

# Selective Recognition of Cobalt (II) Ion by a New Cryptand Compound with N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> Donor Atom Possessing 2-Hydroxy-1-Naphthylidene Schiff Base Moiety

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**Abstract** A new cryptand compound carrying 2-hydroxy-1-naphthylidene Schiff base moiety (**3**) was designed and synthesized by reaction of the corresponding macrobicyclic amine compound (**1**) and 2-hydroxy-1-naphthaldehyde (**2**). The influence of metal cations such as Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Al<sup>3+</sup> and Pb<sup>2+</sup> on the spectroscopic properties of the new fluoroionophore was investigated in acetonitrile-dichloromethane solution (9.5/0.5) by means of absorption and emission spectrometry. The blue shifts on the fluorescence spectrum were observed for all metal cations at 504nm. At the same time the fluorescence spectrum of the ligand showed quenching in the intensity of the signal at 504 nm for all metal cations except for Zn<sup>2+</sup>. Interaction of Co<sup>2+</sup> with the ligand caused quenching of naphthyl fluorescence higher than 84%. The method showed good selectivity and sensitivity for Co<sup>2+</sup> with respect to other metal cations with linear range and detection limit of  $1.5 \times 10^{-7}$  to  $3.3 \times 10^{-6}$ M and  $4.8 \times 10^{-8}$ M respectively.

**Keywords** Cryptand · 2-hydroxy-1-naphthaldehyde · Fluorescence spectroscopy · Co<sup>2+</sup> cation

## Introduction

Cobalt is a natural earth element present in trace amounts in soil and plants. It usually occurs in association with other metals such as copper, nickel and manganese. The toxicity of cobalt is quite low compared to many other metals in soil. At the same time it is part of vitamin B-12, and plays a key role in synthesis of this essential vitamin in organism. Therefore cobalt is essential in trace amounts for human life. However exposure to very high levels of cobalt can cause health effects. Effects on the lungs, including asthma, pneumonia, and wheezing, have been found in workers who inhaled high levels of cobalt in the air [1–3]. Nowadays, it is released to the environment by burning coal and oil and by industrial processes that use the metal or its compounds. For human health, it is important to detect and determine hazardous metal cations such as cobalt (II) in environmental sources.

The numerous analytical methods for the detection of cations, atomic absorption spectrometry, ion sensitive electrodes, electron microprobe analysis, are mostly expensive and often require samples of large size. However the methods based on fluorescent sensors possess some advantages such as sensitivity, selectivity and response time. Therefore, considerable efforts are being made to develop selective fluorescent sensors for cation detection [4–8].

Fluorescent sensors are generally three component systems consisting of a signaling unit (fluorophore), a reception unit (guest-binding site) and a spacer group. The fluorophore and the guest-binding site are usually separated by a spacer group. Once the target metal cation binds to the receptor, some significant changes to the photophysical properties of the fluorophore occur. For example, PET sensors show a very large change in fluorescence intensity such as enhance-

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ment or quenching upon cation binding. However, PCT sensors cause a red or blue shift on the absorption and fluorescence spectra upon cation binding [8].

Crown ether and cryptands have served as the structures of cation binding, especially for alkali and alkaline earth cations [9–13]. In many types of fluorescent sensors, the linker belongs to both the fluorophore and receptor. However, there are some examples of fluorescent sensor in which the functional part of the fluorophore participates in the complexation [14–15]. For example, Valeur *et al.* reported the direct interaction between the bound cation and the carbonyl group of the coumarin 153 linked to diaza-18-crown-6 [14]. Similarly, Li *et al.* showed that the oxygen of the carbonyl group is also bound to cation in some flavone lariat-crowns and the interaction between the bound cation and the carbonyl group of the flavone fluorophore causes the enhancement of a cation-induced intramolecular charge transfer process [15].

In this study, we report the preparation of a novel macrobicyclic ligand with nitrogen-oxygen-sulfur mixed donor carrying ortho hydroxy naphthalimine part (**3**), and present the photophysical changes upon complexation of the ligand with  $\text{Co}^{2+}$ . The complex stability constant and the complex composition were determined by using spectrophotometric and spectrofluorimetric titrations in acetonitrile-dichloromethane (9.5/0.5). During the measurements we expected that some of the tested transition metal cations would interact with the ortho hydroxy naphthalimine part of the ligand.

## Experimental

### Chemicals

Acetonitrile and dichloromethane from Merck (spectrometric grade) were the solvents for absorption and fluorescence measurements. All metal perchlorates purchased from Acros were of the highest quality available and vacuum dried over blue silicagel before use.

