



Study on changes in optical properties of phenylbenzothiazole derivatives on metal ion binding

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ABSTRACT

The UV–visible and fluorescence properties of hydroxy substituted benzothiazole derivatives change on interactions with zinc(II), cadmium(II) and mercury(II) ions. The binding of 2-(2'-hydroxyphenyl)benzothiazole is specific to zinc(II) over cadmium(II) and mercury(II). Similar type of interactions of zinc(II), cadmium(II) and mercury(II) with 2-(2',3',4'-trihydroxyphenyl)benzothiazole is observed in their UV–visible absorptions, whereas 2-(4'-hydroxyphenyl)benzothiazole shows interactions with mercury(II) over the other two ions.

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1. Introduction

Benzimidazole occupies a major status as fluorescence probes [1–7]. The optical properties of analogous derivatives of benzothiazole are relatively less explored, which leaves scope for further study [8–13]. Among them, the hydroxybenzothiazoles are of special interest as presence of OH-group along with a ring containing nitrogen and sulphur atoms at two side of the heterocyclic ring can control coordination modes in a tuneable manner. Moreover, it would be possible to switch fluorescence or UV–visible properties of a hydroxyphenylbenzothiazole derivative by the affinity of a metal ion to either form chelate through lone pair of electrons on S and O atoms or N and O atoms as illustrated in Scheme 1. From the hard acid–soft base principle it is obvious that soft metal ions will preferentially bind to S-coordinating site, while hard ions will prefer the N-coordinating site. The emission and absorption properties of dimeric N-coordinating complex of zinc(II) derived from 2-(2'-hydroxyphenyl)benzothiazole are reported, however, the selectivity in binding to other metal ions is not studied [8]. With an intention of looking at the selectivity in metal binding with tuneable property of hydroxyphenylbenzothiazole derivatives (Fig. 1) we have prepared 2-(2'-hydroxyphenyl)benzothiazole (**1**), 2-(4'-hydroxyphenyl)benzothiazole (**2**), and 2-(2',3',4'-trihydroxyphenyl)benzothiazole (**3**) and studied their interactions with zinc(II), cadmium(II) and mercury(II) ions using UV–visible absorptions and fluorescence emission properties.

2. Materials and methods

2.1. General

All reagents and solvents were purchased commercially and were used without further purification, unless otherwise stated. ¹H NMR data were recorded with a Varian 400 MHz FTNMR spectrometer. The FT-IR spectra were recorded using a Perkin Elmer spectrometer in the KBr pellets in the range 4000–400 cm^{−1}. The UV/visible spectra were recorded using Perkin Elmer Lambda 750 spectrometer. The fluorescence spectra were recorded with a Perkin Elmer LS 55 fluorescence spectrophotometer. Mass spectra were recorded in a Water LC–MS in negative mode.

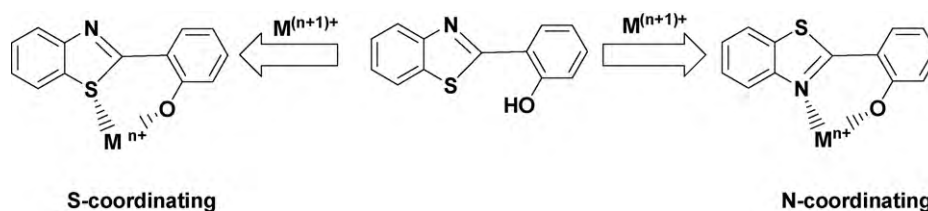
2.2. Synthesis of the compounds **1**, **2** and **3**

2.2.1. 2-(2'-hydroxyphenyl)benzothiazole (**1**)

