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Photophysical properties of the interaction of lower rim 1,3-bis(aminoethoxy)-calix[4]arene derivative with Pb^{2+}, Hg^{2+} and Cd^{2+}ions: Recognition of Hg^{2+}

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Abstract

Interaction of heavy metal ions, viz., Pb^{2+}, Hg^{2+} and Cd^{2+} with 1,3-bis(aminoethoxy)-calix[4]arene was studied using emission spectroscopy and the corresponding binding parameters were derived. Based on the changes observed in the fluorescence during titration with these metal ions, two types of species were proposed, viz., one in which the metal ion is bound at the lower rim, the other in which the metal ion interacts through the hydrophobic arene cavity. The extent to which these species were present depends upon the type of the metal ion as well as the number of metal ion equivalents added. The results were compared with unmodified calix[4]arene titration data. Based on these studies, Hg^{2+} can distinctly be recognized from the other heavy metal ions.

Keywords: 1,3-Bis(aminoethoxy)-calix[4]arene derivative; Lower rim of calix[4]arene; Fluorescence quench; Arene cavity bound species; Recognition of Hg^{2+}

1. Introduction

Calixarenes and their derivatives are currently receiving prominence in the chemistry literature owing to their diverse structural and binding capabilities that could be used in sensing different kinds of species [1] and a recent review covers cation recognition by calixarene based molecules [2]. The lower rim oxygen donor centers have been used in recognizing alkali cations owing to their hydrophilic as well as hard base character [3]. The calixarenes can be functionalized accordingly to suit the binding requirements. Thus, the presence of relatively soft base donor sites, such as nitrogen in the binding core can bring preference towards transition and post-transition ions over the others. Hg^{2+} was selectively recognized as well as extracted using calix[4]arene-sulfonamide derivatives and thioether and ester derivatives [4–9]. Silica functionalized calix[4]arene derivative was used for sensing Hg^{2+} in aqueous medium [10]. Variety of derivatives of calix[4]arene including those coated on electrodes and imbedded in membranes have been used for sensing Pb^{2+} ions [11–15]. Potentiometric sensing of Pb^{2+} has been reported with some derivatives of calix[4 and 6]arene [16,17]. While carboxylic derivatives were used for extraction of Pb^{2+} [18], the fluorophore bound derivatives were used for sensing Pb^{2+} [19]. A thia-calix[4]arene derivative coated on carbon electrode was shown to sense both Cd^{2+} and Pb^{2+} ions [20]. Crystal structures of eight coordinated Pb^{2+} and Cd^{2+} with the tetraethylester and tetramethyl ketone derivatives of calix[4]arene were reported [21].

Recent work from our group clearly demonstrated the role of chelation of imine together with –OH moiety of a lower rim 1,3-di-derivative in recognizing Zn^{2+} selectively [22] over its non-chelating counterpart where only the imine moiety is present but not the –OH in conjunction with the imine [23]. In this paper, we demonstrate the ability of the lower rim di-amine derivative (1,3-di-derivative) synthesized through *O*-alkylation towards recognizing Cd^{2+}, Hg^{2+} and Pb^{2+}, as the out come may have influence in the detection of these toxic heavy metal ions. In order to study the interaction between the calix[4]arene derivative and these metal ions, emission spectral methods were employed. It was the intrinsic fluorescence of the arene moi-

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eties of the derivative that was monitored during the emission studies.

2. Experimental

2.1. Materials

Metal salts, viz., $Cd(ClO_4)_2{\cdot}6H_2O$, $Hg(ClO_4)_2{\cdot}4H_2O$, $Pb(ClO_4)_2{\cdot}3H_2O$ (caution: perchlorate salts are expected to be handled with appropriate care!) were purchased from Sigma–Aldrich Chem. Co. Analytical grade $CHCl_3$ and CH_3OH were obtained from local sources and were purified and dried by routine procedures immediately before use.