### Apparatus

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 200 A spectrometer, using  $\text{CDCl}_3$  with TMS as the internal reference. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer using KBr pellets. The absorption spectra of the solutions were recorded using a Varian Cary 5E spectrophotometer. Mass spectra of the ligand were measured on a Micromass Quattro LC-MS /MS spectrometer. Elemental analysis was performed on Costech 4010 CHNS instrument. A Photon Technologies International Quanta Master Spectrofluorimeter (model QM-4/2006) was used for all fluorescence measurements.

### Measurements

Absorption spectra of fluoroionophore (**3**) with a concentration of  $2.58 \times 10^{-5}\text{M}$  in acetonitrile-dichloromethane solution (9.5/0.5) containing 100 molar equivalents of appropriate metal perchlorate salt were measured using 1-cm long absorption cell. Fluorescence spectra of the same solutions were measured in 1-cm quartz cell. Excitation wavelength was 398 nm. Fluorescence emission spectra were recorded in the range 400–600 nm with slit width of 1.0 nm.

The complex stoichiometry for  $\text{Co}^{2+}$  ion was determined by using the molar-ratio method from both absorption and fluorescence measurements.

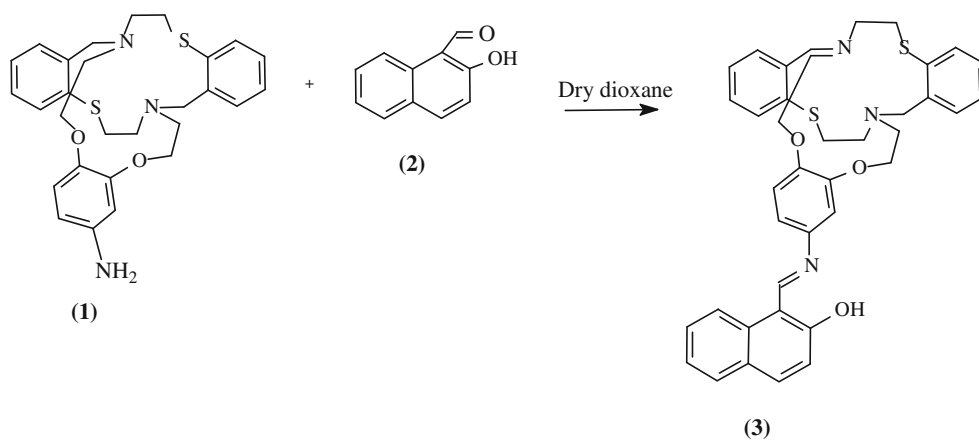
### Synthesis of compound (**3**)

Compound (**1**) (0.142 g, 0.28 mmol) was dissolved in dry dioxane (15 mL) and purged under nitrogen atmosphere in a Schlenk system connected to a vacuum line. A solution of 2-hydroxy-1-naphthaldehyde (**2**) (0.048 g, 0.28 mmol) in dry dioxane (15 mL) was added dropwise to this solution for 30 min at 40 °C. The reaction mixture was refluxed and stirred at reflux temperature for 39 h, monitored by TLC [silica gel (petroleum ether:acetone) (1:2)]. At the end of this period, the pale yellow solution was concentrated on an evaporator to 10 mL and the yellow solid formed was filtered off, washed with hot ethanol and cold diethyl ether, then dried *in vacuo*. The yellow solid product (0.138 g, 74%) was obtained by recrystallization from ethanol-chloroform, mp 130–132 °C. Anal. Calc. for  $\text{C}_{39}\text{H}_{39}\text{N}_3\text{O}_3\text{S}_2$ : C, 70.77; H, 5.94; N, 6.35; S, 9.69%. Found: C, 70.32; H, 6.16; N, 6.04; S, 9.28%. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3435 (O-H), 3049 (Ar-H), 2912–2793 (C-H), 1621 (C=N).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): ( $\delta$ ) 15.71 (s, 1H, O-H), 9.28 (s, 1H, CH=N), 7.53–8.14 (m, 6H, naphth.-H), 6.83–7.49 (m, 11H, macrocyc.-H) 4.22 (s, 4H, Ar- $\text{CH}_2$ ), 3.79 (t, 4H, O- $\text{CH}_2$ ), 3.37–2.66 (m, 8H, N- $\text{CH}_2$ ), 2.53 (t, 4H, S- $\text{CH}_2$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): ( $\delta$ ) 169.62, 153.54, 148.92, 147.22, 141.01, 138.17, 136.21, 135.77, 134.61, 133.13, 132.11, 129.36, 127.90, 127.23, 123.36, 122.19, 118.89, 112.57, 111.41, 108.74, 105.60, 65.87, 59.80, 53.20, 51.11, 33.71, 29.70, MS (EI):  $m/z = 662.25$  [M+1].