To a well stirred solution of 2-aminothiophenol (534 μl, 5 mmol) in methanol (20 ml) salicylaldehyde (532 μl, 5 mmol) was added. The reaction mixture was then allowed to stir for 12 h. The reaction progress was monitored at regular intervals using TLC. After completion of the reaction the solvent was removed under reduced pressure that gave a yellow solid. The product was purified by recrystallization from dichloromethane. Yield: 92%. IR (KBr, cm^{−1}): 3443 (b), 3058 (w), 1622 (m), 1589 (m), 1487 (s), 1458 (m), 1315 (m), 1271 (m), 1219 (s), 1033 (m), 756 (m), 742 (s). ¹H NMR (CDCl₃, 400 MHz, ppm): 12.5 (1H, b), 8.0 (1H, d, *J* = 8.0 Hz), 7.9 (1H, d, *J* = 8.0 Hz), 7.7 (1H, d, *J* = 8.0 Hz), 7.5 (1H, m), 7.4 (2H, dd, *J* = 8.4 Hz, 8.8 Hz), 7.1 (1H, d, *J* = 8.4 Hz), 6.9 (1H, t, *J* = 7.6 Hz). LC–MS [*M*−1]: 226.94.

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Scheme 1. Two different types of chelates.

2.2.2. 2-(4'-hydroxyphenyl)benzothiazole (**2**)

To a well stirred solution of 2-aminothiophenol (534 μ l, 5 mmol) in methanol (20 ml) 4-hydroxybenzaldehyde (0.61 g, 5 mmol) was added. The reaction mixture was then allowed to stir for 24 h. The reaction progress was monitored at regular intervals using TLC. After completion of the reaction the solvent was removed under reduced pressure. The crude product was purified by chromatography (silica gel; hexane/ethyl acetate 3:1). Yield: 73%. IR (KBr, cm^{-1}): 3434 (b), 2922 (w), 1605 (m), 1523 (m), 1482 (m), 1454 (m), 1431 (s), 1284 (s), 1250 (m), 1225 (s), 1167 (m), 977 (m), 826 (m). ^1H NMR (DMSO- d_6 , 400 MHz, ppm): 9.7 (1H, b), 7.9 (4H, b), 7.4 (1H, m), 7.3 (1H, m), 6.9 (2H, d, $J=8.0$ Hz). LC-MS [$M-2$]: 225.58.

2.2.3. 2-(2',3',4'-trihydroxyphenyl)benzothiazole (**3**)

The compound **3** was synthesized in a similar procedure as **2**. Yield: 67% IR (KBr, cm^{-1}): 3437 (b), 3012 (w), 1612 (m), 1589 (m), 1488 (s), 1455 (m), 1279 (m), 1229 (s), 759 (m), 732 (m). ^1H NMR (DMSO- d_6 , 400 MHz, ppm): 11.5 (1H, s), 9.8 (1H, s), 8.6 (1H, s), 8.1 (1H, d, $J=7.2$ Hz), 7.9 (1H, t, $J=8.0$ Hz), 7.5 (1H, m), 7.4 (1H, m), 7.3 (1H, d, $J=7.2$ Hz), 6.5 (1H, d, $J=8.8$ Hz). LC-MS [$M-1$]: 259.92.

3. Results and discussion

3.1. Selective detection of zinc(II) by **1** with UV-visible spectroscopy

Ultraviolet absorption as well as the fluorescence emission of the compounds **1**, **2** and **3** was monitored to study their interactions with different commonly available metal ions and among them we could see significant changes with three metal ions viz. Zn^{2+} , Cd^{2+} and Hg^{2+} . It is observed that the methanolic solution of compound **1** (10^{-4} M) absorbs initially at 335 nm. Incremental addition (20 μ l) of a zinc(II) acetate solution (10^{-2} M) to this parent solution results in a red shift. A new absorption peak appears at 380 nm with an obvious isosbestic point at 350 nm. With the gradual addition of Zn^{2+} solution the peak at 335 nm undergoes a hypochromic effect while the peak at 380 nm undergoes a hyperchromic effect (Fig. 2). The presence of the isosbestic point clearly shows the presence of a zinc-[2-(2'-hydroxyphenyl)benzothiazolate] complex in solution which is already reported in the literature [8]. The com-

plex formation is further confirmed by a Job's plot and it is found to be a 1:2 complex (Fig. 2b). The UV-visible spectra of **1** in the presence of cadmium(II) and mercury(II) acetates having similar d-electron configuration does not show significant change. We have also checked the UV-visible spectra of **1** in the presence of toxic elements cadmium and mercury in their +2 oxidation state and found that zinc(II) detection by **1** is unaffected by these ions. Moreover, the compound **1** does not show any changes in visible absorbances with metal ions like Mn, Fe, Co, Ni, Cu at their +2 oxidation state. Thus, zinc(II) can be selectively screened in the presence of these metal ions by **1**.

