

## A structurally characterised chromone-quinoline conjugate motif for colorimetric detection of $\text{Co}^{2+}$ ions in aqueous medium

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A newly designed chromone-quinoline conjugate chemosensor, 2-methoxy-3-(quinolin-8-ylaminomethylene)-chromon-4-one (HL) have been synthesized and crystallographically characterised that acts as colorimetric probing of  $\text{Co}^{2+}$  ions with high selectivity over the other competitive cations and anions in EtOH- $\text{H}_2\text{O}$  (1:3, v/v, pH 7.4). Investigation of the cations recognition behavior showed that the ligand has selective colorimetric sensing properties for cobalt(II) ions by an easy to observe naked-eye color change from colorless to straw-yellow. The probe, in absence or in presence of  $\text{Co}^{2+}$  ions shows pH independency response over a pH range of 7–10.

Keywords: Chemosensor, cobalt(II) ions, colorimetric response, CHEF.

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### Introduction

It is well known that cobalt an essential trace element found in cobalamin and other metalloproteins such as in vitamin  $\text{B}_{12}$  with 4.35% cobalt content<sup>1,2</sup>. This important micronutrient plays so many vital roles in biological systems. It is essential folate and fatty acid metabolism, also play important part in the metabolism of iron and in the synthesis of hemoglobin<sup>3</sup>. In the environment cobalt released from soil, dust, sea water, burning of coal and oil volcanic eruption, chemical and hard metal industries<sup>4</sup>.  $\text{Co}^{2+}$  is also widely used in industry for manufacturing pigments, batteries, and alloys<sup>5</sup>. In addition cobalt is a significant environmental pollutant and  $\text{Co}^{2+}$  pollution of environmental water causes severe effects on humans and animals. Although cobalt play important roles in living organism, exposure to excessive amount of cobalt can cause several toxicological effects, including heart disease, mutagenesis, thyroid enlargement, asthma, decreased cardiac output, lung fibrosis, dermatitis, vasodilation and even can cause inhibition of some enzyme activities<sup>6–9</sup>. The deficiency of  $\text{Co}^{2+}$  leads to anemia, retarded growth, and loss of appetite<sup>10</sup>. The maximum tolerable level of Co is ca. 10 ppm (170 mM)<sup>11</sup>. Therefore development of methods for the detection and determination of cobalt with high selectivity and sensitivity is of great importance.

There are some analytical methods are available for the detection of cations like inductively coupled plasma atomic

emission spectrometry, atomic absorption spectroscopy, fluorescence techniques and electrochemical methods<sup>12–15</sup>. However all these methods require sophisticated equipment, tedious sample preparation procedures and trained operators. Now a days, fluorescence techniques have become a tools for sensing and imaging of several species like cations, anions or even for neutral molecules, present in trace amounts in the environmental sample<sup>16–22</sup>. Up to now, some fluorescent chemosensor molecules are reported for the detection of  $\text{Co}^{2+}$  ions<sup>23,24</sup>. Although showing high sensitivities toward cobalt(II) ions, fluorometric methods are practically difficult for real time detection because of the fluorescence quenching problem. Colorimetric methods on the other hand have attracted much attention for allowing “naked-eye” detection in a uncomplicated and inexpensive manner, offering both qualitative as well as quantitative information<sup>25–28</sup>. However, colorimetric chemosensors for probing cobalt(II) ions are still rare<sup>29–33</sup>. Some of these sensors cannot be used as colorimetric cobalt(II) ions sensing in aqueous medium<sup>14,30,31</sup>. Therefore, there is still a great demand for the development of new colorimetric chemosensors that can detect  $\text{Co}^{2+}$  selectively and sensitively in aqueous solutions.

Considering the above facts, herein, we report a structurally modified chromone-quinoline conjugate probe (HL) as an efficient colorimetric sensor for  $\text{Co}^{2+}$  ions in an aqueous medium. The probe shows remarkably high selectivity to

wards the naked-eye detection of  $\text{Co}^{2+}$  ions without having any interference from competitive cations and anions. The sensor HL detected  $\text{Co}^{2+}$  ions by showing a color change from colorless to straw-yellow in an aqueous medium at biological pH.