## Results and discussion

The synthetic pathway to new macrobicyclic ligand (**3**) is summarized in Scheme 1. Compound (**1**) was prepared according to the previous paper [16]. Compound (**3**) was synthesized by reaction of compound (**1**) with 2-hydroxy-1-naphthaldehyde (**2**) in dry dioxane. The difference between the IR spectra of (**1**) and (**3**) is clear by the absence of characteristic vibration, at 3448–3365  $\text{cm}^{-1}$  belonging to the  $\text{NH}_2$  groups. The spectra show a broad band at 3435  $\text{cm}^{-1}$

**Scheme 1** Synthetic pathway to new macrobicyclic ligand (**3**) used this study



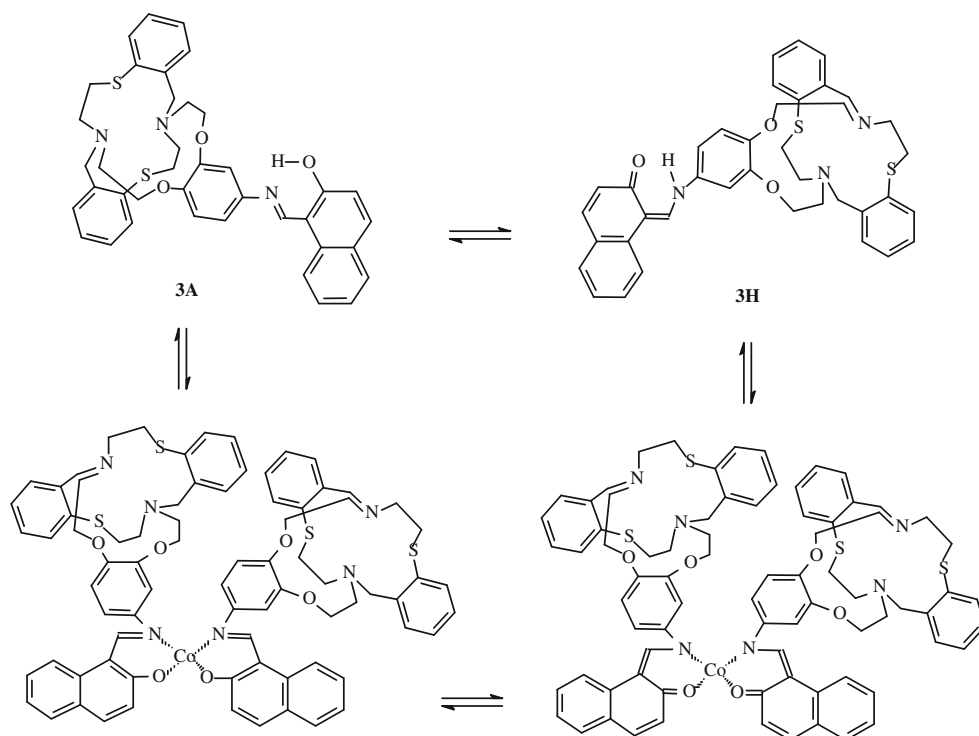
and a narrow band at  $1331\text{ cm}^{-1}$ , respectively, for O-H stretching and phenolic C-O vibrations. However, the O-H band is shifted towards  $2,725\text{ cm}^{-1}$ , due to the increasing strength of the OH...N hydrogen bond. In addition, the two strong bands at  $1,621\text{ cm}^{-1}$  and  $1,602\text{ cm}^{-1}$  can be assigned to stretching of the C=N groups due to different azomethine moieties [17]. Further evidence for the keto-amine tautomer (3H in Scheme 2) stems from the stretching vibrations of the skeleton NH-C=C-C=O at about  $1,536\text{ cm}^{-1}$  and  $1,508\text{ cm}^{-1}$  [18]. These results confirm the coexistence of both phenol-imine form (3A in Scheme 2) and keto-amine form (3H in Scheme 2) tautomers for the Schiff base ligand (**3**) in solid state.

In the <sup>1</sup>H-NMR spectrum of (**3**), there is a singlet at  $\delta = 9.28\text{ ppm}$  for the proton of azomethine group indicating the formation of a Schiff base. The absence of the singlet at  $\delta =$

