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# A benzimidazole-based $Co^{3+}$ complex for electrochemical and spectroscopic recognition of I<sup>-</sup> and HSO<sub>4</sub><sup>-</sup> in semi-aqueous media

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#### ABSTRACT

A benzimidazole-based  $Co^{3+}$  complex was synthesized and evaluated as a sensor for  $I^-$  and  $HSO_4^-$  in aqueous media. The complex showed electrochemical changes with  $I^-$  over other anions, whereas it had a ratiometric response to  $HSO_4^-$  with UV-visible spectroscopy even in the presence of other anions. © 2013 Published by Elsevier Ltd.

The design and synthesis of receptors for selective anion sensing are of great interest in many areas such as environmental chemistry and biology.<sup>1</sup> Iodide plays important roles in neurological activities and thyroid function. Iodide deficiency causes physiological disorders, which lead to growth and maturation of organ systems.<sup>2</sup> Thus, it is strongly desirable to develop selective and sensitive receptors to detect iodide. However, it is difficult to design receptors for iodide detection because iodide anion has a large ionic radius, low charge density, and low hydrogen-bonding ability, which is reflected in the few reports of iodide sensors.<sup>3</sup> Hydrogen sulfate release from industrial processes has a deleterious effect on the environment.<sup>4</sup> Thus, quantifying these anions in biological and environmental samples is of great importance.<sup>5</sup>

Developing a receptor to detect anions in aqueous media is challenging because of competition between anions and water molecules for the receptor binding sites.<sup>6,7</sup> Thus, most hydrogen bonding-based receptors for anions are not compatible with an aqueous system. Metal complexes have been used to overcome this problem. Metal displacement from a complex<sup>8</sup> or electrostatic interactions between the metal center of a complex and an anion can cause changes in its photophysical properties.<sup>9</sup> UV-vis and fluorescence spectroscopic analysis techniques are frequently employed to detect these changes.

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In the last few years, we have reported benzimidazole-based imine receptors that act as sensors for anions and cations.<sup>10</sup> It had been thought that insertion of a cobalt metal ion into the coordination sphere of a benzimidazole-based receptor could provide sensor activity through electrochemical behavior, and the photophysical profile of the metal complex could offer a second channel for sensor activity. In this Letter, we wish to report the development of a sensor system that can simultaneously detect two anions using the photophysical properties of the sensor as well as its electrochemical profile. The combination of photophysical properties with electrochemistry may increase the scope of such a sensor, since electrochemistry has many advantages including a lower detection limit and a measurement of redox potential.<sup>11,12</sup> Anion binding to the benzimidazole-based Co<sup>3+</sup> complex leads to observable changes in its ring current and redox potential. Moreover, this approach has the added advantage that electrostatic interactions between the metal center and an anion can be interpreted even in the presence of competing solvent molecules including water. To the best of our knowledge, this is the first attempt to use a benzimidazole-based sensor to recognize two different anions via these two different analysis techniques.

Ligand **2** was synthesized by a condensation reaction of 2-aminobenzimidazole and 2-hydroxybenzaldehyde.<sup>13</sup> Reaction of ligand **2** with  $Co(NO_3)_2$  gave a complex, which was further subjected to air oxidation to obtained the desired complex **1** (Scheme 1). Complex **1** was characterized by <sup>1</sup>H NMR, IR, elemental analysis, and mass spectroscopy.