## Experimental

### Materials and instrumentation:

The different analytical grade solvents, reagent grade chemicals and high-purity HEPES buffer, used here were purchased from commercial sources. These chemicals were used without further purification (if not mentioned). Here, Milli-Q 18  $\Omega$  water was used throughout the experiments. UV-Vis and IR spectral data were collected using a Shimadzu (model UV-2450) spectrophotometer and a Prestige-21 Shimadzu FT-IR spectrometer, respectively. A Bruker Avance DPX 400 MHz spectrometer using  $\text{DMSO}-d_6$  solution  $^1\text{H}$  NMR spectrum was recorded. Different solution of different pH values were prepared adjusted using either 50 mM HCl or NaOH solution and the pH values were recorded by using a Systronics digital pH meter (model 335). To record the electrospray ionization mass spectra, a Thermochem Exactive plus mass spectrometer was used. The C, H, N elemental analyses were performed on a Perkin-Elmer model 2400 elemental analyzer. Room temperature magnetic susceptibilities were recorded using a vibrating sample magnetometer PAR 155 model. Molar conductance ( $\Lambda_M$ ) was measured in a Systronics conductivity meter 304 model in methanol with a complex concentration of  $-10^{-3}$  mol  $\text{L}^{-1}$ .

### General methods:

The absorbance properties of the probe HL were studied in EtOH 10 mM HEPES (1:3, v/v, pH 7.4) at 30°C. To investigate the effect of different pH on absorbance of HL, in absence or in presence of  $\text{Co}^{2+}$  ions, pH study was performed in 10 mM HEPES buffer solution by maintaining the pH using 50 mM HCl or 50 mM NaOH solution. For the selectivity study of HL, the stock solutions ( $\sim 10^{-2}$  M) of different metal ions were prepared taking nitrate salts of  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ; acetate salt of  $\text{Mn}^{2+}$ ; chloride salts of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$  and sulphate salt of  $\text{Fe}^{2+}$ ; in EtOH/ $\text{H}_2\text{O}$  (1:5, v/v) 10 mM HEPES buffer. In this selectivity study, the amount of the metal ions was 50 times greater than that of the probe used. UV-Visible titration spectra of the probe HL was carried out using cobalt(II) chloride hexahy-

drate in EtOH- $\text{H}_2\text{O}$  (1:3, v/v) at pH 7.4. All the absorbance spectra were taken after 15 min of mixing the  $\text{Co}^{2+}$  ions and HL to acquire the optimized spectra at room temperature.

### Synthesis of 2-methoxy-3-(quinolin-8-ylaminomethylene)-chroman-4-one (HL):

To a colorless stirred methanolic solution of 3-formyl chromone (1 mmol, 174.15 mg), solution of 8-aminoquinoline (1 mmol, 144.18 mg) in methanol was added dropwise. The resulting mixture turned immediately into yellowish-green and this mixture was then further refluxed 6 h. After that solution kept at room temperature for overnight. As a result of which niddle shaped yellow colored crystalline compound obtained which was then washed 2–3 times with cold methanol and dried *in vacuo*. Yield: 72%. m.p 121–122°C.

$\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3$  (HL): Yield: 82–85%; Anal. Calcd.: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.99; H, 4.54; N, 8.71; ESI-MS:  $[\text{M}+\text{Na}]^+$ ,  $m/z$  355.1885 (100%) (Calcd.:  $m/z$  355.1059); FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{NH}}$ , 3219,  $\nu_{\text{C=O}}$ , 1639;  $^1\text{H}$  NMR ( $\delta$ , ppm in  $\text{DMSO}-d_6$ ): 12.94 (N-H), 8.97 (d, 1H), 8.37 (m, 1H), 8.20 (m, 1H), 7.88 (m, 1H), 7.81 (m, 1H), 7.63 (m, 3H), 7.48 (m, 1H), 7.12 (m, 1H), 7.02 (d, 1H), 6.22 (s, 1H), 2.05 (s, 3H).