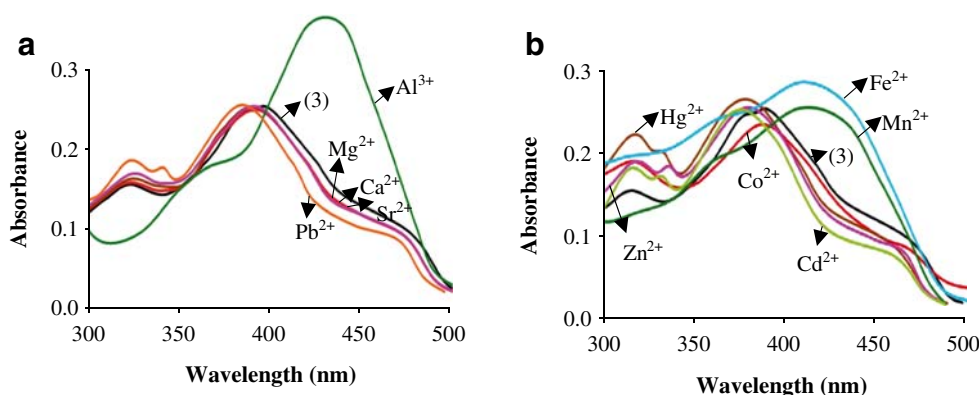
4.60 ppm belonging to the primary aromatic amine groups of the starting material supports the formation of the compound (**3**). The resonance of the moving hydroxyl group were observed at  $\delta = 15.71\text{ ppm}$ .

More detailed information about the structure of compound (**3**) is provided by its <sup>13</sup>C-NMR spectrum. The carbon resonance of azomethine group and the resonance of carbon atom linked with the -OH group are found at  $\delta = 153.54\text{ ppm}$  and  $\delta = 169.62\text{ ppm}$ , respectively. The value of the chemical shift of the phenolic carbon atom is sensitive to the relative population of both tautomers [19]. Alarcon *et al.* adopted the value of 180 ppm as characteristic of the pure H form and the value of 155 ppm as characteristic of the pure A form in solution for N-(2-hydroxynaphthylidene)arylamines [19]. An equilibrium shift from A form to H form with a chemical shift between 155 ppm and 180 ppm. For ligand (**3**), the value of

**Scheme 2** Probable tautomeric equilibriums for ligand (**3**) and its Co (II) complex



**Fig. 1** The effect of metal cations on the absorption spectra of **(3)** in acetonitrile-dichloromethane solution (9.5/0.5): **(a)** for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$ ; and **(b)** for  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$



the chemical shift of the phenolic carbon atom at  $\delta = 169.62$  ppm suggests the coexistence of two forms. These results point to the existence of a tautomerization equilibrium in  $\text{CDCl}_3$  for the ligand **(3)**. On the other hand, the mass spectral analysis of **(3)**, which shows a peak at  $m/z = 662.25$   $[\text{M}+1]$ , confirms the proposed structure.

#### Absorption spectra

In acetonitrile-dichloromethane solution (9.5/0.5), ligand **(3)** exhibits three absorption bands at 326 nm, 398 nm and 475 nm (Fig. 1). In solution the phenol-imine  $\leftrightarrow$  keto-amine tautomeric equilibria is always observed when the Schiff base is derived from 2-hydroxy-1-naphthaldehyde [20–21]. The absorption bands above 400 nm on the absorption spectra of some 2-hydroxy Schiff base belong to the keto-amine form [20–22]. The broad 475 nm absorption band of ligand **(3)** probably belongs to the keto-amine form. The 398 nm absorption band may result from phenol-imine form [21].

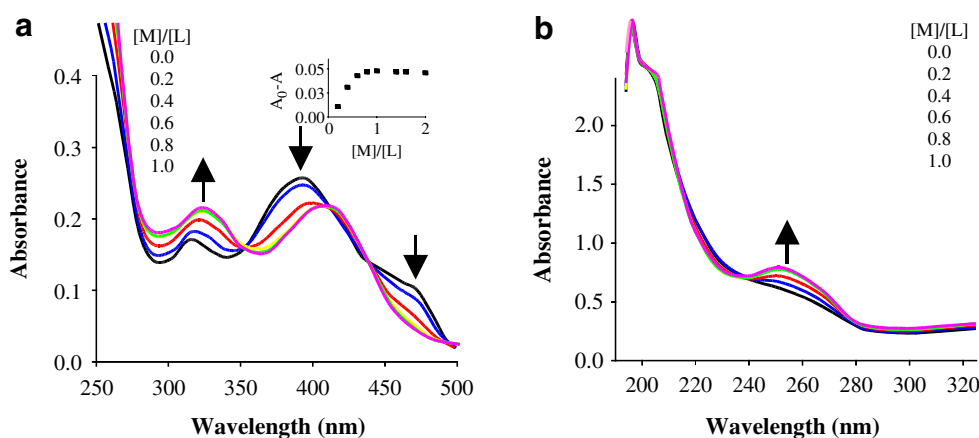
As seen from Fig. 1(a), the presence of 100 equivalents of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  produces little changes in the absorption of **(3)**. However the effect of  $\text{Al}^{3+}$  on the absorption spectra of **(3)** is pronounced in Fig. 1(a). The new band was observed at about 430 nm with absorption enhancement. At the same time the absorption intensity is

decreased at 398 nm. Therefore, the interaction of  $\text{Al}^{3+}$  with ligand **(3)** shifts the phenol-imine form to keto-amine form.  $\text{Pb}^{2+}$  shifts the 398 nm absorption band to the shorter wavelength by about 11 nm.

