

Synthesis of new chromogenic calix[4]arene based molecular receptors for palladium and platinum

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Abstract Four new chromogenic alkylthiophenylazo-calix[4]arenes (**3–6**) have been synthesized. It has been observed that methylthioazocalix[4]arene (**6**) has a potential for developing into molecular diagnostics for Pd(II) and Pt(II).

Keywords Alkylthioazocalixarenes · Molecular receptors · Platinum ions · Palladium ions

Introduction

The presence of distinct hydrophobic and hydrophilic domains and adjustable cavity dimensions in calixarene molecular architecture has enhanced their potential use in recognition of metal ions of biological [1, 2], medicinal [3, 4], radioactive [5, 6] and environmental significance [7]. Easy functionalization of hydrophobic region (upper rim) or hydrophilic region (lower rim) further creates opportunities for development of efficient and specific molecular hosts for complexation of cations [8–11], anions [12–14] and neutral species [15–17]. A large volume of research work has been accomplished on the use of calixarenes for developing receptor of alkali and alkaline earth metal ions. For example, Chawla et al. [18] have reported calix[4]-crowns which have shown considerable selectivity for potassium over sodium. Similarly, Martin et al. [19] have reported *p*-phosphonic acid substituted calix[*n*]arenes and their *O*-alkylated lower rim analogues for selective stabilization and protection of nano-particles and graphene

sheets, encapsulation of bioactive molecules and binding of calcium ions. Although calixarene derivatives have been used for the development of receptors for heavy metal ions, research on their use is limited [20, 21].

In recent years development of chromogenic receptors have attracted considerable attention for use as analytical reagents and chemical sensors [22]. Azo chromophore (–N=N–) has been variously utilized in the development of chromogenic compounds for applications in dyeing [23], coloring and optical sensing [20, 24] as well as construction of molecular devices [20]. Coupling of azo group to the unique architecture of calixarenes, introduces a desirable specificity and selectivity which in principle can result in highly sensitive and selective receptors for metal ions especially the development of sensors for monitoring toxic metal ions in the environment and help keep the environment green and clean while attempting large scale organic synthesis. During recent years many diazo-coupled calixarenes have been reported which have also been used for selective extraction of metal ions [25–28]. For example, Karakus et al. [29] have reported removal of heavy metal ions (Ag⁺, Hg⁺, Hg²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺ and Cr³⁺) from aqueous solution by azocalix[4]arenes.

We believe that soft binding sites having large affinity for the guest ions should be useful to achieve optical transduction through azo groups even when they are present in the calix[4]arene molecular architecture [30–33]. It has been well established by us [34–36] as well as by others [37–40] that attachment of ionisable chromogenic azo groups in positions adjacent to the polar cavity of calixarenes yield useful materials that exhibit both coloring and binding attributes. Working on this line, we have recently reported the development of chromogenic calixarenes that exhibit selective interaction with mercury and platinum ions [36]. Deligoz and coworkers [41] have

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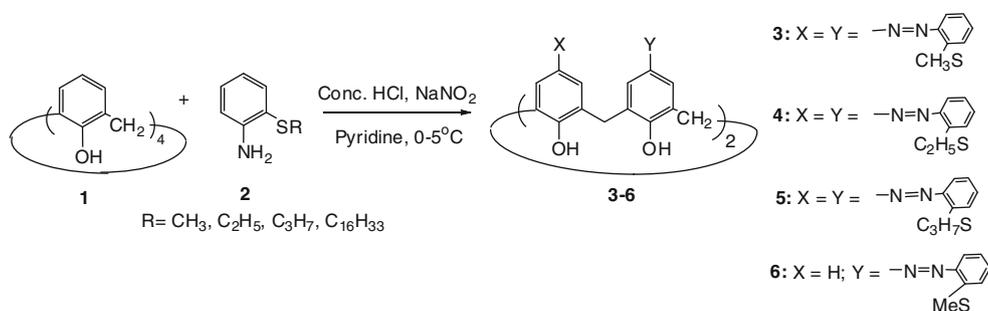
utilized azocalixarene derivatives for extraction of transition metal ions (Ag^+ , Hg^{2+} and Hg^+) from aqueous solution. Similarly a calixarene carboxyphenylazo derivative has been synthesized by Lu et al. [42] as a diagnostic for lead. While a large number of azo calixarenes have been reported in the literature [20, 22, 43], there is very little information about azocalixarenes with additional sulphur hetero atom that interact specifically with palladium and platinum ion. There seems to be very less work on interaction of palladium and platinum ions by calixarene based molecular receptors. In this paper we report the synthesis of five new calixarene derivatives containing multi heteroatoms as potential diagnostics for heavy and precious metal ions especially with special reference to their interaction with Pd^{2+} and Pt^{4+} ions through use of NMR and UV-vis spectroscopic measurements.

Results and discussion

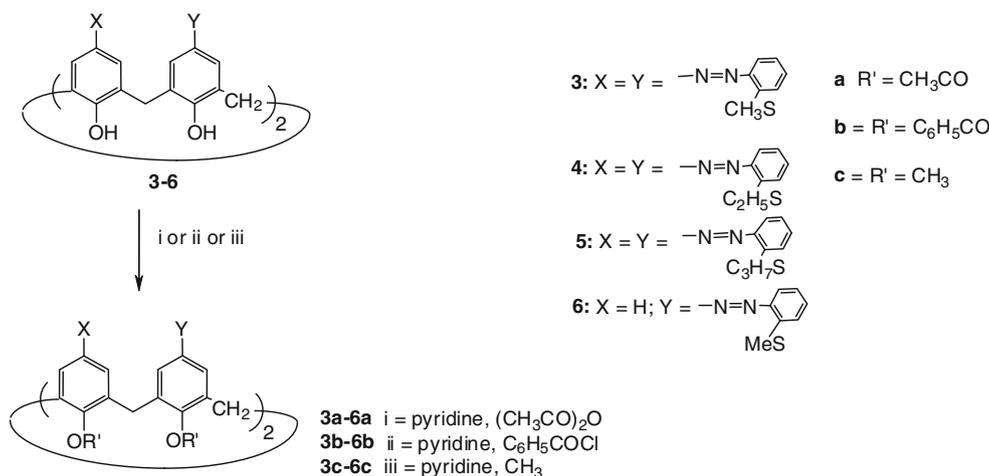
The new calix[n]arene dyes, **3–6** were synthesized by coupling calix[4]arene and 2-alkylthiobenzenediazonium