### Preparation of cobalt(II) complex ( $\text{L}_2\text{Co}$ ):

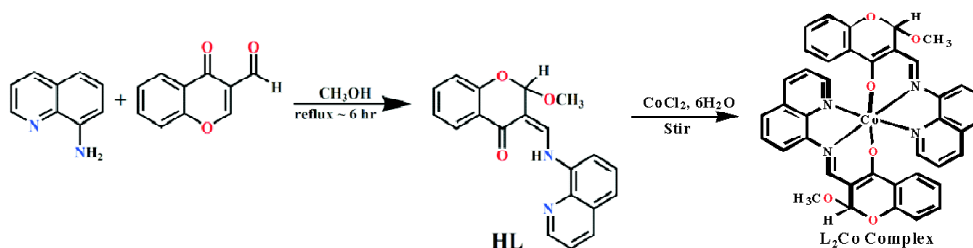
To the methanolic solution of HL (332.0 mg, 1.0 mmol) cobalt(II) chloride hexahydrate (118.5 mg, 0.5 mmol) was added very slowly with vigorous stirring and then the reaction mixture was stirred at ambient temperature for another 6.0 h taking usual precaution. The resulting solution thus obtained was then kept aside for slow evaporation at room temperature. After a few days, a deep brown coloured complex was precipitated out duly washed with cold methanol and water thoroughly and then dried *in vacuo* for characterization purpose.

$\text{C}_{40}\text{H}_{30}\text{CoN}_4\text{O}_6$  ( $\text{L}_2\text{Co}$ ): Yield: 71–74%; Anal. Calcd.: C, 66.58; H, 4.19; N, 7.76. Found: C, 67.18; H, 4.01; N, 7.99; ESI-MS in methanol:  $[\text{M}+\text{Na}]^+$ ,  $m/z$  722.3484 (Obsd. with  $\sim 100\%$  abundance) (Calcd.:  $m/z$  722.1576) where  $\text{M} = [\text{L}_2\text{Co}]$ ; FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{C=N}}$ , 1600. Magnetic moment ( $\mu$ , B.M.): 4.71. Conductivity ( $\Lambda_0$ ,  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) in MeOH: 64.

## Results and discussion

### Synthesis and characterization:

The probe (HL) was synthesized by condensing 3-formyl chromone with 8-amino quinoline in methanol (Scheme 1).



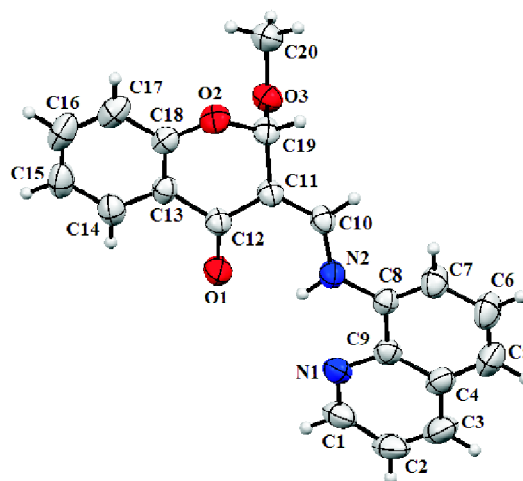
**Scheme 1.** Synthetic strategy of probe HL and its cobalt(II) complex ( $L_2Co$ ).

Bright yellow colored crystalline compound was obtained from the reaction mixture after slow evaporation of the solvent in few days. HL was characterised by different physico-chemical and spectroscopic tools which supports the formulation of HL (Figs. S1–S2). This probe HL is highly soluble in common polar organic solvents and sparingly soluble in water.

The ESI mass spectrum of the probe (HL) in methanol shows a peak at  $m/z$  355.1885 with ~100% abundance assignable to  $[M+Na]^+$  (calculated value at  $m/z$  355.1059) where  $M$  = molecular weight of HL (Fig. S1) conforming the formation of the probe. Also the  $^1H$  NMR and FTIR spectral data of HL are in accordance with the structural formula of HL in the solution state (Fig. S2).

Single crystals of HL suitable for single crystal X-ray crystallography were obtained from the methanolic solution of HL on slow evaporation at room temperature. X-Ray data were collected on a Bruker's Apex-II CCD diffractometer using  $Mo\ K\alpha$  ( $\lambda = 0.71069$ ). The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. A total of 3408 reflections were measured out of which 3072 were independent. The structure was solved by direct methods using SIR-92 and refined by full-matrix least squares refinement methods based on  $F^2$ , using SHELX-97<sup>34,35</sup>. All non-hydrogen atoms were refined anisotropically. All calculations were performed using Wingx package<sup>36</sup>. Important crystal and refinement parameters are given in Tables S1 and S2. Fig. 1 shows the ORTEP view of the crystal HL. Crystallographic data for the structural analyses of HL have been deposited with the Cambridge Crystallographic Data Centre bearing the CCDC No. 1876255. Copies of this information are available on request at free of charge from CCDC, 12, Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>).