Figure 1(b) shows the effect of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  on the absorption spectra of ligand **(3)**.  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions caused dramatic changes in the absorption spectra. These ions shift the 398 nm absorption band to the longer wavelength by 20 nm. The shape of these bands is very broad. These results show that  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions interact with the phenol-imine form of the ligand. An absorption enhancement was also observed in this wavelength for  $\text{Fe}^{2+}$ . In contrast,  $\text{Co}^{2+}$  caused a decrease in the intensity of the 398 nm absorption band with very little red shift. However, the same cation caused an absorption enhancement in the 326 nm. Similar changes in this wavelength were observed for  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ . Only  $\text{Mn}^{2+}$  caused a decrease in the intensity of the 326 nm absorption band.

The change in the absorption spectra of ligand **(3)** with increasing concentrations of  $\text{Co}^{2+}$  is shown in Fig. 2. Figure 2(a) shows the change in the absorption spectra between 190 nm and 320 nm. The absorbance around 250 nm of compound **(3)**, attributed to the benzo-crown moiety, increased together with the blue-shift upon the addition of  $\text{Co}^{2+}$  up to the  $[\text{M}]/[\text{L}] = 1:1$  ratio. These changes can result from the disruption of the  $\pi$ -conjugat-

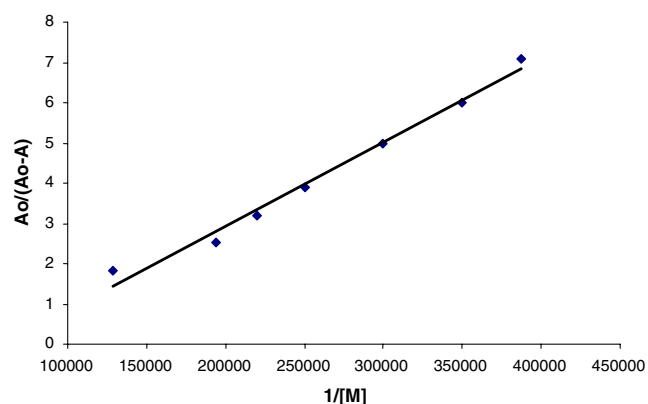
**Fig. 2** Absorption spectra of **(3)** complexed with  $\text{Co}^{2+}$ . **(a)** between 190 and 320 nm; and **(b)** between 250 and 500 nm. The spectral changes during the addition of 0–1 equiv of  $\text{Co}(\text{ClO}_4)_2$ . Ligand concentration:  $2.58 \times 10^{-5} \text{M}$



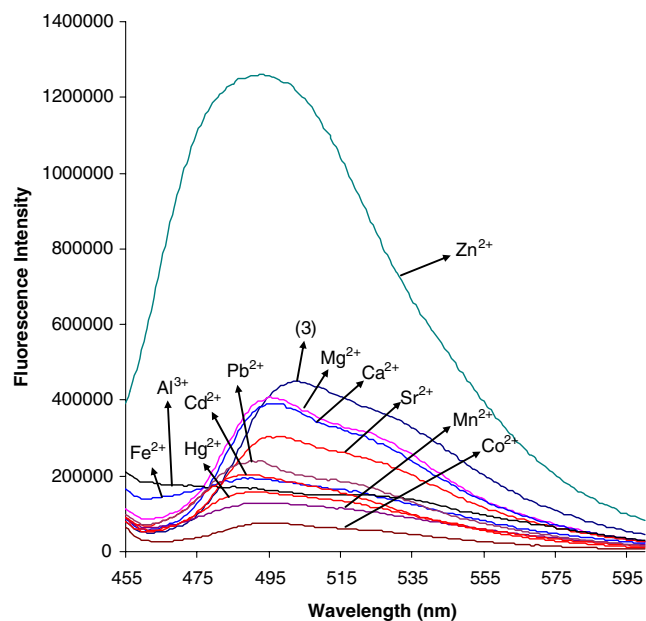
ed system between benzene and azomethine bond due to the binding of  $\text{Co}^{2+}$ . Hama *et al.* observed similar changes in the absorption spectrum of benzo-15-crown-5 possessing 1-naphthaleneacetamide moiety in the binding of  $\text{Mg}^{2+}$  [23]. The isobestic point at 235 nm was not clear when it was observed in detail. This seems to be due to the presence of small amounts of free ligand. Figure 2(b) shows the change in the absorption spectra between 250 nm and 500 nm with increasing amounts of  $\text{Co}^{2+}$  ions. Three isobestic points were observed at 355 nm, 415 nm and 442 nm. Totally, four isobestic points were found in the absorption spectrum as a result of the  $\text{Co}^{2+}$  binding. These results indicated that there were four equilibriums during the complexation. Scheme 2 shows probable tautomeric equilibriums for ligand (3) and its Co (II) complex. As seen from the Fig. 2(b), the isobestic points at 355 nm and 442nm were well-pronounced isobestic points (Fig. 2b).