chlorides at 0–5 °C. All the products were further purified by extensive chromatography (silica gel) to provide new chromogenic calixarenes in good yields (Scheme 1). The structures of synthesized molecular receptors were established by analyzing their spectral and physical characteristics as well as chemical derivatization. For instance, while presence of azo group in the synthesized receptor ($\text{R}'=\text{CH}_3$) was confirmed from its UV spectrum (λ_{max} 356 nm with a shoulder at 400 nm in methanol) and characteristic IR absorption ($1,593\text{ cm}^{-1}$), chemical derivatization of **3–6** (reaction with benzoyl chloride, methyl iodide, acetyl chloride) and spectral identification of synthesized derivatives, (Scheme 2) confirmed the gross structure assigned to it.

^1H NMR spectrum of **6** showed two broad signals at δ 4.30 and 3.65 (which became sharper at low temperatures and on derivatization) to reveal that phenyl rings in **6** are in a syn orientation and the compound could undergo temperature dependent conformational isomerization. This conclusion was confirmed by its HSQC spectrum (Fig. 1). Cone (or near cone) conformation of **6** was confirmed by the observation of ^{13}C NMR signal for methylene carbons



Scheme 1 Synthesis of chromoionophore **3–6**



Scheme 2 Further chemical derivatization of chromoionophore **3–6**

Fig. 1 Aromatic (a) and methylene (b) regions of ^1H - ^{13}C -HSQC spectrum of **6** (CDCl_3 , 300 MHz, r.t.)

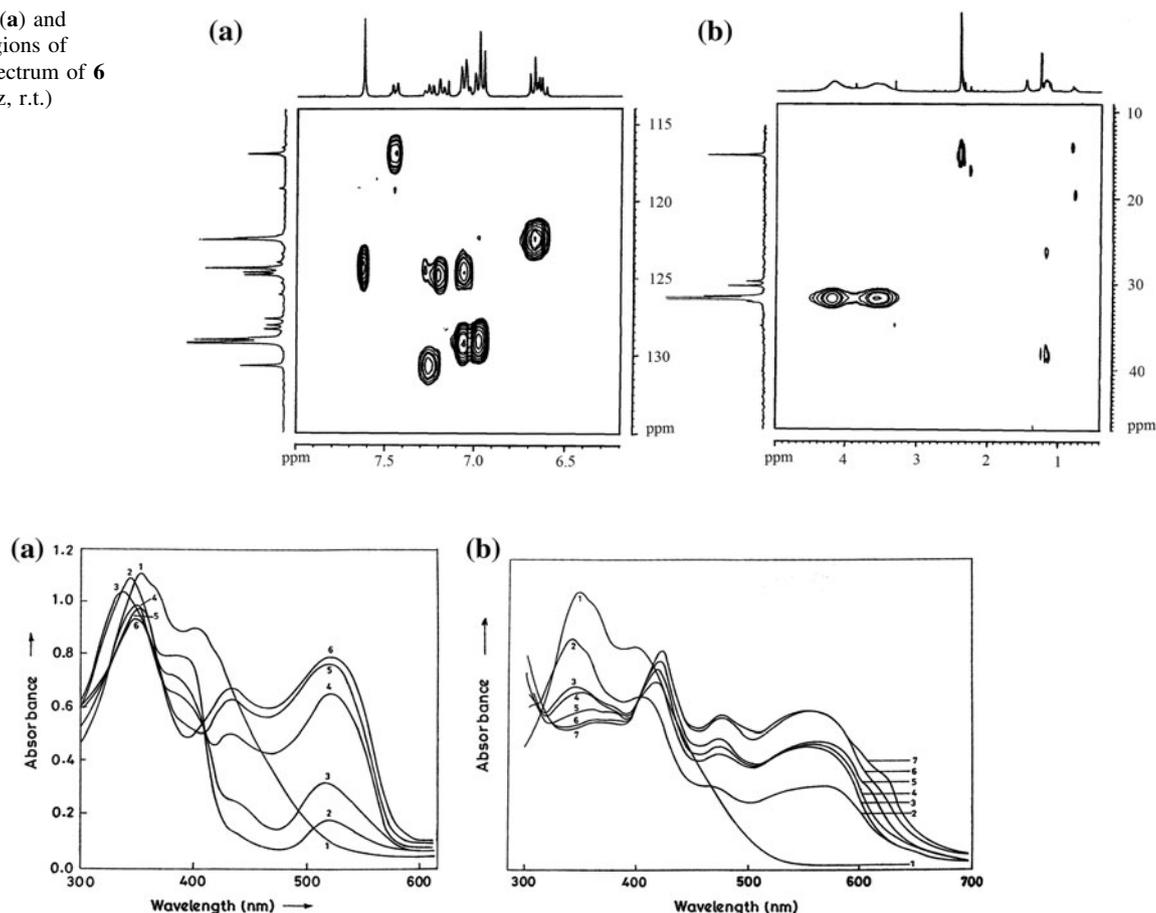


Fig. 2 a Changes in the absorption spectrum of $4.6 \times 10^{-7} \text{ mol dm}^{-3}$ solution of **6** in methanol (1) resulting from the addition of the following concentrations (in mol dm^{-3}) of Na_2PdCl_4 in methanol, 2, 0.6×10^{-7} ; 3, 1.2×10^{-7} ; 4, 3.59×10^{-7} ; 5, 4.79×10^{-7} ; 6, 17.95×10^{-7} . **b** Changes in the

absorption spectrum of $4.6 \times 10^{-7} \text{ mol dm}^{-3}$ solution of **6** in methanol (1) resulting from the addition of the following concentrations (in mol dm^{-3}) of K_2PtCl_4 in methanol, 2, 2.29×10^{-7} ; 3, 4.5×10^{-7} ; 4, 6.0×10^{-7} ; 5, 7.24×10^{-7} ; 6, 9.36×10^{-7} ; 7, 13.24×10^{-7}

of calix[4]arene at δ 31.75 which is in consonance with similar literature precedents as well as analysis of ^1H , ^{13}C -HSQC-NMR spectra (Fig. 1) [36, 44].