The solid state complex ( $L_2Co$ ) was isolated from the re-



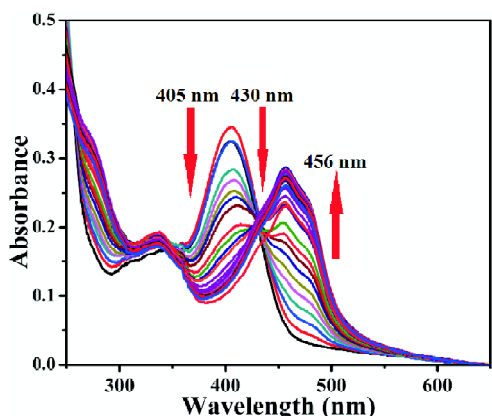
**Fig. 1.** ORTEP view of HL [Bond length (Å): N1-C1, 1.319(3); N1-C9, 1.368(3); O2-C19, 1.436(2); C10-N2, 1.340(3); N2-C8, 1.411(3); C19-O3, 1.408(3); C12-O1, 1.238(3). Bond angles (°): C10-N2-C8, 125.93(19); C1-N1-C9, 117.2 (2); C18-O2-C19, 115.54(17)].

action of HL with cobalt(II) chloride hexahydrate in 2:1 molar ratio in the methanol medium at room temperature at stirring condition with usual precaution. The complex is soluble in methanol, acetonitrile, DMF and DMSO etc. The conductivity measurement of the complex in methanol showed the conductance values in the range of  $64\ \Lambda_0\ mol^{-1}\ cm^{-1}$  at 300 K, which suggests that the complex exists as non-electrolyte in solution. At room temperature the magnetic moment of  $L_2Co$  complex is 4.71 B.M. indicating a high-spin octahedral cobalt(II) complex. The ESI mass spectrum of the complex ( $L_2Co$ ) in methanol shows a peak at  $m/z$  722.3484 with ~100% abundance, assignable to  $[M+H]^+$  (calculated value at  $m/z$  722.1576), where  $M = [L_2Co]$  (Fig. S3).

#### *Photophysical studies and ion selectivity:*

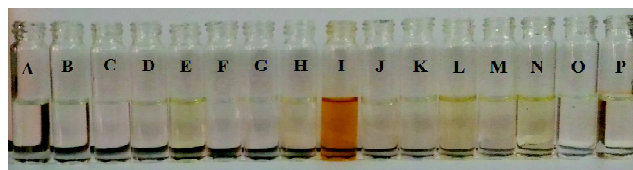
The UV-Vis spectrum of the probe (HL) alone showed the characteristic absorption band at ca. 405 nm in 10 mM

HEPES buffer (EtOH/water: 1/3 v/v) at pH 7.4 and after addition of  $\text{Co}^{2+}$  ions to the colourless solution of HL a new peak generates at 456 nm. These UV-Vis absorption changes account for the changes in solution color from colorless to straw yellow, which can be used for selective colorimetric detection of  $\text{Co}^{2+}$  ions in aqueous environments. On gradual addition of the  $\text{Co}^{2+}$  ion, the intensity of the peak at 405 nm decreases while the intensity of the peak at 456 nm increases (Fig. 2), having appearance of a clear isosbestic point at 430 nm, indicating the formation of a single compound after interaction of HL with  $\text{Co}^{2+}$  ions. This new peak intensity gradually increases due to the formation of the  $\text{L}_2\text{Co}$  complex in the solution state. During these measurements probe concentration was 11.5  $\mu\text{M}$  and  $\text{Co}^{2+}$  ions were added upto 2 equivalent that of probe HL.

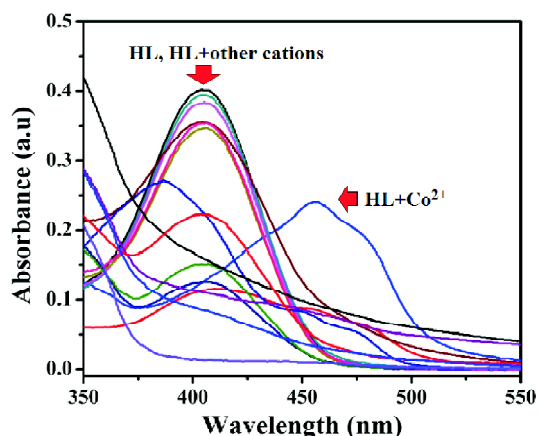


**Fig. 2.** UV-Vis titration spectra of HL with gradual addition of  $\text{Co}^{2+}$  ions in 10 mM HEPES buffer (EtOH/water: 1/3 v/v) at pH 7.4 at 30°C.