3.2. Selective detection of zinc(II) by **1** with fluorescence spectroscopy

Similar study is carried out by fluorimetric titration of compound **1** with different metal ion solutions. Fluorescence emission spectra of **1** in methanol (10^{-4} M) in the presence of zinc(II), cadmium(II) and mercury(II) show distinct changes. Upon excitation at 270 nm compound **1** emits at two wavelengths, one at 375 nm and other at 449 nm. On addition of a zinc(II) acetate solution in methanol the fluorescence emission at 375 nm decreases, while the emission intensity at 449 nm increases. Control addition of a solution of zinc(II) acetate results in an isoemissive point at 410 nm (Fig. 3a). The fluorescence changes support the observation of UV-visible study where zinc complex formation is shown. Titration of the compound **1** with relatively higher concentration of cadmium(II) acetate solution (10^{-2} M) results in changes in the fluorescence emission (Fig. 3b). Since change in this case is not observed in the UV-visible spectra, it can be attributed to the difference in sensitivity of the two tools. However, fluorescence study shows significant differences with mercury(II) ions over the observations made in the case of zinc(II) and cadmium(II). With incremental addition of mercury(II) acetate (10^{-2} M in methanol) to a solution of **1** the fluorescence emission intensity at 449 nm decreases (Fig. 3c). Zinc(II) and cadmium(II) being comparatively harder than mercury(II), they are expected to prefer binding to **1** through the N and O atoms to form chelate while mercury(II) will prefer binding through the S and O atoms. From these studies it may be inferred that in the case of zinc and cadmium **1** forms chelate

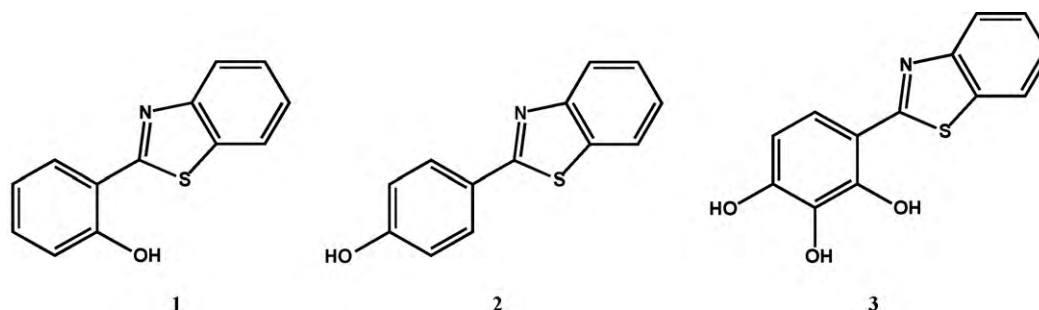


Fig. 1. Structure of the hydroxybenzothiazoles.

