimental Section”. The values fall in the range of 4.71–23.6  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , which is the expected range for the complexes

**Scheme 2** Suggested possible structures of the metal complexes

**Fig. 1** ORTEP view of the ligand (HL) showing the atom numbering scheme. Ellipsoids represent thermal displacement parameters at the 40 % probability level. Dashed line indicates H bonding geometry



to behave as non-electrolytes [39]. Thus, the present complexes are non-electrolytic in nature as evidenced by the involvement of chloride in coordination. This result was further confirmed from the chemical analysis of  $\text{Cl}^-$  ion, not precipitated by addition of  $\text{AgNO}_3$ .

#### Infrared Spectral Studies

In order to characterize the binding mode of the Schiff base to the metal ion in the complexes, the IR spectrum of the free ligand was compared with the spectra of the metal complexes. The characteristic IR bands for the synthesized ligand and its transition metal (II) complexes were listed in “Experimental Section”. The ligand shows broad band at  $\sim 3,450\text{ cm}^{-1}$  attributed to free  $\nu(\text{O-H})$  vibrations [23, 40]. The free ligand shows a sharp intense band at  $1,621\text{ cm}^{-1}$  assigned to the  $\nu(\text{C=N})$  of the benzothiazole ring [41, 15]. The azomethine of benzothiazole vibration of the ligand at  $1,616\text{ cm}^{-1}$  shifted to  $1,604\text{--}1,609\text{ cm}^{-1}$  after complexation, confirming the formation of a bond from the benzothiazole ring nitrogen to the metal. A sharp intense band at  $1,103\text{ cm}^{-1}$  in the ligand is assigned to  $\nu(\text{C-O})$ , which has shown positive shift of about  $15\text{--}27\text{ cm}^{-1}$  in all the complexes indicating the coordination of  $-\text{OH}$  to the metal ion upon complexation [41]. The metal (II) complexes also show a broad band between at  $3,450\text{--}3,500\text{ cm}^{-1}$  due to presence of water molecules in the complexes [40, 42]. Further, the non-ligand bands in the region  $502\text{--}521\text{ cm}^{-1}$  and  $422\text{--}433\text{ cm}^{-1}$  are due to the formation of  $\text{M-O}$  and  $\text{M-N}$  bonds, respectively [40, 41, 43]. In conclusion, these data suggest a NO bidentate behavior of the ligand. Noninvolvement of sulfur of the benzothiazole in coordination is assumed in all these complexes, which is in accordance with earlier reports [44] on the benzothiazole complexes with various transition metal

ions, this is because the sulfur is a poor Lewis base compared to nitrogen in the benzothiazole [23].

#### NMR Spectral Studies

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the ligand were carried out at room temperature in  $\text{CDCl}_3$  and the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data are listed in “Experimental Section”. In the  $^1\text{H}$  NMR spectrum of the ligand exhibits singlet signal in the 14.01 ppm which are attributed to the azomethine group ( $-\text{CH}=\text{N}-$ ) proton [43]. Spectrum of the ligand shows other signals at 8.31 (bs, 2H, Ar-H), 8.12 (d,  $J=7.9\text{ Hz}$ , 2H, Ar-H), 7.99 (d,  $J=7.0\text{ Hz}$ , 2H, Ar-H), 7.56 (dt,  $J=7.0\text{ Hz}$ , 2H, Ar-H), 7.45 (dt,  $J=7.9\text{ Hz}$ , 2H Ar-H) ppm for aromatic protons and 1.50 (s, 9H) *tert*-butyl protons. The  $^{13}\text{C}$  NMR spectrum of the ligand displayed characteristic signal at 154.0 ppm was due to azomethine carbon of the benzothiazole ring. Moreover, the spectrum of the ligand showed peaks in the region of 151.6–31.5 ppm (151.6, 142.3, 134.4, 128.6, 126.2, 125.2, 122.5, 121.5, 119.4, 34.6 and 31.5 ppm) due to aromatic and aliphatic carbons.