The synthesized chromogenic calixarenes appended with sulfur and nitrogen heteroatoms in addition to oxygen are expected to coordinate with heavy or transition metal atoms. Based upon this expectation, experiments were carried out with **6** and transition metal ions such as Pt^{2+} , Pd^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , and Fe^{2+} . To rule out binding with soft metal ions, we have also examined interactions with alkali metal ions (Na^+ and K^+). It has been observed that **6** can interact with platinum and palladium ions but not with aqueous methanolic solutions containing iron, copper, nickel, cobalt, sodium and potassium ions. For example, addition of palladium(II) and platinum(II) salts to a methanolic solution of **6** gave an immediate color change from yellow to red. Differential spectral response to these ions obeyed Lambert–Beer relationship at 10^{-3} M concentration of calix[4]arene derivative. The **6**-metal ion interaction

could be followed spectrophotometrically when significant bathochromic shifts were observed in λ_{max} of **6** (350, 400 nm) on addition of K_2PdCl_4 (330, 430, 520 nm) and K_2PtCl_4 (420, 470, 560(br) nm) respectively (Fig. 2). However, A slight deviation has been observed for free ligand in Fig. 2 and a clear isobestic point was not observed presumably due to in situ conformational morphosis (this point is being investigated) [45] in the synthetic receptor. Evaluation of mole ratio plots provided $[\text{6}]/[\text{Pd}]$ and $[\text{6}]/[\text{Pt}]$ ratio as 1:1 or 1: 2 respectively which was confirmed by investigations through Jobs plots (Figs. 3, 4) [36].

The NMR titrations indicated that addition of Pd(II) solution (Na_2PdCl_4) of **6** caused a down field shift of thio-methyl (S–Me) protons from δ 2.17 to 2.93 while addition of Pt(II) solution (K_2PtCl_4) caused a similar shift from 2.17 to 2.50 ppm (Fig. 5). The aromatic region of the NMR spectrum became quite complex in both the cases and hydroxyl protons of the lower rim of the calixarene σ -framework in **6** remained unaltered.

Fig. 3 **a** Mole ratio plot for the formation of **6**-Pd complex. **b** Job's continuous variation plot for the formation of **7**-Pd complex

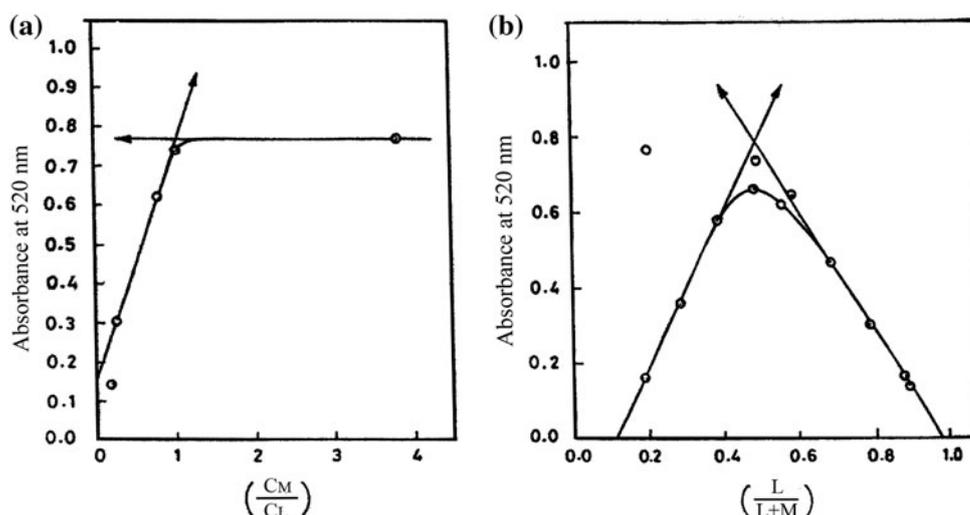
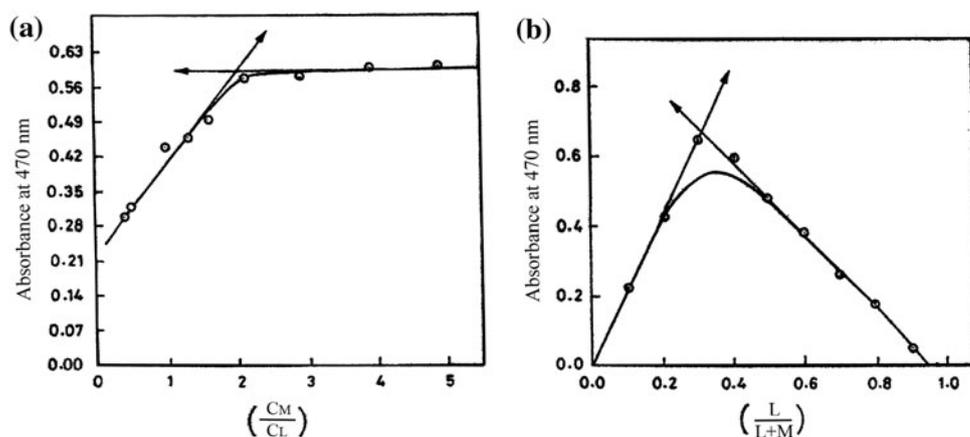


Fig. 4 **a** Mole ratio plot for the formation of **6**-Pt complex. **b** Job's continuous variation plot for the formation of **7**-Pt complex



An equimolar solution of the metal ion and the synthesized molecular receptor on slow evaporation in a desiccator left a residue which was not found to be suitable for single crystal X-ray but the residue showed a considerable reduction in the $\nu_{N=N}$ stretch frequency, e.g. to $1,550\text{ cm}^{-1}$ for **6**-palladium complex and to $1,565\text{ cm}^{-1}$ for **6**-platinum complex indicating the involvement of azo group in metal-receptor interaction [36]. Strangely, metal-carbon and ν_{S-C} absorptions were also observed at 759 and 720 cm^{-1} in the case of **6**-Pd(II) and 738 and 695 cm^{-1} in the case of **6**-Pt(II) compounds respectively. Preliminary observations on selectivity of **6** for Pd(II) and Pt(II) were made on their mixture with diverse transition metal ions (Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+}) and alkali metal ions (K^+ , Na^+ and Cs^+) by following the methods described in the literature [46]. The observed selectivity (as determined by measuring the shift in the absorption maximum of **6**) followed the sequence $\text{Pd} > \text{Pt} > > > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{2+} - \text{Fe}^{3+} > > > \text{K}^+ > \text{Na}^+$. Further functionalization and evaluation of **6** and

related compounds to obtain suitable sensor components for precious metal ions is in progress.