To investigate the selectivity of the probe (HL) towards cations, solution of alkaline earth metal ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ), several transition metal ions ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$ ) were added to the probe solution in 10 mM HEPES buffer (EtOH/water: 1/3 v/v) at pH 7.4. It has been observed that only  $\text{Co}^{2+}$  ions after interaction with HL showed a very easily observable naked-eye color change from almost colorless to straw-yellow color (Fig. 3). Only after interaction of HL with  $\text{Co}^{2+}$  ions, a new peak appears in the UV-Vis spectrum at 456 nm (Fig. 4). After interaction with the most common biologically relevant anions this colorimetric chemosensor molecule neither shows any colour change nor generates new peak (Fig. S4). It also has been found that this probe can detect the presence of  $\text{Co}^{2+}$



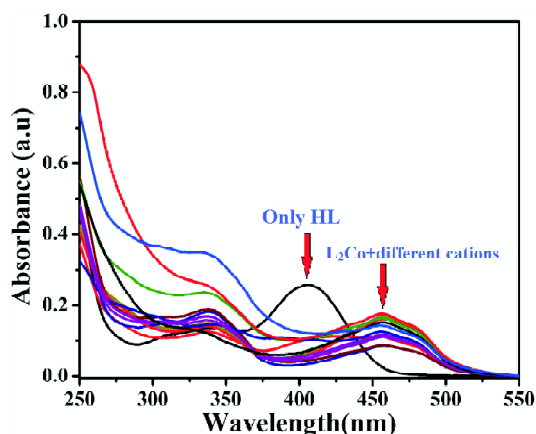
**Fig. 3.** Visual color change of HL upon addition of different cations in 10 mM HEPES, 1:3 EtOH/ $\text{H}_2\text{O}$ , at pH 7.4 (A = only HL, B =  $\text{Mg}^{2+}$ , C =  $\text{Ca}^{2+}$ , D =  $\text{Sr}^{2+}$ , E =  $\text{Al}^{3+}$ , F =  $\text{Cr}^{3+}$ , G =  $\text{Mn}^{2+}$ , H =  $\text{Fe}^{2+}$ , I =  $\text{Co}^{2+}$ , J =  $\text{Ni}^{2+}$ , K =  $\text{Cu}^{2+}$ , L =  $\text{Zn}^{2+}$ , M =  $\text{Cd}^{2+}$ , N =  $\text{Hg}^{2+}$ , O =  $\text{Pb}^{2+}$ , P =  $\text{Fe}^{3+}$ ).



**Fig. 4.** Absorbance response of HL in presence of different cations in 1:3 EtOH/ $\text{H}_2\text{O}$ , 10 mM HEPES buffer, pH 7.4 (different cations are  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ).

ions with almost no interference even in the presence of 50 equivalent concentration of different biologically relevance cations and anions (Figs. 5 and S5). It reveals that the organic moiety (HL) has an excellent selectivity and specificity towards  $\text{Co}^{2+}$  ions over the other cations and can be used for colorimetric detection of  $\text{Co}^{2+}$  ions.

We have investigated the effect of pH on the absorbance response of receptor HL to  $\text{Co}^{2+}$  ions. A series of buffer with pH values ranging from 4 to 10 were prepared by mixing sodium hydroxide solution and hydrochloric acid in HEPES buffer. The UV-Vis spectra of probe HL was measured at various above mentioned pH in presence and in absence of  $\text{Co}^{2+}$  ions at room temperature. Both HL and  $\text{L}_2\text{Co}$  species exhibited a pH independency over the pH range 7.0 to ~10.0 (Fig. S6). It is also found that the absorbance of the organic moiety HL in presence of  $\text{Co}^{2+}$  ions is higher than that in absence of  $\text{Co}^{2+}$  ions.



**Fig. 5.** Effect of presence of different cations on the absorbance property of  $L_2Co$  complex in 1:3 EtOH/ $H_2O$ , 10 mM HEPES buffer, pH 7.4 (other cations includes  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{3+}$ ).