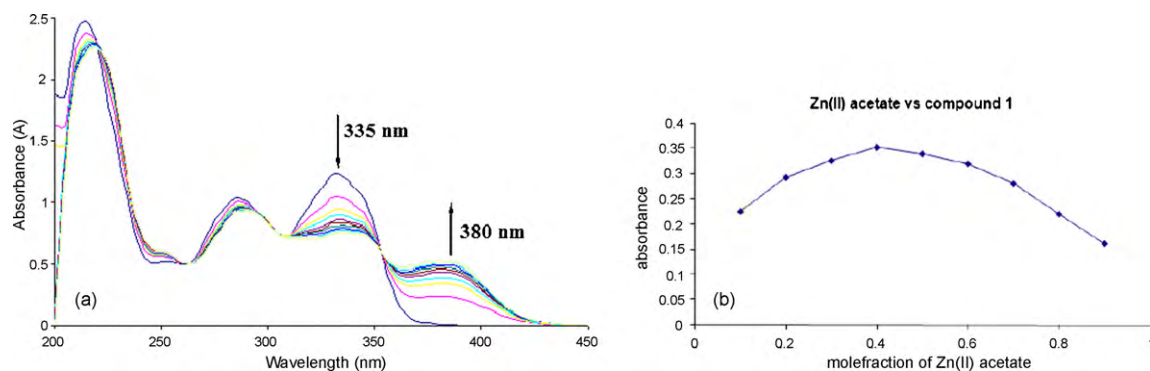


Fig. 2. (a) UV–visible spectra of **1** in methanol solution (10^{-4} M) in the presence of different concentrations of zinc(II) acetate (10^{-2} M in methanol in 20 μ l aliquot). (b) Job's plot of **1** against zinc(II) acetate to show the formation of an 1:2 complex.

through N and O atoms and there is an enhancement in fluorescence emission at 449 nm and 454 nm respectively (Fig. 3). Whereas in the case of mercury high thiophilicity of mercury leads to chelates through S and O atoms as well as N and O atoms (Scheme 1); in the presence of excess of ligand chelation through S and O atom is favoured and consequently quenching in fluorescence emission intensity at 449 nm is observed.

3.3. Selective detection of mercury(II) by **2**

The UV–visible spectroscopic study is not a suitable tool to show binding property of **2** with either of zinc(II), cadmium(II) or mercury(II) as no significant changes in the visible absorption of **2** is observed upon interaction with these ions. The changes in the fluorescence emission of **2** with incremental addition of zinc(II) and cadmium(II) are also not systematic (please refer to [Supplementary materials](#)). This could be due to flexible ambidentate interaction of **2** with the metal ions due to the absence of chelating effect. However mercury having higher affinity for sulphur shows decrease in emission of a methanolic solution of **2** at 375 nm with increase in concentration of mercury(II) acetate (Fig. 4).

3.4. Detection of zinc(II), cadmium(II) and mercury(II) by **3**

Compound **3** shows interesting UV absorption on interaction with metal ion (Zn^{2+} , Cd^{2+} and Hg^{2+}) solutions. The UV–visible absorption of this compound is affected by interaction with zinc(II), cadmium(II) and mercury(II) acetates. The UV–visible spectrum of **3** with increasing amount of mercury(II) is shown in Fig. 5c. It is observed that the methanolic solution of compound **3** (10^{-4} M) absorbs initially at 335 nm. The spectra show red shift near to 380 nm with incremental addition of mercury(II) acetate solution.

Moreover the band at 335 nm undergoes a hypochromic effect with the addition of the metal ion. An isosbestic point at 355 nm appears suggesting the formation of mercury(II) complex with **3**. The complex formation in solution is further confirmed by a Job's plot and it is found to be a 1:4 complex (please refer to [Supplementary materials](#)). Similar changes in absorbance of **3** on addition of with zinc(II) and cadmium(II) along with the appearance of isosbestic points are observed (Fig. 5a and b) and the complexes in solution are found to be of 1:1 and 1:2 composition from their Job's plot (please refer to [Supplementary materials](#)). These results

