

Synthesis and characterization of complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and UO_2^{2+} with *p*-tert-butylcalix[4]arene bearing two imine pendants linked through salicylyl moiety at the lower rim

Mishtu Dey^a, Jugun Prakash Chinta^a, Gary J Long^b & Chebrolu P Rao^{a,*}

^aBioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India
Email: cprao@iitb.ac.in

^bDepartment of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409-0010, USA

Received 22 September 2009; revised and accepted 21 October 2009

Metal ion complexes of the double-armed *p*-tert-butylcalix[4]arene derivative possessing imine functionality linked through salicylyl moiety at the lower rim has been synthesized for the first time and characterized by analytical, spectral and magnetic methods. The 1, 3- di-calix[4]arene-imine conjugate exhibits variable coordination behavior, from tetradentate to hexadentate, depending upon the metal ion to which it is bound, by always acting as di-anionic. While it uses both the ether oxygens of the pendants to coordinate in the case of Fe(III), Co(III) and Ni(II) complexes, it uses only the pendant salicylidene moieties in the case of Cu(II) and Zn(II) complexes. The Zn(II) complex catalysis ester hydrolysis through the formation of Zn(II)-hydroxo species.

Keywords: Coordination chemistry, Calixarenes, Calix[4]arene-imine conjugates, Iron, Cobalt, Nickel, Copper, Zinc, Uranium, FAB mass spectrometry, Magnetic susceptibility, Electron paramagnetic resonance, Mossbauer spectroscopy

IPC Code: Int. Cl.⁹ C07F1/08; C07F3/06; C07F5/00; C07F15/00

Calix[4]arenes have received considerable attention for host-guest chemistry¹ particularly for their ability to bind metal ions. In order to develop such chemistry, functional groups need to be introduced. It is indeed true that the calix [4]arene framework serves as platform for developing derivatives² possessing necessary binding and/or ligating groups³. Hence, currently there is immense interest in the development of calix[4]arene derivatives, which can be used as an ideal platform for the development of fluorescent chemosensors for alkali, alkaline earth and transition metal ions as reported recently in the literature⁴.

Our research group recently demonstrated the selective recognition^{5(a-e)} of some biologically relevant M^{2+} , viz., Zn^{2+} , Ni^{2+} and Cu^{2+} as well as environmentally relevant heavy metal ion, viz., Hg^{2+} , by suitable derivatization at the lower rim of calix[4]arene. In contrast, azomethine linked calix[4]arene and its metallo-derivatives have received scant attention though some solution studies of metal ion interactions have been reported⁶. The present study has been taken up since calix[4]arene conjugates provide coordination environment for transition metal ions and the resulting complexes tend to exhibit interesting properties. We report herein the

synthesis and characterization of the complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and UO_2^{2+} of azo-methine conjugate of calix[4]arene.

Materials and Methods

The metal precursors and the chemicals used in the synthesis were purchased from commercial sources. All the solvents were dried prior to use.

Synthesis of the ligand

The calix[4]arene dinitrile derivative was synthesized as reported in the literature, with some modification⁷. A mixture of *p*-tert-butylcalix[4]arene (1.0g, 1.55mmol), K_2CO_3 (0.853g, 6.17 mmol), NaI (0.925g, 6.17 mmol) and chloroacetonitrile (0.478g, 6.33 mmol) in 50ml dry acetone was refluxed under nitrogen atmosphere for 7h. The reaction mixture was allowed to cool down to room temperature and filtered through celite to obtain clear light brown solution. This was concentrated to give a brown solid, which was recrystallized from chloroform/methanol to give a white crystalline solid. Yield: 86%. ¹H NMR (CDCl_3) δ 0.88, 1.33 (s, 18H each, $\text{C}(\text{CH}_3)_3$), 3.45, 4.22 (2d, 8H, ArCH_2Ar), 4.81 (s, 4H, OCH_2N), 5.56 (s, 2H, Ar-OH), 6.73, 7.12 (2s, 8H, Ar-H) ppm.