#### Magnetic Susceptibility and Absorption Spectral Studies

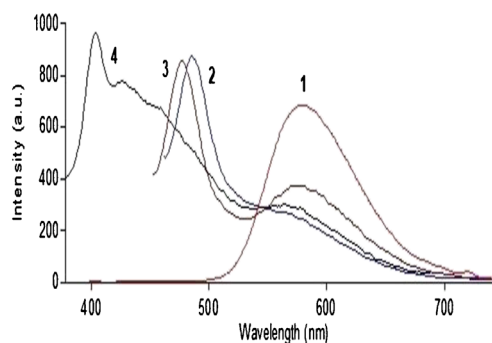
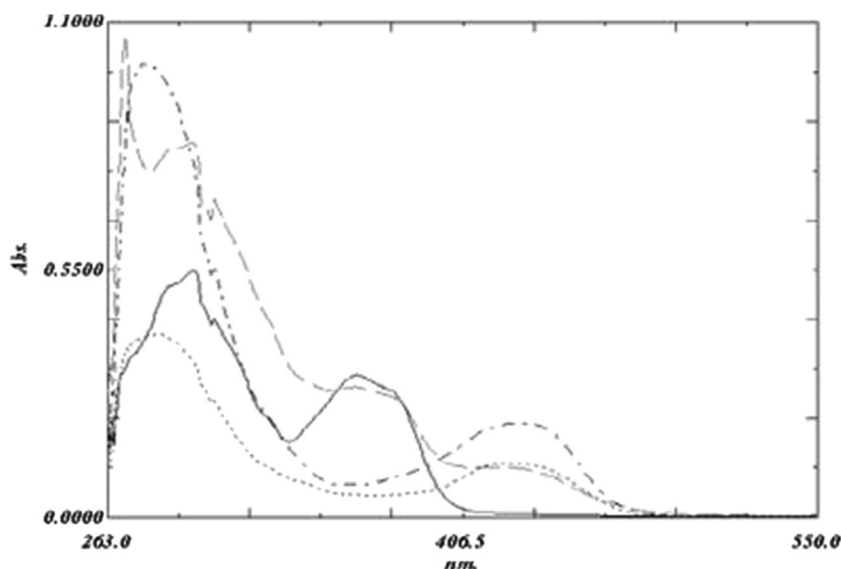
The magnetic moments of the complexes recorded at room temperature for the Cu (II), Ni (II) and Co (II) complexes are 3.99, 3.01 and 1.88 BM, respectively. Electronic absorption spectra of all the compounds were recorded in DMF solution over the range 200–800 nm at room temperature. The electronic absorption spectra provides reliable information about the ligand arrangement in transition metal complexes. The electronic spectra of the free ligand exhibits absorption bands at 218 and 284 nm, which are due to the intraligand  $\pi\text{-}\pi^*$  transitions, these bands remain almost unchanged in the spectra of complexes [23, 45]. Absorptions in the 362 nm is attributed to the  $n\text{-}\pi^*$  transition associated with azomethine,

the bathochromic shift of this absorption upon complexation is due to the donation of a lone pair of electrons to the metal ion, indicating the coordination of azomethine nitrogen of benzothiazole ring [41, 45]. The bands at 458 and 484 nm can be assigned to the transition within the molecule, essentially an intramolecular charge transfer interaction [16]. [CoHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O complex possesses a magnetic moment of 3.99 BM, which is in agreement with values reported for three unpaired electrons in an octahedral environment. The lowest energy band at 674 nm was due to  $^4T_{1g} \rightarrow ^4A_{2g}$  and broad band near 434 nm were assigned to  $^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$  transition, supporting an octahedral geometry for the complex [41, 42, 45, 46]. However, [NiHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O exhibits a magnetic moment of 3.01 BM, consistent with octahedral geometry [41, 45]. The electronic spectrum of [NiHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O displayed d-d transitions around 448 nm, assignable to  $^3A_{2g} (F) \rightarrow ^3T_{1g}$  transition, indicating an octahedral geometry. The [CuHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O complex in the present study shows a  $\mu_{\text{eff}}$  value of 1.88 B.M., corresponding to one unpaired electron [45, 47, 48]. The absorption spectrum of this complex exhibits weak d-d electronic band centred at 684 nm, assignable to  $^2E_g \rightarrow ^2T_{2g}$  transition [41, 43, 45]. Absorptions in this region are typical of species with distorted octahedral geometry around the Cu (II) ions [49–51].

#### Fluorescence Features

The absorption and emission properties of the benzothiazole-based ligand and its complexes with Cu (II), Ni (II) and Co (II) were investigated in toluene, tetrahydrofuran (Figs. 2 and 3) and ethylacetate and the results obtained are summarized in Table 1.

**Fig. 2** Absorption spectra of Ligand (HL) (—) ( $1 \times 10^{-5}$  M); [CuHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (—) ( $1 \times 10^{-5}$  M) [NiHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (.....) ( $1 \times 10^{-5}$  M); and [CoHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (—) ( $1 \times 10^{-5}$  M) in tetrahydrofuran



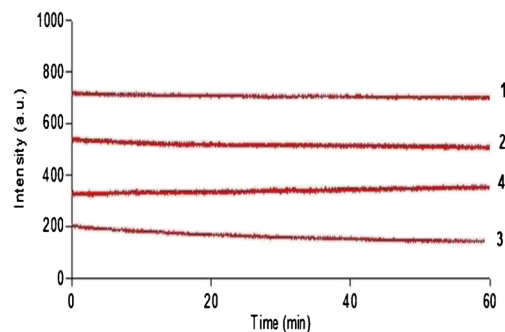
**Fig. 3** Fluorescence spectra of Ligand (HL) (1), [CuHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (2), [NiHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (3) and [CoHLC<sub>l</sub>Cl<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (4) in tetrahydrofuran at  $1 \times 10^{-5}$  M

The benzothiazole-based ligand has two absorption maxima in all the solvents studied; the first one is between 297–298 nm and the second one is between 363–367 nm. For the metal complexes derived from the ligand, while the first absorption maxima appeared in the same region, the second absorption maxima shifted to longer wavelengths between 417–432 nm, presumably due to the complete transfer of the electron from the ligand to the metal ions. The extinction coefficients at the shorter absorption maxima are higher than the extinction coefficients at the longer absorption maxima for ligand and all the complexes.