2.2. Synthesis of the lower rim 1,3-diamino derivative of calix[4]arene (L)

As reported by us earlier [7,8], L was synthesized by carrying out two consecutive reactions starting from simple *p*-tert-butyl-calix[4]arene as shown in Scheme 1. While it was the $BrCH_2CN$/acetonitrile combination that was used in the earlier case, in the present case it was the combination of $ClCH_2CN$/acetone that was used. Satisfactory analytical results were obtained for the characterization of L as reported earlier.

2.3. Emission studies

Fluorescence emission spectra were measured on Perkin-Elmer LS55 by exciting the solutions at 240 nm and the emission spectra were recorded in 250–400 nm range. The bulk concentration of L in $CHCl_3$ was 1.5 mM and that of the Cd^{2+}, Hg^{2+} and Pb^{2+} perchlorates in CH_3OH were 15 mM. All the measurements were made in 1 cm quartz cell and maintained a final L concentration of 50 μM. During the titration, the concentration of metal perchlorate was varied accordingly in order to result in requisite mole ratios of metal ion to L and the total volume of the solution was maintained constant at 3 mL in each case by adding appropriate volume of a mixture of 95% CH_3OH–5% $CHCl_3$. Normalized emission (relative fluorescence) intensities (I/I_0) (where I_0 is the intensity with no metal ion addition; I is the intensity at different metal ion to L mole ratios) were plotted against the mole ratio of metal ion to the L. The binding constants of the complexes formed in the solution have been quantitatively estimated by plotting $\log[(I-I_0)/(I^*-I)]$ versus $\log[S]$ (where I_0 and I have the same meaning as earlier; I^* is the maximum Intensity; S is the concentration of the metal salt added). The slope of the straight line gives the ratio of metal cation versus L in the fully saturated case and pK_{ass} for the complex equals to the value of $\log[S]$ at $\log[(I-I_0)/(I^*-I)]=0$, where K_{ass} is association constant.

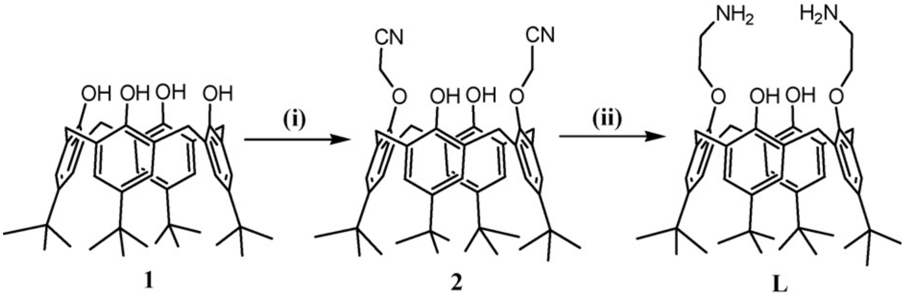
3. Results and discussions

Ligand L was studied for its complexation behavior towards three toxic metal ions, viz., Pb^{2+}, Hg^{2+} and Cd^{2+} using emission spectroscopy.

3.1. Emission studies

The ligand L shows a single emission band at 312 nm arising from the $\pi^* \rightarrow \pi$ transition of the phenyl core of the calix[4]arene derivative. However, in the presence of Hg^{2+}, the fluorescence emission intensity was quenched sharply at low equivalents and a complete quench was noticed at very high equivalents. Thus, in the titration of Hg^{2+} saturation was reached only beyond 50–100 equivalents indicating an equilibrium-shift reaction between Hg^{2+} and L. The corresponding emission spectra (Fig. 1a) and the relative fluorescence intensity plots (Fig. 1b) were shown in Fig. 1. The logarithmic plot in case of Hg^{2+} titration data did not result in a straight line (Fig. 1c) and can be fitted into two straight lines indicating a variation in the type of species present. While the lower ratio yields a K_{ass} of 25,120 M^{-1}, that of the higher yields a K_{ass} of 5010 M^{-1}. However, an average straight-line fit of this data yields a K_{ass} of 19,050 ± 2100 M^{-1} and the slope corresponds to 1:1 species.