Experimental

General procedure for coupling reaction of tetrahydrocalix(4)arene with diazotized 2-alkylthioaniline

A solution of 2-alkylthiobenzenediazonium chlorides prepared from 2-alkylthioaniline (10 mmol) and concentrated HCl (2.5 ml) in water (15 ml), at $0-5\text{ }^\circ\text{C}$ was added drop wise to an ice-cold solution of calix(4)arene (1.0 g, 2.36 mmol) in pyridine (25 ml) with constant stirring to give red suspension. After stirring the suspension for 5 min at the same temperature range, it was gradually allowed to attain the room temperature. The reaction mixture was kept for 15 min at room temperature and then the suspension

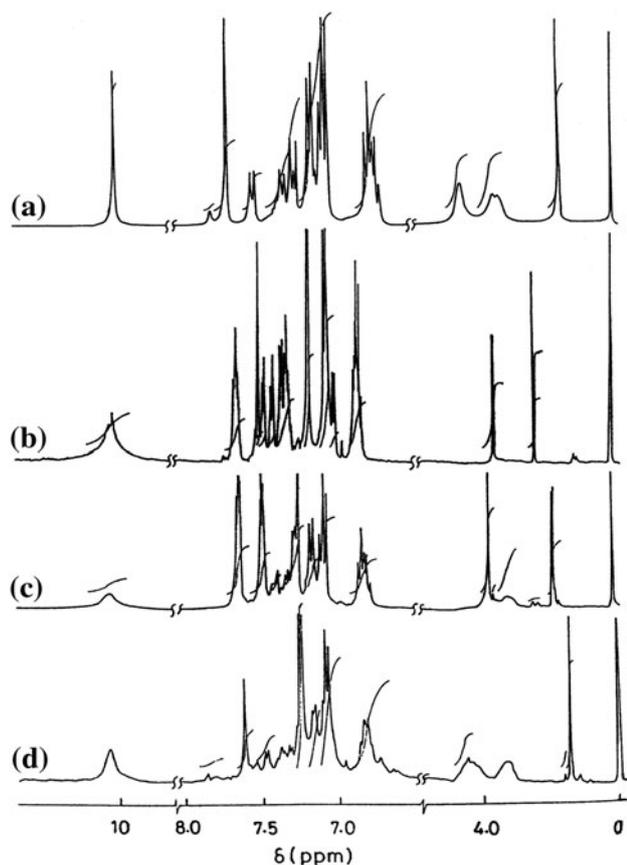


Fig. 5 $^1\text{H-NMR}$ spectrum of **6** (a) and its change upon addition of Pd(II) (b) Pt(II) (c) and Cu(II) (d) solutions

was poured into 500 ml of water followed by acidification with concentrated HCl. The mixture was warmed to 60 °C for 30 min to produce azo calixarenes in moderate to poor yields as red solids which were filtered and subsequently washed with water and methanol. The compounds were finally dried and used for further studies.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetra(2-thiomethylphenylazo)calix[4]arene: 3

A solution of 2-methylthioaniline (1.40 g, 10 mmol) (prepared from 2.5 g of 2-aminothiophenol and iodo methane), sodium nitrite (1.0 g, 15 mmol) and concentrated HCl (2.5 ml) in water (15 ml) was slowly added (over a period of about 30 min) into an ice-cold solution of tetrahydroxycalix(4)arene (1.0 g, 2.36 mmol) in 20 ml of pyridine at 0–5 °C to give red suspension. The reaction was worked out as described in the general procedure. It was purified by crystallization from THF and methanol to give **3** (1.23 g, 51%) as a red solid. m.p. > 300 °C. (Calculated for $\text{C}_{56}\text{H}_{58}\text{N}_8\text{O}_4\text{S}_4$: C, 65.60; H, 4.72; N, 10.93; S, 12.5. Found: C, 66.50; H, 4.02; N, 11.53; S, 11.5. Mol. mass

(vapour pressure osmometry): 1055 (Calculated 1025). UV (λ_{max} , DMSO): 412 nm. IR (KBr; ν_{max} , cm^{-1}): 3456(bs), 1584(s), 1567(m), 1482(m), 1436(w), 1372(w), 1276(w), 1212(w), 762(m), 620(w). $^1\text{H-NMR}$ (DMSO- d_6 ; δ , ppm): 9.03 (4H, bs, exchangeable with D_2O , OH), 7.60–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH_2Ar), 2.44 (12H, s, CH_3).

25,26,27,28-Tetrahydroxy-5,11,17,23-tetra(2-thioethylphenylazo)calix[4]arene

A solution of 2-ethylthioaniline (1.53 g, 10 mmol) (prepared from 2.5 g of 2-aminothiophenol and iodoethane), sodium nitrite (1.0 g, 15 mmol) and concentrated HCl (2.5 ml) in water (15 ml) was slowly added (over a period of about 30 min) into an ice-cold solution of tetrahydroxycalix(4)arene (1.0 g, 2.36 mmol) in 25 ml of pyridine at 0–5 °C to give red suspension. The reaction was worked out as described in the general procedure. It was purified from THF and methanol to give **4** (0.53 g, 21%) as a red solid. m.p. > 250 °C. (Calculated for $\text{C}_{60}\text{H}_{56}\text{N}_8\text{O}_4\text{S}_4$: C, 66.64; H, 5.22; N, 10.36; S, 11.86). Found: C, 66.50; H, 5.02; N, 10.53; S, 11.56. Mol. mass (vapor pressure osmometry): 1,108 (Calculated 1,081). UV (λ_{max} , DMSO): 420 nm. IR (KBr; ν_{max} , cm^{-1}): 3456(bs), 1578(m), 1567(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). $^1\text{H-NMR}$ (DMSO- d_6 ; δ , ppm): 8.70 (4H, bs, exchangeable with D_2O , OH), 7.61–6.83 (24H, m, ArH), 4.10 (8H, bs, ArCH_2Ar), 2.44 (8H, s, SCH_2), 1.44 (12H, s, CH_3).