The calix[4]arene diamine derivative was synthesized as per the reported procedure.⁷ To a vigorously stirred solution of calix[4]arene dinitrile derivative (1.0 g, 0.34 mmol) in 40 mL dry THF, LiAlH₄ (0.12 g, 3.56 mmol) was added and the reaction mixture was refluxed for 5 h. After that, 20% NaOH solution (0.33ml) and H₂O (1.0ml) were added to quench excess of LiAlH₄. The white precipitate that was formed was filtered and the filtrate was evaporated. The residue was recrystallized from CHCl₃-MeOH mixture to give diamine derivative as white crystals. Yield: 78%; m.pt. 200°C (decomp.). ¹H NMR (CDCl₃): δ 1.10, 1.25 (s, 18H each, C(CH₃)₃), 3.30 (br, 4H, NCH₂), 3.37, 4.31 (2d, 8H, ArCH₂Ar), 4.07 (br, 4H, OCH₂), 6.97, 7.04 (2s, 8H, Ar-H) ppm. ESMS: *m/z* 734 ([M]⁺, 45%).

The ligand, 5,11,17,23-Tetra-*tert*-butyl-25,27-bis-{2-[N-(2-hydroxybenzylidene)amino]ethoxy}-26,28-dihydroxycalix[4]arene (**L**) was prepared as follows: A mixture of calix[4]arene diamine (100 mg, 0.136 mmol) and salicylaldehyde (33.2 mg, 0.272 mmol) were stirred in EtOH at room temperature for 12 h. The yellow precipitate thus formed was isolated through filtration, washed with methanol and dried under vacuum. Yield: 77%; m.pt. 193-194°C. FTIR (KBr): 3448 (ν_{OH}), 1634 (ν_{C=N}) cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 1.28, 0.95 (s, 18H each, C(CH₃)₃), 3.32 (d, 4H, J=13.0, ArCH₂Ar), 4.15 (t, 4H, J= 5.5 Hz, CH₂N), 4.22 (d, 4H, J=13.0, ArCH₂Ar), 4.30 (t, 4H, J=5.5, OCH₂), 6.76 (s, 4H, Ar-H), 6.94-6.80 (m, 4H, Ar H), 6.97 (s, 2H, Ar OH), 7.01 (s, 4H, Ar H), 7.36-7.24 (m, 4H, ArH), 8.50 (s, 2H, HC=N) ppm. FAB-MS: *m/z* 943 ([M+H]⁺, 100%). UV-vis: γ_{max}/nm, (ε/Lmol⁻¹cm⁻¹), (CHCl₃/CH₃OH, 1:9): 224 (190000), 256 (21490), 284 (9530), 291 (8880), 316 (6800) and 394 (305).

Synthesis of complexes (1) to (6)

(1): To the ligand, (**L**) (0.100 g, 0.104 mmol) in CH₂Cl₂ (10 mL), was added Fe(ClO₄)₃.9H₂O (0.0516g, 0.1 mmol) in C₂H₅OH (2 mL) dropwise when the dark yellow colored solution turned to maroon color. The reaction mixture was stirred at room temperature under N₂ atmosphere for about 29 h. The solvent was removed *in vacuo* to yield a paste-like product. This was treated with ethanol by stirring at room temperature for 5 h to yield the product (**1**). A second crop of the product was obtained from the filtrate. Yield: 0.0538 g (52%);

m.pt.: >270°C. FTIR (KBr, cm⁻¹): 3450 (ν_{OH}), 1621 (ν_{C=N}), 1091 (ν_{perchlorate}). FAB-MS: *m/z* 998 ([M+2]⁺, 100%). UV-vis, γ_{max}/nm, (ε/Lmol⁻¹cm⁻¹), (CHCl₃/CH₃OH, 1:1): 279 (3210), 320 (1045), 390 (552) and 505 (266). π(mho)=94.5. Anal.: Calc. (%) for C₆₂H₇₂N₂O₆Fe.ClO₄ (1096.0): C, 67.88; H, 6.57; N, 2.56. Found: C, 67.18; H, 6.23; N, 2.06.