As seen from Fig. 2(b), the  $\text{Co}^{2+}$ -induced changes in the absorption spectrum involves the absorbance increments at 326 nm and the absorbance decreases at 398 nm and 475 nm. The peak at 326 nm can be assigned to the  $\pi$  electron transition of the naphthalene fluorophore. The red shifts at 398 nm may result from the interaction of  $\text{Co}^{2+}$  with the phenol-imine form. The binding of  $\text{Co}^{2+}$  cation to the receptor site in the ligand increases the conjugation and shifts the peak to longer wavelength. Also, the absorbance increments at 326 nm and red shifts show the interaction of  $\text{Co}^{2+}$  with the  $\pi$  electron system of naphthalene group during the complexation. The changes in the absorption spectra of ligand (3) between 300–500 nm suggested that a large conformational change occurred around the naphthalene group.

Molar ratio method was used to determine the complex composition for  $\text{Co}^{2+}$ . We could not obtain proper data for the complex composition from the change of absorbance at 326 nm and 398 nm. However there was a good relationship between  $A_0/(A_0-A)$  and  $[M]/[L]$  at 478 nm.  $A_0$  and  $A$  are the absorbance of free ligand and the absorbance of the solution



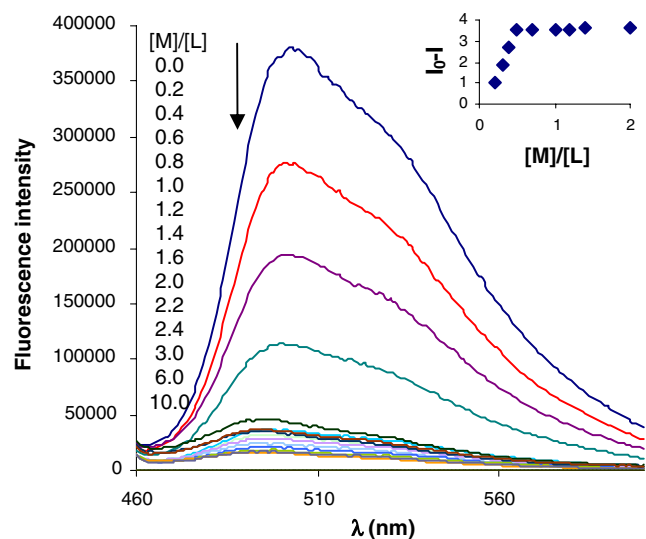
**Fig. 3**  $A_0/(A_0-A)$  versus  $1/[M]$  for the spectrophotometric titration of ligand (3) with Co (II) perchlorate in acetonitrile-dichloromethane (9.5/0.5).  $\lambda$ :478 nm



**Fig. 4** Effects of metal cations on fluorescence spectra of ligand (3) in acetonitrile-dichloromethane solution (9.5/0.5). (Ligand concentration= $2.58 \times 10^{-5}$  M. Metal perchlorate concentrations= $2.58 \times 10^{-3}$  M. Excitation at 398 nm.)

involving  $\text{Co}^{2+}$  cation, respectively. Figure 2(b) (inset) shows the molar ratio plot for  $\text{Co}^{2+}$ . As seen from Fig. 2(b), the inflection point was 0.5 ( $[M]/[L]$ ). It can thus be concluded that ligand (3) formed a stable 1:2 (M:L) complex with  $\text{Co}^{2+}$ .