25,26,27,28-Tetrahydroxy-5,11,17,23-tetra(2-thiopropylphenylazo)calix[4]arene: 5

A solution of 2-propylthioaniline (1.68 g, 10 mmol) (prepared from 3.0 g of 2-aminothiophenol and iodo propane), sodium nitrite (1.0 g, 15 mmol) and concentrated HCl (2.5 ml) in water (15 ml) was slowly added (over a period of about 30 min) into an ice-cold solution of tetrahydroxycalix(4)arene (1.0 g, 2.36 mmol) in 25 ml of pyridine at 0–5 °C to give red suspension. The reaction was worked out as described in the general procedure. It was purified by crystallization from THF and methanol to give **5** (1.52 g, 57%) as a red solid. m.p. 240 °C (decomp.). (Calculated for $\text{C}_{64}\text{H}_{64}\text{N}_8\text{O}_4\text{S}_4$: C, 67.58; H, 5.67; N, 9.85; S, 11.28). Found: C, 67.90; H, 5.20; N, 10.12; S, 11.56. Mol. mass (vapor pressure osmometry): 1,157 (Calculated 1,138). UV (λ_{max} , CHCl_3): 420 nm. IR (KBr; ν_{max} , cm^{-1}): 3430(bs), 2870(m), 1584(s), 1563(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). $^1\text{H-NMR}$ (CDCl_3 ; δ , ppm): 8.70 (4H, bs, exchangeable with D_2O , OH), 7.07–7.00 (24H, bm, ArH), 4.08 (8H, bm, ArCH_2Ar), 2.48 (8H, s, SCH_2), 1.73 (8H, m, SC-CH_2), 1.00 (12H, t, SC.C.CH_3).

25,26,27,28-Tetrahydroxy-5, 17-di(2-thiomethylphenylazo)calix[4]arene: (6)

An ice cold solution of 2-methylthiobenzenediazoniumchloride (0.75 g, 5.79 mmol), concentrated HCl (1.4 ml) in water (1.5 ml) and NaNO₂ (0.4 g, 10.86 mmol) in water (1.9 ml) as added to an ice cold solution of tetrahydroxycalix[4]arene (1.06 g, 2.5 mmol) in pyridine (10 ml) and THF (15 ml) at 0–5 °C with constant stirring. The addition of diazonium salt was done slowly over a period of about 20 min. After addition was complete, the reaction mixture was stirred for additional 30 min at 10–15 °C and then it was gradually brought to room temperature. The reaction mixture was poured into water and stirred well to produce the diazocalix[4]arene as red solid which was filtered, washed successively with water, dilute HCl and ether. The solid obtained was purified by crystallization from CHCl₃ and hexane to give **6** as red solid. The samples of analytical standard were prepared by passing the crude compound through silica gel column using ethyl acetate as eluent. Yield (0.9 g, 49%). m.p. 263–270 °C. Mol. Mass (vapor pressure osmometry): 742 (calcd. 724.9). Anal. calcd. for C₄₂H₃₆N₄O₄S₂: C, 69.59; H, 5.01; N, 7.73; S, 8.85. Found: C, 68.50; H, 5.52; N, 7.53; S, 8.41. UV [CHCl₃; λ_{max} (ε)]: 350 nm (24774), 400 nm (18842) (appears as shoulder). IR (KBr; ν_{max}, cm⁻¹): 3178(bs), 1593(m), 1436(w), 1372(w), 1276(w), 1212(w), 753(m), 620(w). ¹H-NMR (CDCl₃; δ, ppm): 10.21 (4H, bs, exchangeable with D₂O, OH), 7.72–6.71 (18H, m, ArH), 4.30, 3.65 (8H, s, ArCH₂Ar), 2.17 (6H, s, SCH₃). ¹³C-NMR (CDCl₃; δ, ppm): 151.91, 148.65, 130.69, 129.19, 125.32, 124.78, 124.61, 122.45, 122.36, 115.67, 31.75, 31.64, 14.91.

General procedure for the reaction of diazocalix(4)arenes **3–6** with acetic anhydride

A solution of diazocalix(4)arene **3–6** (0.75 mmol) in pyridine (10 ml) was treated with acetic anhydride (5 ml) on boiling water bath for 20 h. The reaction mixture was cooled and poured into ice-cold dilute HCl (5%, 300 ml) to yield a yellow precipitate, which was collected by suction filtration and dissolved in CHCl₃ (30 ml) and charcoaled with active charcoal (2 g). Recrystallization of the product from CHCl₃–methanol (1:1) gave **3a–6a** as yellow crystalline solids.

25,26,27,28-Tetraacetyloxy-5,11,17,23-tetra(2-thiomethylphenylazo)calix[4]arene: 3a

(0.27 g, 30%) m.p. > 250 °C, Calcd. for C₆₄H₅₆N₈O₈S₄: C, 64.41; H, 4.73; N, 9.39; S, 10.75. Found: C, 65.64; H, 5.02; N, 9.60; S, 11.26. Mol. Mass (vapor pressure

osmometry): 1177 (Calcd. 1193). UV (λ_{max}, CHCl₃): 412 nm. IR (KBr; ν_{max}, cm⁻¹): 2908(sh), 1758(s), 1563(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ, ppm): 7.60–6.80 (24H, m, ArH), 4.12 (8H, bs, ArCH₂Ar), 2.44 (12H, s, SCH₃), 2.04 (12H, s, OCCH₃).

25,26,27,28-Tetraacetyloxy-5,11,17,23-tetra(2-thioethylphenylazo)calix[4]arene: 4a

(0.23 g, 25%) m.p. > 250 °C, Calcd. for C₆₈H₆₄N₈O₈S₄: C, 65.36; H, 5.16; Found: C, 65.64; H, 5.22. UV (λ_{max}, CHCl₃): 415 nm. IR (KBr; ν_{max}, cm⁻¹): 2898(sh), 1752(s), 1582(s), 1567(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). ¹H-NMR (CDCl₃; δ, ppm): 7.61–6.83 (24H, m, ArH), 4.10 (8H, bs, ArCH₂Ar), 2.44 (8H, s, SCH₂), 2.13 (12H, s, OCCH₃), 1.44 (12H, s, CH₃).