Titration of L with Pb^{2+} showed a sharp decrease in the fluorescence intensity till the addition of 2 equivalents of this ion. Upon further addition of this ion there is only a marginal increase in the fluorescence intensity and approaches saturation beyond 50–70 equivalents. Corresponding spectral traces were shown in Fig. 2a. Plot of the relative fluorescence intensity (I/I_0) versus $[Pb^{2+}]/[L]$ (Fig. 2b) clearly indicates the interaction of Pb^{2+} with L being schoichiometric and the species formed were 1:1 when considered up to about 5–10 equivalents. Beyond 10 equivalents, the behavior of this curve is different from that observed in case of Hg^{2+}. The logarithmic plot for 0–10 equivalents resulted in a straight line yielding K_{ass} of 21,550 ± 800 M^{-1} for the binding of Pb^{2+} and the slope conforms to 1:1 species. How-



Scheme 1. Synthesis L: (i) **1** (10.0 g, 15.4 mmol), K_2CO_3 (8.52 g, 61.64 mmol), NaI (9.24 g, 61.64 mmol), chloroacetonitrile (4.77 g, 63.18 mmol), 250 mL acetone, reflux under N_2 for 7 h; (ii) **2** (4.70 g, 6.50 mmol), $LiAlH_4$ (2.0 g, 5.1 mmol), 250 mL diethylether, reflux for 5 h.

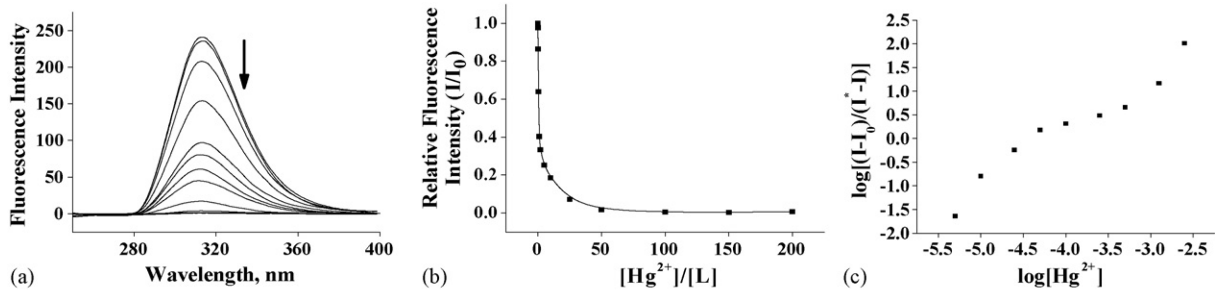


Fig. 1. Fluorescence titration of L with Hg^{2+}: (a) spectral traces, (b) plot of relative fluorescence intensity (I/I_0) vs. $[Hg^{2+}]/[L]$ mole ratio and (c) plot of $\log[(I - I_0)/(I^* - I)]$ vs. $\log[Hg^{2+}]$.