In order to determine the complex stability constant, the ratio of  $A_0/(A_0-A)$  was plotted versus  $1/[M]$ , as in Fig. 3, which gave a good straight line. The stability constant was calculated from the ratio intercept/slope [24]. Log K was 4.76 for the complex. Log K was calculated from the data

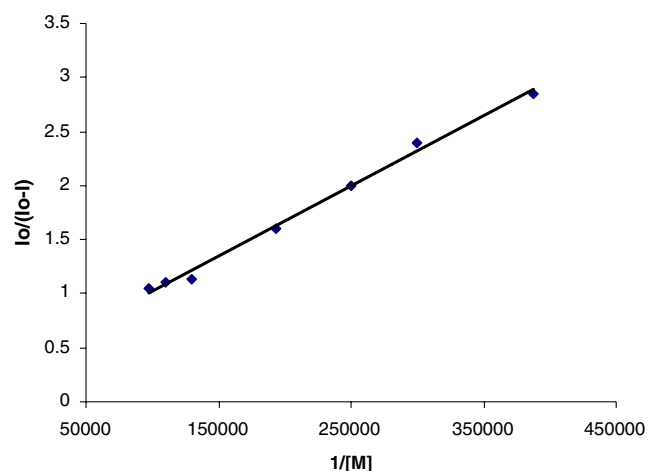


**Fig. 5** Fluorescence spectra ( $\lambda_{\text{exc}}$ :398nm,  $\lambda_{\text{em}}$ :504nm) of ligand (3) in acetonitrile-dichloromethane (9.5/0.5) with increasing amounts of  $\text{Co}^{2+}$  ions.  $[L]$ :  $2.58 \times 10^{-5}$  M. Inset: Molar ratio plot for complex composition

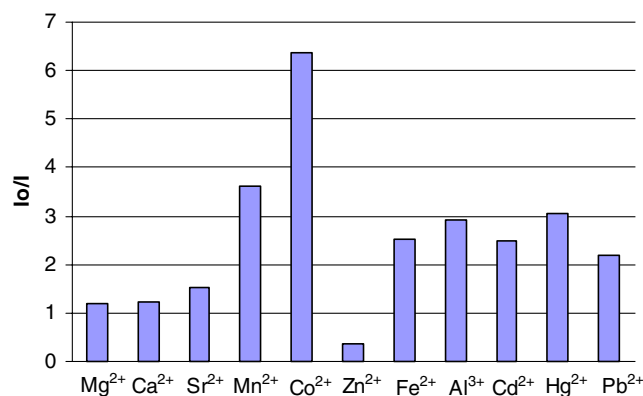
obtained from four independent absorbance measurements. The standard deviation was 0.24. The calculation was carried out at 478 nm.

#### Infra-red spectra

We prepared  $\text{Co}^{2+}$ -ligand (**3**) complex by refluxing a solution of (**3**) in ethanol with a solution containing 1 molar equivalent of  $\text{Co}(\text{ClO}_4)_2$  in acetonitrile to investigate the complexation properties of the ligand (**3**) with  $\text{Co}^{2+}$  ion. The complex was a brown solid with melting point of 288–290 °C. The IR spectra of the prepared complex have broad absorption with a maximum at  $3,483\text{ cm}^{-1}$ , confirming the presence water of hydration. The infrared bands observed at  $1,621\text{ cm}^{-1}$  and  $1,602\text{ cm}^{-1}$  which are assigned to the C=N frequency in the free ligand are shifted to lower frequencies ( $\Delta\nu = 3\text{--}5\text{ cm}^{-1}$ ) after complexation. This shows the coordination of nitrogen of imine moiety of Schiff base to  $\text{Co}^{2+}$  ion. This is further confirmed by the appearance of a medium intensity band in the region  $508\text{--}533\text{ cm}^{-1}$ , characteristic of  $\nu_{\text{M-N}}$  stretching vibrations and bands at about  $471\text{ cm}^{-1}$  are assigned to M-O (phenolic) stretching vibrations [25–26]. Moreover, the band belonging to phenolic C-O at  $1,331\text{ cm}^{-1}$  shifted to  $1,383\text{ cm}^{-1}$ . This shows the OH group incorporated to the complexation. Aryl ether stretching bands are observed at  $1271\text{--}1211\text{ cm}^{-1}$ . For free ligand, these bands appeared at  $1,265\text{--}1,227\text{ cm}^{-1}$ . This shift can result from the contribution of oxygen donor atoms belong to cryptand moiety to the complexation. IR spectra of Co (II) complex display bands attributable to the asymmetric Cl-O stretching vibration at about  $1,120\text{ cm}^{-1}$  and to the symmetric Cl-O bending vibration at  $623\text{ cm}^{-1}$ . The strong broad band at  $1,120\text{ cm}^{-1}$  having the weak splitting indicates that the perchlorate anion is partially involved in the coordination sphere [27].