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The stoichiometry of complex 1 was established by a Job's plot,<sup>14</sup> which had a maximum at 0.7 that corresponded to a 2:1 (host:guest) stoichiometry (Fig. S1). In spite of our numerous efforts, we were unfortunate to grow the single crystals to determine the exact structure of new material. The obtained crystals were in a range of sub-micrometer size. We analyzed the sample with powder diffraction technique. The data interpretation is much simpler in powder diffraction when the purpose is to compare the sample with pure metal ion and pure organic receptor. Figure S2 represents the comparison of PXRD pattern of ligand 2, complex 1, and cobalt nitrate. The diffraction pattern of ligand 2 shows scattering angles (20) 10.04, 11.50, 14.13, 17.13, 19.52, 20.27, 21.07, 23.34, and 28.35 and cobalt nitrate has sharp peaks at  $(2\theta)$  15.25, 16.40, 19.31, 27.20, 28.31, 29.18, 30.71, and 41.43. However, the diffraction pattern of complex 1 ((20) 8.98, 10.37, 11.65, 17.49, 17.91, 21.60, 22.09, 23.61, 24.36, 24.83, and 30.82) neither matches with ligand **2** nor with cobalt nitrate. It implies that metal complex 1 has unique composition and represents the new material. The formula of the metal complex was supported by mass spectra showing a m/z peak at 684.2 ([1(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>OH)(NO<sub>3</sub><sup>-</sup>)]+Na<sup>+</sup>) (Fig. S3). The coordination sphere of  $Co^{3+}$  consisted of a weakly bound anion  $(NO_{2}^{-})$  and solvent molecules  $(H_{2}O \text{ and } CH_{3}OH)$ . These ligands can easily be replaced with other anions. Thus, the complex had the potential of being an anion sensor. In order to investigate the effect of pH on the sensing behavior of complex 1, pH titrations were performed. In acidic medium, the absorption profile of complex 1 remained intact up to pH 4.0, and further lowering of the pH resulted in the development of a new band at 400 nm and a decrease in the absorbance at 350 nm as shown in Figure S4A. An increase in pH beyond 9.5 resulted in the development of a new band at 372 nm (Fig. S4B). Therefore, the pH range between 4.0 and 9.5 is favorable for the optimum operation of complex **1**. The effect of ionic strength on the absorption profile of complex 1 was studied with different concentrations of tetrabutylammonium perchlorate. It was found that the absorption profile of complex 1 was not significantly modulated even with up to 100 mM of tetrabutylammonium perchlorate (Fig. S5). The absorption spectra of complex 1 were recorded in different solvents such as MeOH, EtOH, DMSO, THF, and DMF to examine a possible solvatochromic effect. It was noticed that a new band at 365 nm was observed in polar solvents such as DMSO and DMF (Fig. S6). The effect of water content was investigated with different ratios of MeOH/H<sub>2</sub>O (Fig. S7). It was observed that water content greater than 20% led to the formation of aggregates. Particle size analysis via dynamic light scattering (DLS) revealed that these aggregates were approximately 50 nm in size (Fig. S8). Therefore, all recognition studies were carried out in MeOH/H<sub>2</sub>O (8:2, v/v).

The interaction of complex **1** with tetrabutylammonium salts of various anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $l^-$ ,  $NO_3^-$ ,  $CN^-$ ,  $CH_3COO^-$ ,  $HSO_4^-$ , and  $H_2PO_4^-$ ) was investigated by differential pulse voltammetry (DPV)



**Figure 1.** Changes in the DPV profile of complex 1 (1  $\mu$ M) upon addition of various tetrabutylammonium anion salts (40  $\mu$ M) in MeOH/H<sub>2</sub>O (8:2, v/v).



**Figure 2.** CV profile of complex **1** (1  $\mu$ M) and complex **1** + I<sup>-</sup> in MeOH/H<sub>2</sub>O (8:2, v/ v). Reference electrode: AgNO<sub>3</sub>/Ag; supporting electrolyte: (<sup>*n*</sup>Bu)<sub>4</sub>NClO<sub>4</sub>.



Figure 3. Changes in the DPV profile of complex 1 (1  $\mu$ M) upon continuous addition of tetrabutylammonium iodide (0–40  $\mu$ M) in MeOH/H<sub>2</sub>O (8:2, v/v).

and cyclic voltammetry (CV) in MeOH/H<sub>2</sub>O (8:2, v/v). Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. The DPV profile of complex **1** showed an oxidation peak at -0.235 V (Fig. 1). Upon the addition of various anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) to the solution of complex **1**, only I<sup>-</sup> caused a change in the electrochemical signal. The CV profile of complex **1** showed one reversible oxidation wave with  $E_{1/2} = -0.752$  V and an irreversible oxidation peak at 0.121 V as shown in Figure 2. The irreversible CV peak at 0.121 V disappeared upon the addition of I<sup>-</sup>, and simultaneously, there was a shift in  $E_{1/2}$  from -0.752 to -0.897 V.

Changes in the DPV profile of complex **1** upon the addition of various amounts of  $I^-$  are shown in Figure 3. Upon the addition

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**Figure 4.** DPV profile of complex  $1 + I^-$  and complex  $1 + I^- +$  other anions in MeOH/ H<sub>2</sub>O (8:2, v/v). Reference electrode: AgNO<sub>3</sub>/Ag; supporting electrolyte: TBACIO<sub>4</sub>.