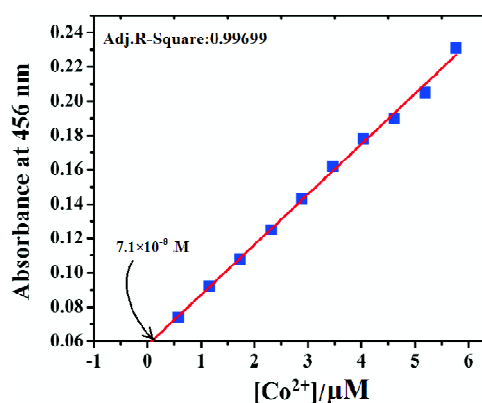
The binding stoichiometry of HL was achieved from the Job's method on the basis of absorbance. In which, Job's plot was produced by continuously varying the mole fraction of  $Co^{2+}$  from 0 to 1. The Job's plot analysis revealed that the mole fraction of  $Co^{2+}$  is around 0.33 which indicates a 2:1 stoichiometry for the  $L_2Co$  complex (Fig. S7). To better understand the binding mode of HL with  $Co^{2+}$ , ESI mass spectra of probe in the presence of metal ion was performed and the observed  $m/z$  peak for HL in the presence of  $Co^{2+}$  at 722.3484 corresponding to  $L_2Co$  complex (viz. Fig. S3). The mass data therefore also confirmed the binding of  $Co^{2+}$  to HL with 1:2 stoichiometry.

The binding constant of HL for  $Co^{2+}$  was determined using a modified Benesi-Hildebrand equation:  $(A_{max} - A_0)/(A_x - A_0) = 1 + (1/K)(1/[M]^n)$ , where  $A_{max}$ ,  $A_0$ ,  $A_x$  are absorbance values for HL in the presence of  $Co^{2+}$  at saturation, in the absence of  $Co^{2+}$  and at any intermediate  $Co^{2+}$  ions concentration, respectively. A plot of  $(A_{max} - A_0)/(A_x - A_0)$  vs  $1/[M]^n$  (here  $n = 1/2$ ) yields the binding constant value as  $2.86 \times 10^2 M^{-1/2}$  (Fig. S8).

On the basis of all the experimental observations, it is revealed that during the reaction with  $Co^{2+}$  ions, at first the N-H proton gets deprotonated forming a new species L which then binds with the  $Co^{II}$  ion in a 2:1 stoichiometric ratio to form the  $L_2Co$  complex (Scheme 1). Here, HL behaves as a tridentate monobasic ligand through the rearrangement during chelation with cobalt(II) ion. In this rearrangement, the amine (NH) and carbonyl group changed to imine-N and

phenolic-OH (i.e. the  $O1=C12-C11=C10H-N2H-$  transformed into  $O1H-C12=C11-C10H=N2-$  viz. Fig. 1) respectively, and as a result  $L_2Co$  complex (viz. Scheme 1) is formed through deprotonation of the *in situ* formed O-H group of HL prior to coordination with the  $Co^{II}$  ion.

The detection limit of the probe HL for the detection of  $Co^{2+}$  ions also determined from the curve (Fig. 6). The LOD value has been found to be  $7.1 \times 10^{-8} M$  which is good for quantitative determination.



**Fig. 6.** Detection limit of receptor HL in EtOH- $H_2O$  (1 : 3, v/v, pH 7.4, 10 mM HEPES buffer) in sensing of  $Co^{2+}$  ion.

## Conclusion

In conclusion, herein we have presented a newly designed and structurally characterized probe (HL) which acts as a colorimetric chemosensor for  $Co^{2+}$  ions in 10 mM HEPES buffer EtOH- $H_2O$  (1:3, v/v) at biological pH. All the processes have been evidenced by thorough experimental findings. The probe HL shows highly specific and selectivity towards  $Co^{2+}$  ions as low as  $7.1 \times 10^{-8} M$  with almost no interference of other competitive cations and anions. The receptor HL binds with  $Co^{2+}$  ions in a 2:1 stoichiometric manner with binding constant value of  $2.86 \times 10^2 M^{-1/2}$ . The absorbance profile of HL in absence or presence of  $Co^{2+}$  ions also shows a pH independency over a range of pH 7–10.

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