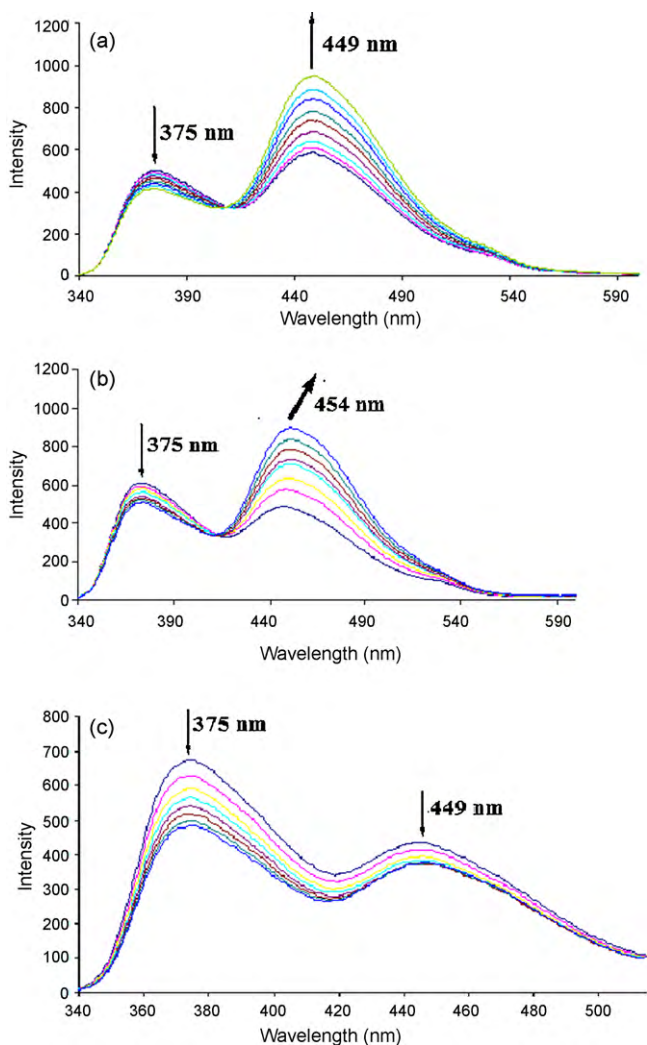


Fig. 3. Fluorescence emission spectra (λ_{ex} 270 nm) of **1** in methanol (10^{-4} M, 2 ml) solution in the presence of different concentrations of (a) zinc(II) (10^{-3} M), (b) cadmium(II) (10^{-2} M), and (c) mercury(II) (10^{-2} M) in 20 μ l each aliquot.

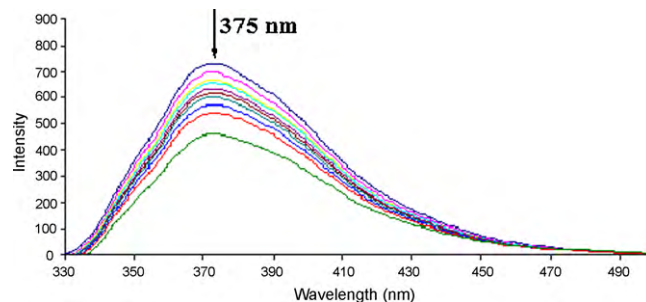


Fig. 4. Changes in the fluorescence emission of **2** (λ_{ex} 270 nm, 10^{-6} M in methanol solution) on addition of mercury(II) (10^{-2} M in methanol).

