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Evaluation of Complexation Behavior of Calix[4]arene Derivative

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Abstract

In this article we have explored the solvatochromic behavior including solvent selection, time study and complexation ability of 5,11,17,23-Tetrakis(N-piperidinomethyl)-25,26,27,28-tetrahydroxycalix[4]arene (**3**). The complexation behavior of **3** toward the selected transition metals has been explored through FT-IR, UV-visible and fluorescence spectroscopic techniques. It has been found that the ligand **3** has remarkable complexation ability for all selected transition metal (Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}) ions used in the experiment with exceptionally high affinity for Hg^{2+} ions. Besides this, by applying method of continuous variation, i.e. Job's method; the stoichiometric ratio for the complexation between **3** and Hg^{2+} ion in acetonitrile has been determined, which indicates that **3** forms a 1:1 metal:ligand complex. The strong complexation behavior of **3** for Hg^{2+} ions was also confirmed by FT-IR and fluorescence spectroscopy. Consequently, it has been deduced that **3** is a versatile compound and can be used in diverse fields such as analytical/environmental chemistry and sensor technology.

***Keywords**:* Calixarene; Transition metals; Complexation; Liquid-Liquid Extraction; Job's plot.

Introduction

Heavy metals pollution is a serious threat to human health. Their entrance to the food chain and accumulation in various tissues causes many adverse effects to all living organisms [1]. Contamination level of these metals is increasing very quickly because of rapid industrialization and other anthropogenic activities [2]. They are released by many processes such as smelting, mining, paper and pulp industries etc. Among these metals, mercury and cadmium in all forms are highly toxic. Both metals have been used for centuries because of their vast applications in many fields like artisanal mining and in electrode technology [3, 4]. Their main sources of entrance to the environment are mining activities, dentistry, coal fired power plants, volcanoes, urban wastes, and industrial processes such as chloro-alkali processes and batteries manufacturing [5-7]. From these sources, it enters ultimately to marine life where it bioaccumulates in the tissues of marine and thus makes their way to food chain; while amalgam fillings is a source of direct ingestion to human body [8, 9]. They offer many adverse effects such as parentheses, cerebral palsy and, nervous system damages, tetratogenesis, geno-toxicity and even death [10, 11]. Cadmium accumulation in cells, liver and kidneys brings physiological disorders and causes lung, prostate, and renal cancers [12, 13]. Because of these toxic effects towards human beings, there is an intense need for designing innovative material to complex these metals. The complexation of metals through different ligands has enormous application in various fields [14, 15].

However, supramolecular chemistry provides new strategies for developing novel ionophores/ligands for the complexation of toxic metals. Calixarenes are an important class of macrocyclic compounds in supramolecular chemistry, which offer an emerging base/platform for synthesizing new and efficient ligands. They

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have wide application in selective transportation and host-guest complexation [16-21]. Their three-dimensional structure and selective functionalization of both upper and lower rims with ligating podands make them efficient ionophores, which can extract or bind target metal ions selectively [22]. Thus, in continuation to our previous work in this field [23-26] herein, we have developed a strategy to incorporate calix[4]arene platform with relatively soft, donor ligating sites that can selectively bind with the target metal ions.

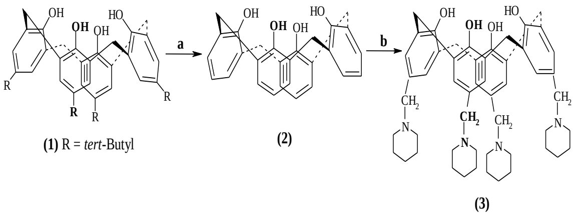
Experimental

Apparatus

Melting points were determined on a Gallenkamp apparatus (UK) in a sealed glass capillary tube and are uncorrected. IR spectra were recorded on a Thermo Nicollet AVATAR 5700 FT-IR spectrometer using KBr pellets in the spectral range 4,000-400. UV–visible spectra were recorded on a Perkin Elmer Lambda-35 UV–visible spectrophotometer using standard (1.00 cm) quartz cells. Gallenkamp (HZ-662l) mechanical shaker with temperature controller was used for shaking. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer. Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}).