25, 26, 27, 28-Tetraacetyloxy-5,11,17,23-tetra(2-thiopropylphenylazo)calix[4]arene: 5a

(0.21 g, 21%), m.p. > 223 °C (decomp.), Calcd. for C₇₂H₇₂N₈O₈S₄: C, 66.23; H, 5.56. Found: C, 67.64; H, 5.22. UV (λ_{max}, CHCl₃): 420 nm. IR (KBr; ν_{max}, cm⁻¹): 2898(sh), 1733(s), 1572(m), 1453(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ, ppm): 7.60–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH₂Ar), 2.38 (8H, s, SCH₂), 2.06 (12H, s, OCCH₃), 1.68 (8H, m, SCCH₂), 1.18 (12H, t, SC.C.CH₃).

25,26,27,28-Tetraacetyloxy-5,17-di(2-thiomethylphenylazo)calix[4]arene: 6a

(0.15 g, 22%). m.p. > 250 °C (decom.); Mol. Mass (vapor pressure osmometry): 845 (calcd. 839). Anal. calcd. for C₅₀H₄₄N₄O₈S₂: C, 67.25; H, 4.97; N, 6.27; S, 7.18. Found: C, 67.64; H, 4.02; N, 6.60; S, 7.86. UV (λ_{max}, CHCl₃): 412 nm. IR (KBr; ν_{max}, cm⁻¹): 2998 (sh), 1750 (s), 1560(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ, ppm): 7.60–6.80 (18H, m, ArH), 4.30, 3.65 (8H, d, ArCH₂Ar), 2.26 (12H, s, OCOCH₃), 2.18 (6H, s, SCH₃).

General procedure for the reaction of diazocalix(4)arenes **3–6** with benzoyl chloride and pyridine

A solution of diazocalix(4)arene **3–6** (0.75 mmol) was taken in pyridine (15 ml) and benzoyl chloride (0.60 g, 4.25 mmol) was added to it. After heating on boiling water bath for 15 h, the reaction mixture was cooled and poured into crushed ice (200 g) and the yellow precipitate obtained was collected by suction filtration. It was dissolved in

CHCl₃ (30 ml) and washed with dilute HCl, saturated NaHCO₃ solution and water. The residue obtained on evaporation was recrystallized from CHCl₃–methanol (1:1) gave **3b–6b** as pale yellow crystalline solids.

25,26,27,28-Tetrabenzoyloxy-5,11,17,23-tetra(2-thiomethylphenylazo)calix[4]arene: 3b

(0.32 g, 30%), m.p. > 250 °C, Calcd. for C₈₄H₆₄N₈O₈S₄: C, 69.98; H, 4.47; N, 7.77. Found: C, 68.64; H, 4.22; N, 7.36. Mol. Mass (vapor pressure osmometry): 1450 (Calcd. 1442). UV (λ_{\max} , CHCl₃): 410 nm. IR (KBr; ν_{\max} , cm⁻¹): 2978(sh), 1740(s), 1684(m), 1560(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 1120(s), 762(m), 620(w). ¹H-NMR (CDCl₃; δ , ppm): 7.73–7.62 (20H, m, ArH), 7.60–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH₂Ar), 2.44 (12H, s, SCH₃).

25, 26, 27, 28-Tetrabenzoyloxy-5, 11, 17, 23-tetra(2-thioethylphenylazo)calix[4]arene: 4b

(0.25 g, 22%), m.p. > 245–247 °C, Calcd. for C₈₈H₇₂N₈O₈S₄: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.64; H, 4.22; N, 7.36. Mol. Mass (vapor pressure osmometry): 1500 (Calcd. 1498). UV (λ_{\max} , CHCl₃): 410 nm. IR (KBr; ν_{\max} , cm⁻¹): 2889(sh), 1756(s), 1696(m), 1573(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 1120(m), 765(m), 635(w). ¹H-NMR (CDCl₃; δ , ppm): 7.73–7.52 (20H, m, ArH), 7.51–6.83 (24H, m, ArH), 4.10 (8H, bs, ArCH₂Ar), 2.42 (8H, q, SCH₂), 1.44 (12H, t, CH₃).

25,26,27,28-Tetrabenzoyloxy-5,11,17,23-tetra(2-thiopropylphenylazo)calix[4]arene: 5b

(0.24 g, 21%), m.p. > 243 °C (decomp.), Calcd. for C₉₂H₈₀N₈O₈S₄: C, 71.11; H, 5.19; N, 7.21. Found: C, 70.12; H, 5.96; N, 8.12. Mol. Mass (vapor pressure osmometry): 1601 (Calcd. 1554). UV (λ_{\max} , CHCl₃): 420 nm. IR (KBr; ν_{\max} , cm⁻¹): 2898(sh), 1962(s), 1752(m), 1560(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ , ppm): 7.73–7.52 (20H, m, ArH), 7.42–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH₂Ar), 2.44 (8H, m, SCH₂), 1.62 (8H, m, SCCH₂), 1.02 (12H, t, SC.C.CH₃).

25,26,27,28-Tetrabenzoyloxy-5,17-di(2-thiomethylphenylazo)calix[4]arene: 6b

(0.22 g, 26%), m.p. > 250 °C; Mol. Mass (vapor pressure osmometry): 1131 (calcd. 1141). Anal. calcd. for C₇₀H₅₂N₄O₈S₂: C, 73.66; H, 4.59; N, 4.91; S, 5.62. Found: C, 73.94; H, 4.22; N, 4.36; S, 5.16. UV (λ_{\max} , CHCl₃):

410 nm. IR (KBr; ν_{\max} , cm⁻¹): 2998 (sh), 1720(s), 1543(m), 1470(m), 1426(w), 1372(w), 1256(w), 1212(w), 1120(s), 1090(w), 762(m), 635(w). ¹H-NMR (CDCl₃; δ , ppm): 8.01–7.81 (38H, m, ArH), 4.32, 3.67 (8H, d, ArCH₂Ar), 2.24 (6H, s, SCH₃).