(2): To (**L**) (0.100 g, 0.104 mmol) in CH₂Cl₂ (25 mL) was added Co(OAc)₂.4H₂O (0.0249 g, 0.100 mmol) in CH₃OH (5 mL) drop-wise and the resultant light brown colored reaction mixture was stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the residue was suspended in CH₃OH and stirred at room temperature for 12 h to yield a dirty green colored product (**2**), which was recrystallized from CHCl₃/CH₃OH. Yield: 0.048 g (43%); m.pt.: >250°C. FTIR (KBr, cm⁻¹): 3432 (ν_{OH}), 1622 (ν_{C=N}). FAB-MS: *m/z* 1000 ([M+1]⁺, 100%), 1057 ([M+CH₃COO]⁺, 30%). UV-vis, γ_{max}/nm, (ε/Lmol⁻¹cm⁻¹), (CHCl₃/CH₃OH, 1:9): 273 (10270), 385 (2150) and 612 (255). π(mho)=105.6. Anal.: Calc. (%) for C₆₂H₇₂N₂O₆Co.CH₃COO.2CH₂Cl₂ (1229.3): C, 64.49; H, 6.48; N, 2.28. Found: C, 64.20; H, 6.94; N, 2.18.

(3): To (**L**) (0.100 g, 0.104 mmol) in CH₂Cl₂ (20 mL), was added Ni(ClO₄)₂.6H₂O (0.0366 g, 0.1 mmol) in CH₃OH (4 mL) dropwise to result in a pale green solution. Upon stirring the reaction mixture at room temperature for 5h, no change was observed. It was then refluxed for 3h to result in the formation of a green precipitate. The product obtained (**3**) was purified by washing several times with methanol and dried *in vacuo*. Yield: 0.075 g (75%); m.pt.: >250°C. FTIR (KBr, cm⁻¹): 3449 (ν_{OH}), 1617 (ν_{C=N}). FAB-MS: *m/z* 999 ([M]⁺, 20%). UV-vis, γ_{max}/nm, (ε/Lmol⁻¹cm⁻¹), (CHCl₃/CH₃OH, 1:9): 226 (216700), 272 (50600), 333 (7020), 418 (230) and 609 (130). Anal.: Calc. (%) for C₆₂H₇₂N₂O₆Ni.CH₂Cl₂.CH₃OH (1117.0): C, 68.82; H, 7.04; N, 2.51. Found: C, 68.21; H, 7.12; N, 2.38.

(4): Complex (**4**) was synthesized following the procedure given for (**3**) except that the metal precursor used was Cu(OAc)₂.H₂O (0.0200 g, 0.10 mmol). Yield: 0.062 g (60%); m.pt., 152-154°C. FTIR (KBr, cm⁻¹): 3439 (ν_{OH}), 1621 (ν_{C=N}) cm⁻¹. FAB-MS: *m/z* 1005 ([M+1]⁺, 75%). UV-vis, γ_{max}/nm, (ε/Lmol⁻¹cm⁻¹), (CHCl₃/CH₃OH, 1:9): 227 (217600), 275 (89800), 367 (16050), 453 (1790) and 611 (336). Anal.: Calc. (%) for C₆₂H₇₂N₂O₆Cu.CH₃OH (1036.8): C, 72.99; H, 7.39; N, 2.70. Found: C, 72.88; H, 7.05; N, 2.53.

(5): Complex (5) was synthesized by adopting the procedure given for (3) except using $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.0227 g, 0.1035 mmol) Yield: 0.086 g (81%); m.pt.: $>220^\circ\text{C}$. FTIR (KBr, cm^{-1}): 3456 (ν_{OH}), 1623 ($\nu_{\text{C}=\text{N}}$). FAB-MS: m/z 1005 ($[\text{M}]^+$, 100%). UV-vis, $\gamma_{\text{max}}/\text{nm}$, ($\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$), ($\text{CHCl}_3/\text{CH}_3\text{OH}$, 1:1): 280 (816) and 315 (499). Anal.: Calc. (%) for $\text{C}_{62}\text{H}_{72}\text{N}_2\text{O}_6\text{Zn}$ (1005.0): C, 74.17; H, 7.23; N, 2.79. Found: C, 74.35; H, 7.50; N, 2.61.