Synthesis and characterization

Syntheses of starting material *p*-*tert*-butylcalix[4]arene (**1**), calix[4]arene (**2**) and *p*-piperidinomethylcalix[4]arene (**3**) illustrated in Scheme-1 were carried out by the methods described previously [27-29]. Characterization of the compounds was made by various techniques such as, melting point, TLC, FT–IR, and elemental analysis, which confirm the structure and purity of the compounds.



Scheme 1. Methodology for the synthesis of ligand 3. (a) H_5C_6OH-$AlCl_3$ / (dry) Toluene (b) $H_{11}C_5N$-HCHO / Acetic acid: THF.

Analytical procedure

General procedure for UV–visible, fluorescence and FT–IR measurements

The ligand **3** (5×10^{-5} M) and nitrate salts (50 eq.) of selected transition metals were dissolved in acetonitrile. All solutions were stirred for one hour and warmed if needed. Any change in the UV–visible spectra of **3** was recorded by the addition of respective metal nitrates; while its concentration was kept constant in all experiments. In the fluorescence study, a test solution was prepared by placing 100 µl (5×10^{-5} M) of **3** into a cuvette, adding appropriate aliquot (50 eq) of each metal stock and diluting the solution up to 3.5 ml with acetonitrile. For all experiments, widths of both excitation and emission slits were 5 nm and at fixed excitation wavelength, i.e. 348 nm. Moreover, KBr pellets were used to confirm the complex formation in FT–IR study in the given range.

Results and Discussion

Solvatochromic behavior

Variation in the UV–visible spectra of **3** concerning position, intensity and shape of the absorbance bands in various solvents revealed that solvent plays an important role in complexation process [30]. Study of solvatochromic effect helps in selecting the solvent for a particular ligand that could not show similar spectra in various solvents. In particular, calixarene based ligands show aggregations in some solvents depending on the solvent-solute interactions. In order to examine these effects on metal complexation of ligand **3**, a series of solvents ranging from polar to non-polar were used and analyzed by UV–visible spectrophotometry. It has been observed that solvents like CH_3CN, CH_2Cl_2 and DMSO offer good results. In CH_2Cl_2 and CH_3CN, ligand **3** shows significantly different spectral results in terms of disappearance of its aggregated bands and appearance of more intense bands with greater shifts in λ_{max} as compared with DMSO (Fig 1).

As we know that with the increase in polarity of the solvent the absorption bands shift toward longer wavelengths (i.e. positive solvatochromisim). This effect results due to the presence of non-bonding electron pairs of carboxylic, azo or ester groups in the ligand. But in case of ligand **3**, due to the presence of moderately intermediate nature bearing nitrogen atom, it interacts with less polar solvent. That's why it gives blue shifting (i.e. negative solvatochromisim) with appreciable absorption bands in less polar solvent like acetonitrile and dichloromethane in the region 220-250 nm through n→π* transitions. Many attempts have been made to observe the solvatochromic behavior of ligand **3** in different solvents such as CH_3OH, THF, CH_3COCH_3 and DMF even at low concentration; but due to aggregation and too much noise in the spectra, they have been decided as superfluous except CH_2Cl_2 and CH_3CN. Thus, on the basis of stability, solubility of nitrate salts of transition metals and to ascertain effective complexation without the formation of aggregates; CH_3CN was selected as best solvent for complexation study [31].

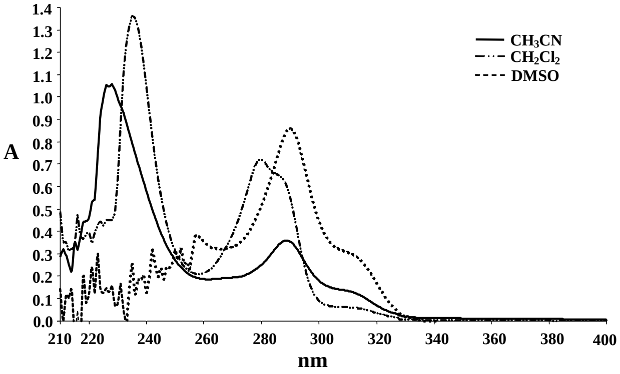


Figure 1. **Absorption spectra of ligand 3 in different solvents (5×10^{-5} M).**