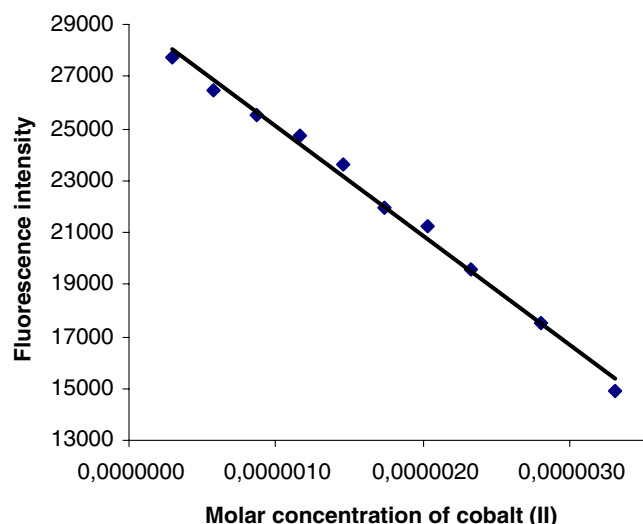
**Fig. 6**  $I_0/(I_0-I)$  versus  $1/[M]$  for the spectrophotometric titration of ligand (**3**) with Co (II) perchlorate in acetonitrile-dichloromethane (9.5/0.5).  $\lambda$ :504 nm



**Fig. 7** The influence of metal perchlorates on relative emission intensity. [L]:  $2.58 \times 10^{-5}$  M, [Metal perchlorate]:  $2.58 \times 10^{-3}$  M, measured at 504 nm

#### Fluorescence spectra

Excitation at 398 nm gives an emission band with a maximum 504 nm for the ligand (**3**). Figure 4 shows the effects of metal cations on fluorescence spectra of ligand (**3**). A dramatical change in the emission intensity of ligand (**3**) was observed upon the addition of 100 M equivalent of metal perchlorates such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$ . The emission band intensities are reduced somewhat by the presence of earth alkaline metal cations and are diminished substantially for interactions with  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$ . A decrease of the fluorescence intensity caused by  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions is probably a result of the “heavy atom effect” [28]. Blue shifts were observed at the 504 nm emission band for all the metal cations. The fluorescence spectrum of the ligand (**3**) showed quenching in the intensity of the signal at 504 nm for all metal cations except for  $\text{Zn}^{2+}$ . Especially, interaction



**Fig. 8** Linear response of the fluorescence intensity as a function of  $\text{Co}^{2+}$  concentration

of  $\text{Co}^{2+}$  with the ligand caused quenching of naphthyl fluorescence higher than 84%.

Figure 5 shows the fluorescence spectra of ligand (3) in acetonitrile-dichloromethane (9.5/0.5) with increasing amounts of  $\text{Co}^{2+}$  ions. The addition of  $\text{Co}^{2+}$  induced a regular quenching in the fluorescence spectra. Maximum fluorescence intensity was observed at 504 nm with excitation at 398 nm. The molar ratio curve obtained clearly showed the formation of a 1:2 (M:L) complex for the ligands with  $\text{Co}^{2+}$  (inset). This result is in agreement with that of absorption measurements as seen from Fig. 2(b) (inset).

The complex stability constant (Log K) was also calculated from fluorescence measurements [24]. For this, the quantity  $I_0/(I_0-I)$  is plotted versus  $1/[M]$ , and the stability constant is given by the ratio intercept/slope.  $I_0$  and  $I$  are the fluorescence intensity of free ligand and the fluorescence intensity of the solution involving  $\text{Co}^{2+}$  cation, respectively. Figure 6 shows  $I_0/(I_0-I)$  versus  $1/[M]$  for ligand (3) ( $2.58 \times 10^{-5}\text{M}$ ) with Co (II) perchlorate. Log K was 4.78 for the complex in this case. Log K was calculated from the data obtained from four independent fluorescence measurements. The standard deviation was 0.15. There is good agreement between the log K values obtained from the changes in absorption and fluorescence spectra.

The relative emission intensity ratio ( $I_0/I$ ) used for measurement of the molecular recognition sensing, changed from 0.4 to 6.4 depending on the nature of metal cations as illustrated in Fig. 7. As seen from Fig. 7, the emission intensity of the ligand decreased with the effect of metal cation except for  $\text{Zn}^{2+}$ . This suggests that the interaction of  $\text{Zn}^{2+}$  with the ligand was carried out upon a different mechanism in the excited state. Molar ratio method was used to investigate the complexation of  $\text{Zn}^{2+}$  with the ligand for both absorption and emission data. There was no expected curve related to the complexation in case of both measurements.

A linear response of the fluorescence intensity as a function of  $\text{Co}^{2+}$  concentration was observed from  $1.5 (\pm 0.1) \times 10^{-7}$  to  $3.3 (\pm 0.1) \times 10^{-6}\text{M}$  with linearly dependent coefficient  $R^2 = 0.9908$  (Fig. 8). The detection limit calculated as three times the standard deviation of the blank signal was found to be  $4.8 \times 10^{-8}\text{M}$ .

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