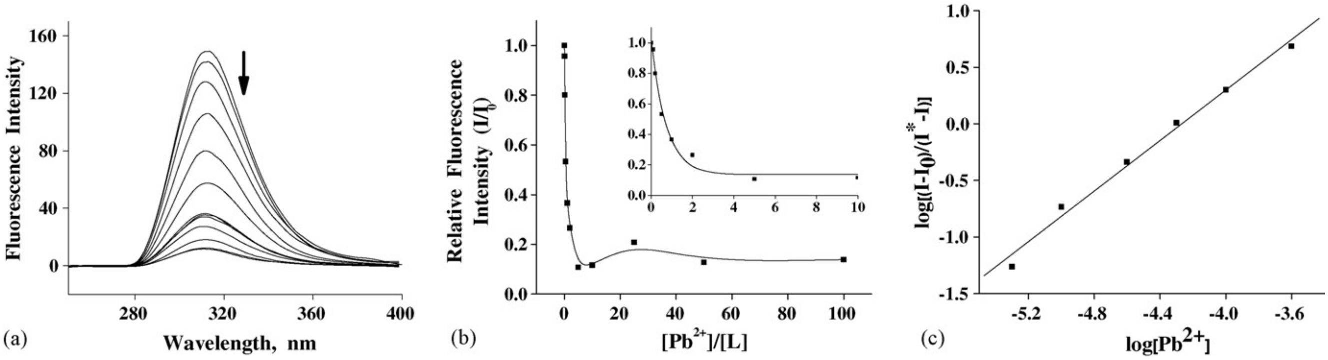


Fig. 2. Fluorescence titration of L with Pb^{2+}: (a) spectral traces, (b) plot of relative fluorescence intensity (I/I_0) vs. $[Pb^{2+}]/[L]$ mole ratio and (c) plot of $\log[(I - I_0)/(I^* - I)]$ vs. $\log[Pb^{2+}]$. Inset in (b) is an expanded version for 0–10 equivalents of Pb^{2+} addition.

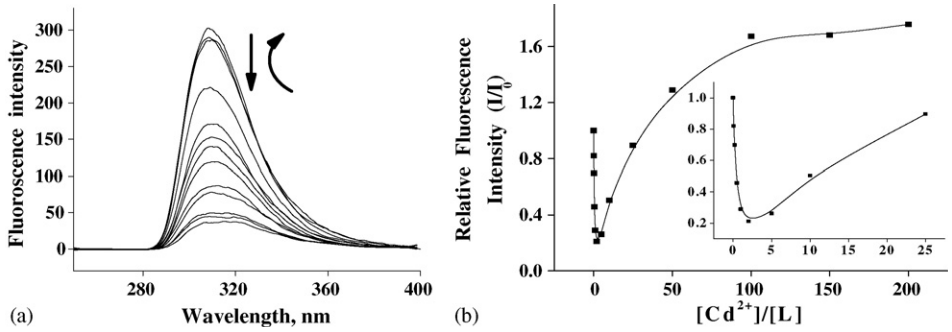


Fig. 3. Fluorescence titration of L with Cd^{2+}: (a) spectral traces (the arrows indicate decrease followed by increase), (b) plot of relative fluorescence intensity (I/I_0) vs. $[Cd^{2+}]/[L]$ mole ratio. Inset in (b) is an expanded version for 0–25 equivalents of Cd^{2+} addition.

ever, an estimation of K_{ass} could not be made for the titration beyond 10 equivalents since the changes in the (I/I_0) were only marginal.

The fluorescence spectra obtained in the titration of L with Cd^{2+} is shown in Fig. 3a. In this titration, the fluorescence intensity initially decreases rapidly by going through a minimum at around 2 equivalents of the metal ion and then gradually increases upon further addition and approaches saturation around 100 equivalents (Fig. 3b). Thus, the titration of L with Cd^{2+} yielded a behavior that is qualitatively comparable with that of Pb^{2+} though there is a lot of difference in their quantitative changes. Further, the fluorescence behavior of Pb^{2+} titration is qualitatively comparable with that of the Hg^{2+} only till about 2–5 equivalents and certainly not beyond. Thus, the initial part (i.e., till 2–5 equivalents) of the titration is qualitatively similar among all the three titrations. The log plot computed for the 0–2 equivalents in case of Cd^{2+} titration yields a K_{ass} of 84,410 M^{-1} and that for the remaining yields a K_{ass} of 935 M^{-1}.

The dual behavior observed in I/I_0 versus mole ratio plot of Pb^{2+} as well as Cd^{2+} titrations can be fitted to two different species, viz., one corresponding to lower mole ratios and another corresponding to higher mole ratios. The behavior of I/I_0 is almost same in lower mole ratios among all the three metal ion titrations and hence same type of species at lower mole ratios. Thus, the distinct fluorescence behavior observed in case of Hg^{2+} titration clearly provides a niche to differentiate Hg^{2+} from the other two heavy ions, viz., Pb^{2+} and Cd^{2+}.