Complexation study

To explore the binding efficiency of ligand **3** towards various metal ions, UV–visible spectroscopic technique was applied. The complexation ability of **3** was examined in acetonitrile (5×10^{-5} M) with the addition of 50 eq of various transition metal ions such as Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+} and Hg^{2+}. A UV–visible spectrum of **3** after the addition of metal ions is shown in Fig 2 (a, b). After complexation, pronounced changes in the absorption spectra have been observed, which shows that **3** has remarkable affinity toward metal ions and in particular with Hg^{2+}. Since, Hg^{2+} forms stronger complex with ligand **3** by showing significant difference in the absorption spectra through the disruption of n-π* transitions in the region 220-280 nm thus; it has been decided that further investigations will be carried out only with Hg^{2+}.

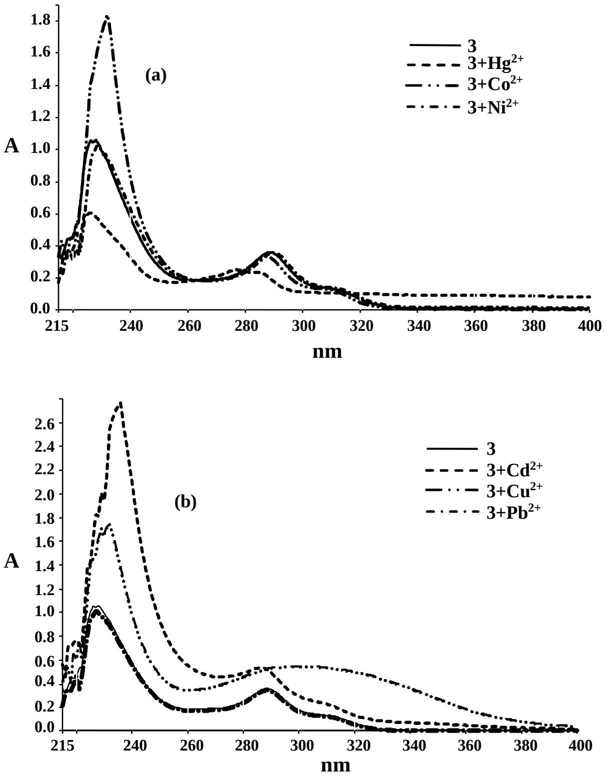


Figure 2. **UV-visible complexation study of 3 (5×10^{-5} M) before and after the addition of different metals (50 eq) in acetonitrile; (a) Hg^{2+}, $Co^{2+}$and Ni^{2+} (b) Cd^{2+}, Cu^{2+} and Pb^{2+}.**

Job's plot

To find stoichiometric ratio between the ligand **3** and Hg^{2+}, method of continuous variation was applied by plotting absorbance verses mole fraction. From (Fig. 3), it is clear that the maximum absorbance is observed at 0.5 mole fraction, which indicates that the complexation involves 1:1 metal:ligand ratio.

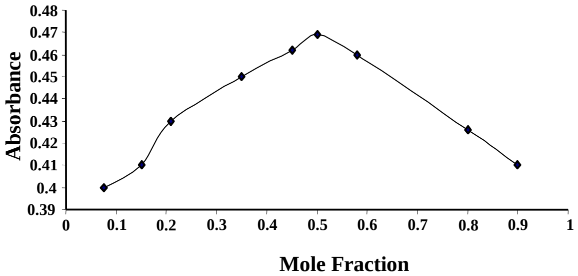


Figure 3. **Job's plot for Hg^{2+} complex of ligand 3.**

From the spectrophotmetric results, it has been revealed that only the size ($Pb^{2+} > Hg^{2+} > Cd^{2+}$) of cation does not play the significant role [32], but the nature of binding sites in the ligand (i.e. hard/soft) and the metal ions (softness follows the order $Hg^{2+} > Cd^{2+} > Pb^{2+}$) also contributes to the complexation process. Moreover, this leads to the idea that nitrogen as donor atom of **3** may prefers Hg^{2+} among rest of metal ions due to its borderline softness nature. This phenomenon may reflect the 'hard and soft acids and bases' concept introduced by Pearson [33]. As this environment exists due to the presence of nitrogen containing functionalities, where lone pair interactions favor the complexation with the more polarizable transition metal ions especially Hg^{2+}, which is known as soft metal cation [34-39]. The proposed model for metal-ligand interaction is given in (Fig. 4).