**Figure 5.** Absorption spectra of complex 1 (1  $\mu$ M) upon addition of different anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) in MeOH/H<sub>2</sub>O (8:2, v/v).

of I<sup>-</sup>, the oxidation potential of complex **1** shifted from -0.235 to -0.512 V. After the addition of 40 equiv of I<sup>-</sup>, the potential became constant. In order to evaluate the practical utility of complex **1**, the selectivity of complex **1** toward I<sup>-</sup> was examined in competition experiments. Testing was performed in the presence of 4 equiv of I<sup>-</sup> and an equimolar amount of another anion (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sup>-</sup><sub>3</sub>, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sup>-</sup><sub>4</sub>, and H<sub>2</sub>PO<sup>-</sup><sub>4</sub>) in MeOH/H<sub>2</sub>O (8:2, v/v) (Fig. 4). The competition experiments illustrate that complex **1** had nearly the same potential changes with I<sup>-</sup> even in the presence of other anions.

It was observed that the addition of HSO<sub>4</sub><sup>-</sup> to a solution of complex 1 gave a visible color change, even though  $HSO_4^-$  had not induced any significant electrochemical changes. This result encouraged us to evaluate the anion binding profile of complex 1 through UV-visible spectroscopy. The anion binding ability of complex **1** toward various tetrabutylammonium anion salts (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) was investigated by UV-visible spectrophotometry. Interestingly, complex 1 showed selectivity for HSO<sub>4</sub>, which was totally different from the electrochemical results (Fig. 5). The addition of  $HSO_4^-$  (200  $\mu$ M) into a stock solution of complex  $1 (1 \mu M)$  produced a new band at 400 nm with a simultaneous decrease of the band at 347 nm. These results afforded a ratiometric determination for HSO<sub>4</sub> with an isosbestic point at 375 nm. A ratiometric estimation is more preferable to monitoring at a single wavelength because such an analysis is free from errors due to receptor concentration and instrumental error.<sup>15</sup> To collect further information on the binding



**Figure 6.** Changes in the absorption profile of complex **1** (1  $\mu$ M) with continuous addition of tetrabutylammonium HSO<sub>4</sub><sup>-</sup> (0–200  $\mu$ M) in MeOH/H<sub>2</sub>O (8:2, v/v).



Figure 7. Detection of  $HSO_4^-$  with complex 1 (1  $\mu$ M) in the presence of an equimolar amount of other anions in MeOH/H<sub>2</sub>O (8:2; v/v) at 400 nm.

mechanism of  $HSO_4^-$  to complex **1**, a titration was performed between complex **1** and  $HSO_4^-$  in MeOH/H<sub>2</sub>O (8:2, v/v) (Fig. 6). The ratiometric changes at 400 and 375 nm are displayed. The emergence of new band at 400 nm attributes to hydrogen bond interaction between  $HSO_4^-$  and N–H of benzimidazole. There are various reports in the literature, which advocate that C–H/N–H–anion interactions are main leading force behind the recognition.<sup>16</sup> The ratiometric changes of complex **1** at 400 and 375 nm were proportional to the amount of added  $HSO_4^-$  at concentrations between 0.01 and 140 µM (Inset of Fig. 6). The stoichiometry of complex **1**.  $HSO_4^-$  was investigated using a Job's plot.<sup>14</sup> The graph was plotted between [HG] and [H]/([H]+[G]), which showed a 1:1 stoichiometry (Fig. S9). The association constant of complex **1** and  $HSO_4^-$ , calculated using the Benesi–Hildebrand plot for a 1:1 H. Sharma et al./Tetrahedron Letters xxx (2013) xxx-xxx

stoichiometry, was 1.2  $(\pm 0.12)\times 10^3\,M^{-1}.^{17}$  The detection limit was found to be 63  $\mu M.$ 

To confirm the selectivity of complex **1** toward  $HSO_4^-$ , competitive titrations were performed. The absorption spectra of complex **1** with  $HSO_4^-$  were measured in the absence and presence of competing anions (Fig. 7). It was found that complex **1** showed high selectivity even in the presence of competing anions such as  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $l^-$ ,  $NO_3^-$ ,  $CH_3COO^-$ , and  $H_2PO_4^-$ .

In summary, a benzimidazole-based  $Co^{3+}$  complex was prepared and evaluated for anion binding in aqueous media using cyclic voltammetry and UV-visible spectrophotometry. Complex **1** showed changes in its electrochemical behavior with iodide and had high selectivity even in the presence of other anions. On the other hand, complex **1** had a different UV-visible spectrophotometry recognition profile, which exhibited a ratiometric response to HSO<sub>4</sub><sup>-</sup> compared to other competing anions.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.08.051.

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