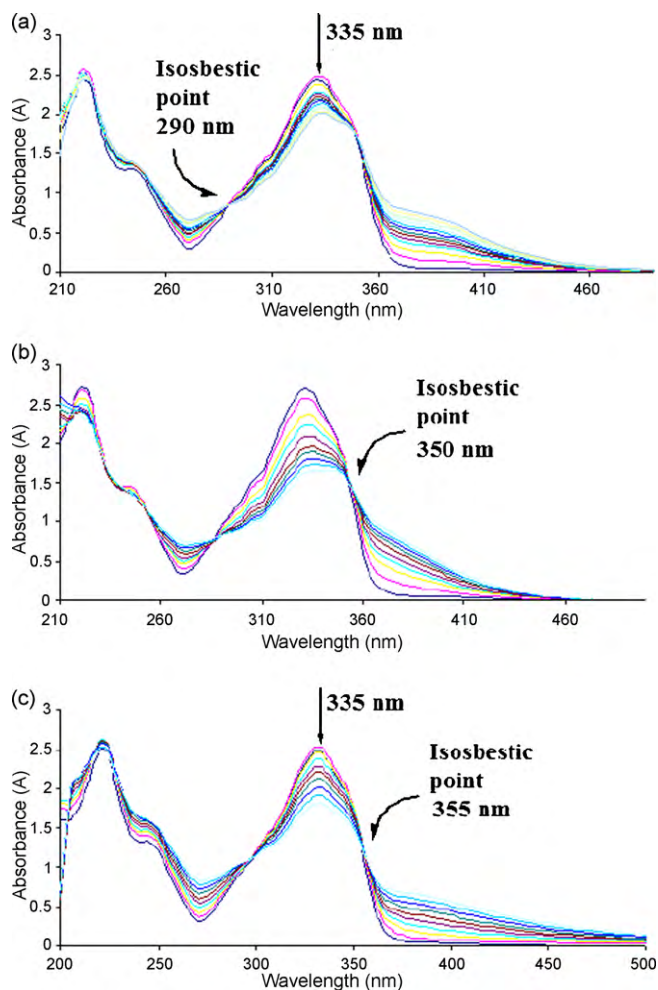


Fig. 5. Changes in UV-visible absorption spectra of **3** in methanol (10^{-4} M, 2 ml) in the presence of different concentrations of (a) zinc(II), (b) cadmium(II), and (c) mercury(II) (10^{-3} M in methanol with 20 μ l aliquot in each case).

show that in case of the ligand **3** chelation through S and O atoms occurs irrespective of the metal ions. It occurs due to the extra hydroxyl groups that participate in hydrogen bonding preventing the other binding modes. The compound **3** does not show fluorescence emission.

4. Conclusions

In conclusion, we have synthesized a few benzothiazole derivatives and studied their optical properties towards selective binding of metals. The optical properties of 2-(2'-hydroxyphenyl)benzothiazole(**1**) change on binding to zinc(II), cadmium(II) and mercury(II) as evidenced from their UV-visible spectra. This compound is found to be selective towards binding to zinc(II) over cadmium(II) or mercury(II). The changes in the fluorescence emission of **1** on addition of zinc(II) is opposite to that of mercury(II) which is attributed to change in coordination mode from N-O type to S-O type of chelate. The compound **2** is useful in studying the role of the 2'-hydroxy group of the benzothiazole derivatives. Compound **2** has a 4'-hydroxy binding site and is found to be less active towards coordination. The interactions of compound **3** with zinc(II), cadmium(II) and mercury(II) are identical, this is in contrast to the selective metal interactions of **1** and **2**.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.04.038.

References

- [1] Y.P. Tong, S.L. Zheng, X.M. Chen, *Inorg. Chem.* 44 (2005) 4271.
- [2] S. Santra, S.K. Dogra, *J. Photochem. Photobiol. A: Chem.* 101 (1996) 221.
- [3] S. Nigam, S. Srivastava, S.K. Dogra, A.K. Mishra, *Indian J. Chem. Sec. A* 33 (1994) 206.
- [4] M. Novo, M. Mosquera, F.R. Prieto, *J. Chem. Soc., Faraday Trans.* 89 (1993) 885.
- [5] P.C. Tway, L.J.C. Love, *J. Phys. Chem.* 86 (1982) 5223.
- [6] L.J. Cline Love, L.M. Upton, *Anal. Chim. Acta* 118 (1980) 325.
- [7] K.S. Rogers, C.C. Clayton, *Anal. Biochem.* 48 (1972) 199.
- [8] G. Yu, S. Yin, Y. Liu, Z. Shuai, D. Zhu, *J. Am. Chem. Soc.* 125 (2003) 14816.
- [9] K. Ghosh, T. Sen, *Tetrahedron Lett.* 50 (2009) 4096.
- [10] S.H. Kim, B.S. Kim, Y.A. Son, *Mol. Cryst. Liq. Cryst.* 498 (2009) 151.
- [11] G.W. Lee, N. Singh, H.J. Jung, D.O. Jang, *Tetrahedron Lett.* 50 (2009) 807.
- [12] M. Qureshi, S.S. Manoharan, S.P. Singh, Y.N. Mahapatra, *Solid State Commun.* 133 (2005) 305.
- [13] Z. Holzbecher, M. Hejtmanek, Z. Sobalik, *Coll. Czech. Chem. Commun.* 43 (1978) 3325.