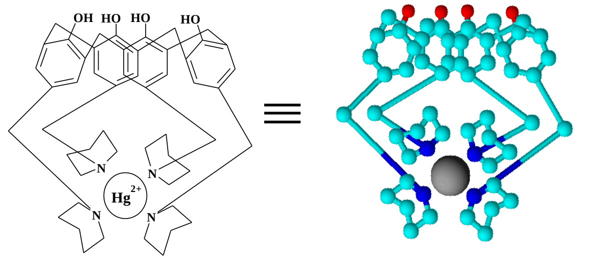


Figure 4. **Proposed model for Hg^{2+}-ligand 3 complex (a) Simple model (b) 3D model.**

Stability of ligand 3 and its complex

To further explore the complexation phenomenon of **3** with Hg^{2+}, the absorption profile as a function of stability of pure ligand and its complex with respect to time was tested. In order to determine the stability of ligand **3** and its Hg^{2+} complex in a selected solvent, i.e. acetonitrile; the UV–visible absorption spectra of ligand **3** were immediately obtained after UV–visible light irradiation from 0 to 200 minutes (Fig. 5). The results show that no spectral change appears in the spectra with the passage of time and hence, it has been concluded that **3** is stable in acetonitrile.

Timely response of chromoionophores or chemosensor is an important phenomenon. Besides this, stability of complex has also given a primary importance because of susceptibility of complex toward decomposition with respect to time, as highly efficient chromoionophore should not be time dependent. The ligand **3** responses very fast and when titrated with $Hg(NO_3)_2$, a prominent band appears with appreciable absorption at near 230 nm very rapidly and remains quite stable with the passage of time (Fig. 6), which indicates the stability of the complex too.

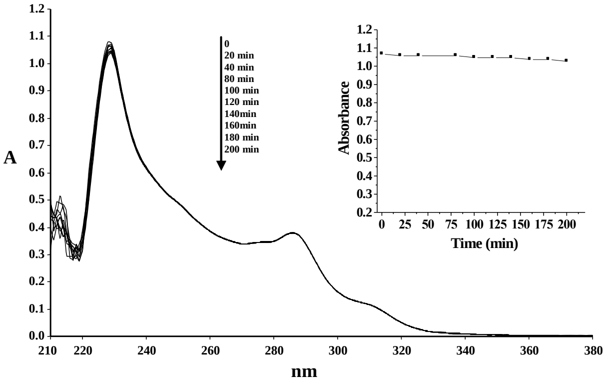


Figure 5. **Stability of 3 in acetonitrile (5×10^{-5} M) with respect to time.**

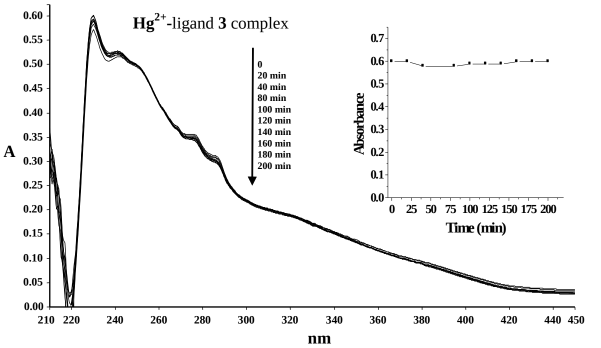


Figure 6. **UV-visible spectra showing stability of Hg^{2+}-ligand 3 complex in acetonitrile along with time study graph.**

Fluorescence spectroscopic study

Since, UV–visible provided clear evidence for high binding affinity of **3** for Hg^{2+} as compared with other transition metal ions. Thus, it was necessary to further confirm the formation of complex with other spectroscopic techniques. For this purpose, the nitrate salt of Hg^{2+} was taken to examine the metal fluorescence sensing ability of ligand **3** in solution using CH_3CN as a solvent. Fluorescence spectrum of ligand **3** shows enhancement of fluorescence intensity from 800 to 1000 nm upon complexation with Hg^{2+} in the region around 340 nm, which confirms the formation of complex between ligand **3** and Hg^{2+} (Figs. 7 and 8).