While the ligand displayed one emission maxima between 577–581 nm, complexes have two emission bands, the first one is between 367–486 nm, and the second one is between 539–578 nm (Table 1). The second emission maxima was blue shifted as the polarity of the solvent increased from toluene to ethyl acetate for all the compounds studied. The emission maxima of the complexes were observed in shorter wavelength in comparison to the emission maxima of the ligand in all

**Table 1** Absorption and emission maxima,  $\lambda$  (nm); molar extinction coefficients,  $\epsilon$  ( $\text{l mol}^{-1} \text{cm}^{-1}$ ); Stokes' shifts,  $\Delta\lambda$  (nm); singlet energies,  $E_s$  (kcal  $\text{mol}^{-1}$ ); and fluorescence quantum yields,  $\Phi$  of ligand (HL),  $[\text{CuHLCI}_2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{NiHLCI}_2 (\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  and  $[\text{CoHLCI}_2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  in toluene, tetrahydrofuran and ethylacetate

Compound	Solvent	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{abs}}$	$\epsilon_{\text{max}}^1$	$\epsilon_{\text{max}}^2$	$\epsilon_{\text{max}}^3$	$\lambda_{\text{max}}^{\text{ems}}$	$\lambda_{\text{max}}^{\text{ems}}$	$\lambda_{\text{max}}^{\text{ems}}$	$\Delta\lambda$	$E_s^1$	$E_s^2$	$\Phi$
(1)	Ligand (HL)	298	367	—	58,370	32,280	—	—	—	—	214	—	49.1	0.1442
	Toluene	298	364	—	54,790	31,650	—	—	—	—	215	—	49.3	0.0676
	Tetrahydrofuran	297	363	—	49,560	28,670	—	—	—	—	214	—	49.5	0.0713
(2)	Ethyl acetate	289	—	432	76,320	—	18,060	486	578	578	146	58.7	49.3	0.0432
	Toluene	277	—	431	100,860	—	20,960	485	565	565	134	58.8	50.5	0.0146
	Tetrahydrofuran	293	—	428	43,460	—	20,490	481	567	567	139	59.3	50.3	—
(3)	Ethyl acetate	290	—	422	18,640	—	440	367	576	576	154	77.7	49.5	0.0106
	Toluene	284	—	423	40,610	—	12,080	477	579	579	156	59.8	49.3	0.0003
	Tetrahydrofuran	275	—	422	37,240	—	7,490	476	562	562	140	59.9	50.8	0.0267
(4)	Ethyl acetate	290	—	—	24,280	—	—	382	575	575	285	74.7	49.6	0.0358
	Toluene	297	363	417	16,638	5,804	2,240	425	565	565	268	67.1	50.5	0.0081
	Tetrahydrofuran	272	—	—	37,880	—	—	394	539	539	267	72.4	52.9	0.0637



**Fig. 4** The photostability test results of Ligand (HL),  $[\text{CuHLCI}_2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{NiHLCI}_2 (\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  and  $[\text{CoHLCI}_2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  in tetrahydrofuran after 1 h of monitoring

the solvents tested. The compounds exhibited moderate Stokes' shift values ranging from 134 to 285 nm, which confers to the advantage of better spectral resolution in emission based studies. Table 1 also lists the fluorescence quantum efficiencies of the ligand and the complexes with a standard of quinine sulfate. The highest quantum yield values were obtained for the ligand compared to its complexes.

The photostability of the compounds in toluene, tetrahydrofuran and ethyl acetate was determined with a steady-state spectrofluorimeter in time-based mode. The data were acquired at their maximum emission wavelengths. According to the data collected after 1 h, there was no significant change in the fluorescence intensities of the compounds (Figs. 3 and 4).

## Conclusion

The symmetrical benzothiazole-based ligand (*2,6-bis(benzothiazol-2-yl)-4-(tert-butyl) phenol*) and its Cu (II), Ni (II) and Co (II) transition metal complexes were synthesized. On the basis of various physico-chemical and spectroscopic data presented and discussed above, the complexes may tentatively suggested to octahedral geometry around Ni (II) and Co (II) complexes, and tetragonal geometry for Cu (II) complex. According to these investigations, the ligand acts as a bidentate compound coordinating through the nitrogen atom of the benzothiazole group and the oxygen atom of the phenol-OH. All the synthesized metal complexes are found to be mononuclear. Moreover, the evaluation of absorption and emission properties of the compounds was carried out in different solvents. The compounds exhibited moderate Stokes' shift values ranging from 134 to 285 nm, which confers to the advantage of better spectral resolution in emission based studies. All derivatives exhibited excellent photostability in tetrahydrofuran, ethyl acetate and toluene.

## Supplementary Material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as the supplementary publication Nos. CCDC-1012083 (for the ligand (HL)). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Acknowledgments** The authors wish to thank Presidency of Scientific Research Projects of University of Yüzüncü Yıl for the financial support.

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