General procedure for the reaction of diazocalix(4)arenes **3–6** with methyl iodide and sodium hydride

A mixture of diazocalix[4]arene **3–6** (0.7 mmol), NaH (0.30 g, 12.5 mmol), methyl iodide (2.79 g, 19.65 mmol) in dry dimethyl formamide (50 ml) was stirred at 60 °C for 20 h. The reaction mixture was cooled and poured into ice cold water (200 ml) to yield yellow coloured precipitate which was collected by suction filtration and dissolved in chloroform (30 ml) and charcoaled with active charcoal (2 g). Recrystallization of the product from chloroform to methanol (1:1) gave **3c–6c** as yellow crystalline solid.

25,26,27,28-Tetramethoxy-5,11,17,23-tetra(2-thiomethylphenylazo)calix[4]arene: 3a

Compound **3c** (0.24 g, 30%). m.p. 255 °C was obtained as yellow crystalline solid from the reaction of diazocalix[4]arene **3** (0.78 g, 0.76 mmol) with methyl iodide (2.79 g, 19.6 mmol) and NaH (0.3 g, 12.5 mmol) by following the general procedure. Mol. Mass (vapor pressure osmometry): 1087 (calcd. 1081). Anal. calcd. for C₆₀H₅₆N₄O₄S₄: C, 66.64; H, 5.22; N, 10.36. Found: C, 67.24; H, 4.98; N, 10.76. UV (λ_{\max} , CHCl₃): 420 nm. IR (KBr; ν_{\max} , cm⁻¹): 2898(sh), 1560(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ , ppm): 7.60–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH₂Ar), 3.51 (12H, s, OCH₃), 2.44 (12H, s, SCH₃).

25,26,27,28-Tetramethoxy-5,11,17,23-tetra(2-thioethylphenylazo)calix[4]arene: 4c

(0.23 g, 27%). m.p. 245–247 °C was obtained as yellow crystalline solid from the reaction of diazocalix[4]arene **4** (0.81 g, 0.75 mmol) with methyl iodide (2.79 g, 19.6 mmol) and NaH (0.3 g, 12.5 mmol) by following the general procedure. Mol. Mass (vapor pressure osmometry): 1147 (calcd. 1138). Anal. calcd. for C₆₄H₆₄N₈O₄S₄: C, 66.64; H, 5.22; N, 10.36. Found: C, 67.58; H, 5.67; N, 9.85. UV (λ_{\max} , CHCl₃): 420 nm. IR (KBr; ν_{\max} , cm⁻¹): 2898(sh), 1584(s), 1567(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). ¹H-NMR (CDCl₃; δ , ppm): 7.61–6.83 (24H, m, ArH), 4.10 (8H, bs, ArCH₂Ar), 3.78 (12H, s, OCH₃), 2.44 (8H, q, SCH₂), 1.44 (12H, t, CH₃).

25,26,27,28-Tetramethoxy-5,11,17,23-tetra(2-thiopropylphenylazo)calix[4]arene: **5c**

(0.21 g, 24%). m.p. 223 °C (decom.) was obtained as yellow crystalline solid from the reaction of diazocalix[4]arene **5** (0.85 g, 0.75 mmol) with methyl iodide (2.79 g, 19.6 mmol) and NaH (0.3 g, 12.5 mmol) by following the general procedure. Mol. Mass (vapor pressure osmometry): 1201 (calcd. 1194). Anal. calcd. for C₆₈H₇₂N₈O₄S₄: C, 68.42; H, 6.08; N, 9.39. Found: C, 67.64; H, 6.22, N, 9.86. UV (λ_{max} , CHCl₃): 420 nm. IR (KBr; ν_{max} , cm⁻¹): 2898(sh), 1560(m), 1452(m), 1436(w), 1372(w), 1256(w), 1212(w), 762(m), 620(w). ¹H-NMR (CDCl₃; δ , ppm): 7.60–6.80 (24H, m, ArH), 4.14 (8H, bs, ArCH₂Ar), 3.51 (12H, s, OCH₃), 2.48 (8H, t, SCH₂), 1.73 (8H, m, SCCH₂); 1.06 (12H, t, SCCH₃).

25,26,27,28-Tetramethoxy-5,17-di(2-thiomethylphenylazo)calix[4]arene: **6c**

(0.23 g, 27%). m.p. 245 °C (decom.) was obtained as yellow crystalline solid from the reaction of diazocalix[4]arene **6** (0.73 g, 1.0 mmol) with methyl iodide (3.72 g, 26.2 mmol) and NaH (0.4 g, 16.6 mmol) by following the general procedure. Mol. Mass (vapor pressure osmometry): 792 (calcd. 781). Anal. calcd. for C₄₆H₄₄N₄O₄S₂: C, 70.74; H, 5.68; N, 7.17. Found: C, 71.20; H, 5.52, N, 7.03. UV (λ_{max} , CHCl₃): 360 nm. IR (KBr; ν_{max} , cm⁻¹): 2823(m), 1593(m), 1482(m), 1436(w), 1372(w), 1276(w), 1212(w), 753(m), 620(w). ¹H-NMR (CDCl₃; δ , ppm): 7.72–6.71 (18H, m, ArH), 4.30, 3.65 (8H, d, ArCH₂Ar), 3.52 (12H, s, OCH₃), 2.17 (6H, s, SCH₃).

UV-VIS spectrophotometric titrations

Preparation of the stock solution of the ligands (**6**) and metals

The chromogenic calix(4)arene (**6**) was weighed (16.62 mg) accurately and dissolved in 2 ml of CHCl₃ in 100 ml standard flask. The rest of the volume was made up to the mark by adding methanol. The concentration of the solution was calculated as 2.2927×10^{-4} M. This solution was labelled as L1. Sodium tetrachloropalladate (II), (Na₂PdCl₄) was weighed (17.6 mg) accurately and dissolved in methanol in a 5 ml standard flask. The concentration of this solution was determined to be 1.1965×10^{-2} M. This solution was labeled as Pd. Potassium tetrachloroplatinate (II), (K₂PtCl₄) was weighed (12.5 mg) accurately and dissolved in methanol containing 1 ml of water in a 25 ml standard flask. The concentration of this solution was determined to be 1.2045×10^{-3} M. This solution was labeled as Pt.