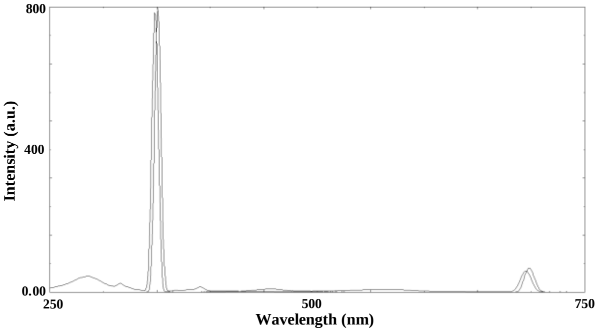


***Figure 7.* Excitation and Emission spectra of ligand 3 in acetonitrile (5×10^{-5} M).**

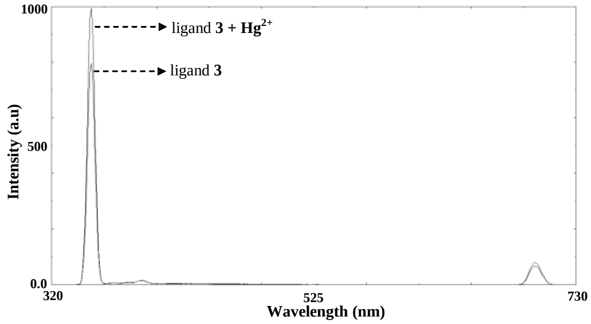


***Figure 8.* Emission spectra of ligand 3 (5×10^{-5} M) before and after complexation with nitrate of Hg^{2+} (50 eq.).**

FT–IR study

Complexation phenomenon of **3** with Hg^{2+} was also studied through FT–IR spectroscopic technique. From (Fig. 9), it is clear that various shiftings in frequencies are taking place after complexation of Hg^{2+} ion with ligand **3**. A peak υ(C-N) which appears at 1330 cm^{-1} shifts to 1382 cm^{-1} after complexation. Similarly, C-H stretching also undergoes into a change and shifts from 2996 cm^{-1} to 2967 cm^{-1}. Merging of several peaks at 1382 cm^{-1} gives informative signs for the formation of complex between ligand **3** with Hg^{2+} [30].

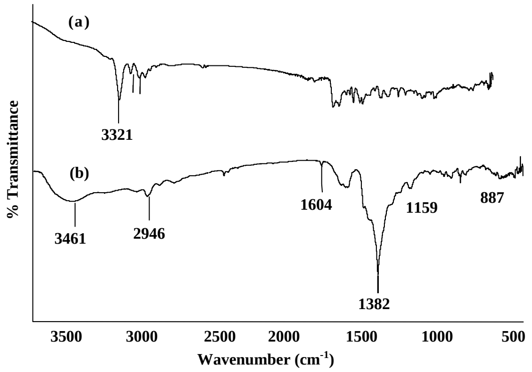


***Figure 9.* Comparative FT–IR studies of (a) ligand 3 (b) Hg^{2+}-complex of ligand 3.**

Conclusions

In the present work, we have investigated the solvatochromic, complexation and sensing properties of ligand **3** by using UV–visible, FT–IR and fluorescence spectroscopic techniques. Ligand **3** shows clear indication of complexation with Hg^{2+} ion. The specificity of Hg^{2+} ion can be attributed to soft nature of both the metal and the binding sites present at the wide rim of ligand **3**. Moreover, geometry of ligand **3** also seems to be attuned in terms of preorganization, size and accommodation of Hg^{2+}.

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