4. Conclusions

The results of fluorescence studies support each other in a sense that there exist one kind of species in the lower equivalent

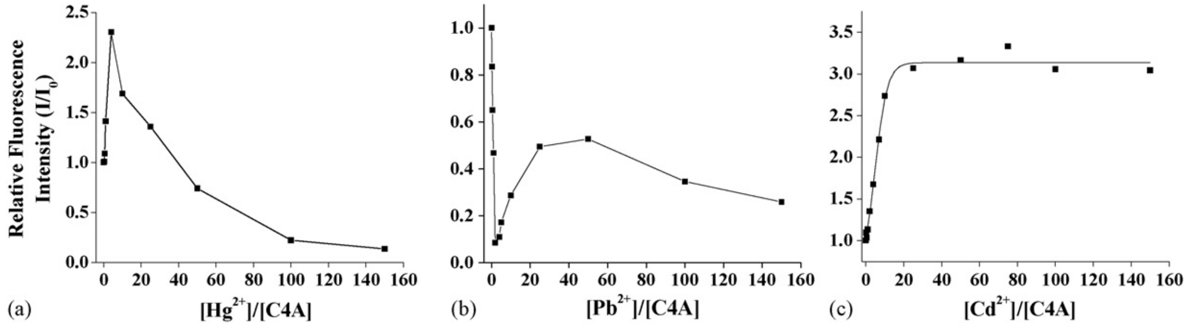
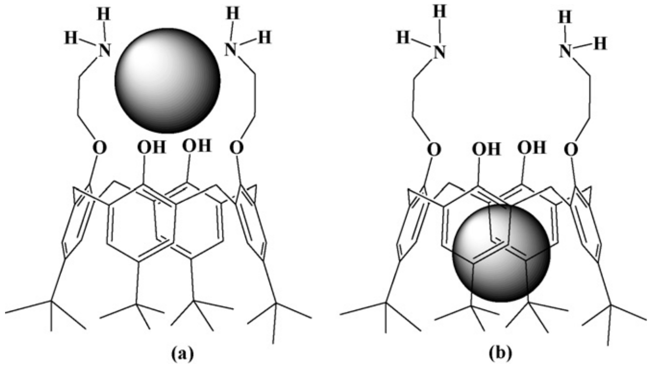


Fig. 4. Plot of relative fluorescence intensity (I/I_0) vs. [M^{2+}]/[C4A] mole ratio in the titration of the unmodified *p*-*t*-butyl-calix[4]arene: (a) Hg^{2+}, (b) Pb^{2+} and (c) Cd^{2+}.



Scheme 2. Proposed species for metal ion interaction with L: (a) lower rim amine bound *species 1* and (b) arene cavity bound *species 2*. Grey sphere indicates the metal ion.

region and a different species at the higher equivalents of metal ion. Number of ways in which a metal ion can interact with L is mainly limited to two types. One is binding through amine terminal of the lower rim and the other is in the hydrophobic arene cavity. Thus, the fluorescence results of the titration of L with these heavy metal ions clearly fits with the presence of two species, viz., species where the metal ion is bound to the amine functions at the lower rim (*species 1*) and another species where the metal ion is present in the hydrophobic arene cavity (*species 2*) as shown in Scheme 2. Similar species were proposed in case of Ag^+ sensing by calix[4]arene derivatives in the literature [24]. While Hg^{2+} primarily shows *species 1* that of the Pb^{2+} and Cd^{2+} show both *species 1* and *2*, of course, to different extents. Thus, Hg^{2+} can be distinctly differentiated from other two heavy ions and this study can provide a means to recognize Hg^{2+}. On the other hand, the titration of the precursor to L, viz., *p*-*t*-butyl-calix[4]arene (C4A) with Hg^{2+} resulted in a fluorescence behavior (Fig. 4a) that is quite different from that observed in case of L. Therefore, the specificity of Hg^{2+} can be attributed to the binding characteristics of the amine moieties present on the pendants at the lower rim in case of L (*species 1*). Comparison of the titration data of L with that of the unmodified *p*-*t*-butyl-calix[4]arene (C4A) clearly showed considerable changes in the fluorescence intensity pattern (Fig. 4b and c) and suggests minimal (Pb^{2+}) or no (Cd^{2+}) interaction at the lower rim owing to the presence of –OH groups instead of $–NH_2$ pendants and as a result the presence of *species 1* is mainly suppressed and *species 2* is dominant.

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