General procedure for spectrophotometric analysis of interaction between **6** and metal ions

The stock solution L1 was diluted 2.5 times to get the optical density (OD) within scale of the spectrophotometer. This solution was divided into several 3 ml portions and 0.5 ml of the solutions of the following metals (in methanol) were added to them followed by a record of UV-VIS spectrum of each solution. The metal ions taken were Pd²⁺ [Na₂PdCl₄] and Pt²⁺ [K₂PtCl₄]. The spectral changes upon addition of Pd(II) and Pt(II) are shown in Fig. 2.

General procedure for quantitative examination of the interaction between chromogenic calixarene (**6**) with metal ions by spectrometry

The metal to ligand ratio of the **6**-metal complexation was ascertained by mole-ratio plots and it was further confirmed by the Jobs continuous variation method.

(a) *Mole-ratio plots for stoichiometry of the platinum and palladium complexes with synthesized calix[4]arene derivatives.* A series of solutions with fixed concentration of ligand and gradually varied concentration of metal ions were prepared. The mixed solutions were shaken well and left for about 5–10 min so as to ensure equilibrium between the ligand and metal ions. The optical spectrum of each solution was recorded. The OD was observed at a wavelength at which neither the metal nor the ligand absorbed (470 nm in the case of Na₂PdCl₄ and 520 nm in the case of K₂PtCl₄). The metal to ligand ratio (M/L) was calculated for each metal ion from the plots of OD and C_M/C_L where C_M is the concentration of the metal ions and C_L is the concentration of the ligand (C_M/C_L).

(b) *Evaluation of interaction of metal ions with molecular receptors by Jobs method of continuous variation.* A series of solutions with varied metal ion and ligand concentrations were prepared. The total ligand and metal ion concentration was fixed which was kept the same for each of them (*i.e.* $C = C_M + C_L$, where C_L , C_M and C are concentrations of the ligand, metal ion and total concentration respectively). The solutions were allowed to stand for about 10 min to attain equilibrium between the metal and the ligand. The OD was measured at 470 and 520 nm for Na₂PdCl₄ and K₂PtCl₄ respectively and was plotted against the mole-fraction of the ligand, $X_L (=C_L/C)$. Assuming that only one complex is formed with a composition ML_{*n*}, the value of *n* was calculated from the X_{max} (mole-fraction of the ligand (X_L) at maximum absorption) from the following relation.

$$n = X_{\text{max}}/1 - X_{\text{max}}$$

Table 1 Solutions of different composition of **6** and Pd solutions

No.	Volume of ligand solution (ml) ^a	Volume of metal solution (ml) ^b	X _L
1	0.0	5.0	0.00
2	0.5	4.5	0.09
3	1.0	4.0	0.19
4	1.5	3.5	0.29
5	2.0	3.0	0.38
6	2.5	2.5	0.49
7	3.0	2.0	0.59
8	3.5	1.5	0.69
9	4.0	1.0	0.79
10	4.5	0.5	0.80
11	5.0	0.0	1.00

^a Concentration of ligand (**6**) solution was 2.2327×10^{-4} M

^b Concentration of metal ion (Na₂PdCl₄) solution was 2.393×10^{-4} M

Interaction between **6** and Na₂PdCl₄

Application of mole-ratio method

A series of solutions containing 2 ml of ligand (**6**) (2.2927×10^{-4} M) and 0.00, 0.05, 0.10, 0.30, 0.40 and 1.5 ml respectively of metal ion solution (1.196×10^{-3} M) were prepared. The spectrum of each solution was recorded as mentioned in the general procedure to produce (Fig. 2a). The OD at 470 nm was plotted against the metal to ligand mole ratio (C_M/C_L) (Fig. 3a) which gave metal to ligand mole ratio as 1.2. This corresponded to around 1.2 indicating the ratio of the ligand to metal (palladium) as 1:1.

Jobs continuous variation method

A series of solutions of the composition mentioned in the Table 1 was prepared and after treating them as described in the general procedure, their OD at 520 nm was recorded. From the plot of OD Vs X_L (Fig. 3b), the value of 'X_{max}' was found to be 0.5 which corresponded to the value of 'n' as one [0.5/(1 - 0.5)].

Interaction between **6** and K₂PtCl₄

Application of mole-ratio method

A series of solutions containing 2 ml of ligand (**6**) (2.2927×10^{-4} M) and 0.00, 0.19, 0.38, 0.50, 0.60 and 0.80 ml respectively of metal ion solution (1.2045×10^{-3} M) were prepared. The spectrum of each solution was recorded as mentioned in the general procedure (Fig. 2b). The OD of these solutions at 470 nm was plotted against the metal to ligand mole ratio (C_M/C_L) (Fig. 4a). From this

Table 2 Solutions of different composition of **6** and Pt solutions

T. No.	Volume of ligand solution (ml) ^a	Volume of metal solution (ml) ^b	X _L	Absorbance (OD) at 470 nm
1	0.0	5.0	0.00	0.00
2	0.5	4.5	0.10	0.22
3	1.0	4.0	0.20	0.42
4	1.5	3.5	0.30	0.66
5	2.0	3.0	0.40	0.60
6	2.5	2.5	0.50	0.48
7	3.0	2.0	0.60	0.38
8	3.5	1.5	0.70	0.26
9	4.0	1.0	0.80	0.18
10	4.5	0.5	0.90	0.05
11	5.0	0.0	1.00	0.00

^a Concentration of ligand (**6**) solution is 2.2927×10^{-4} M

^b Concentration of metal (K₂PtCl₄) solution is 2.2653×10^{-4} M

plot, metal to ligand mole ratio was determined to be 2.2 that corresponded to approximately 1:2 ratio of ligand to metal (platinum).

Application of Jobs continuous variation method

A series of solutions of the compositions mentioned in Table 2 were prepared and after treating them as described in the general procedure, their OD at 470 nm was recorded. From the plot of OD Vs X_L (Fig. 4b), the value of 'X_{max}' was found to be 0.33 that gave the value of 'n' as approximately 0.5 [0.33/(1 - 0.33)].

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