(6): This complex was synthesized by adopting the procedure given for (3) except using $\text{UO}_2(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.0439 g, 0.1035 mmol). Yield: 0.047 g (38%); m.pt.: $128\text{--}132^\circ\text{C}$; FTIR (KBr, cm^{-1}): 3461 (ν_{OH}), 1624 ($\nu_{\text{C}=\text{N}}$), 896 ($\nu_{\text{U}=\text{O}}$). FAB-MS: m/z 1211 ($[\text{M}+1]^+$, 100%). UV-vis, $\gamma_{\text{max}}/\text{nm}$, ($\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$), ($\text{CHCl}_3/\text{CH}_3\text{OH}$, 1:1): 279 (10254) and 346 (1857). Anal.: Calc. (%) for $\text{C}_{62}\text{H}_{72}\text{N}_2\text{O}_8\text{U}$ (1210): C, 61.49; H, 5.60; N, 2.32. Found: C, 61.88; H, 5.74; N, 2.65.

Potentiometric pH titration

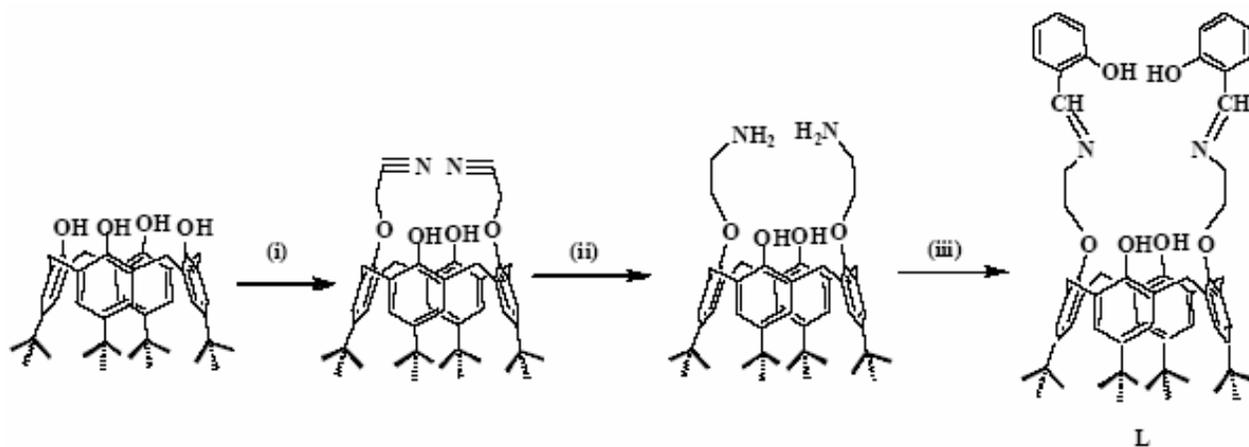
Titrations were carried out at $25 \pm 0.2^\circ\text{C}$ by means of a Cyberscan 1000 pH meter with a combined glass electrode. The electrode was calibrated using standard aqueous buffers immediately before use. Solutions were made of aqueous methanol (33%, v/v) and the ionic strength was adjusted to 0.1M using NaNO_3 . The solution of (L) (1.00 mM) with four equivalents of HCl (4.00 mM) in the absence and in the presence of one equivalent of salt of the respective metal ion was titrated against 0.1 M NaOH aqueous solution. During the titration, each increment of NaOH (50 μl) was added with an equilibration time of 60s.

Hydrolysis of *p*-nitrophenyl acetate (*p*-NPA)

The hydrolysis rate of *p*-NPA in the presence of $[\text{Zn}(\text{H}_2\text{L})]$, (5), was measured by an initial slope method following the absorbance increase in the 400 nm band of the released *p*-nitrophenolate species at 25°C . Such experiments were carried out at a solution pH of 8.27, 9.08, 9.42 and 10.16, maintained using TRIS (20 mM) with an ionic strength of 0.1 mM KNO_3 . To increase the solubility of *p*-NPA, 10% $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution was used. In a typical experiment, *p*-NPA ($c=0.2$ mM) and the complex, $[\text{Zn}(\text{H}_2\text{L})]$ ($c=0.02\text{--}0.08$ mM) in 10% $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution were mixed at appropriate pH (the control experiment does not contain the Zn(II) complex) and the UV-vis absorption spectra were measured as a function of time until no substantial increase was observed in the absorbance of the 400 nm band. Initial slopes were determined from the plots of the measured absorbance at 400 nm versus time.

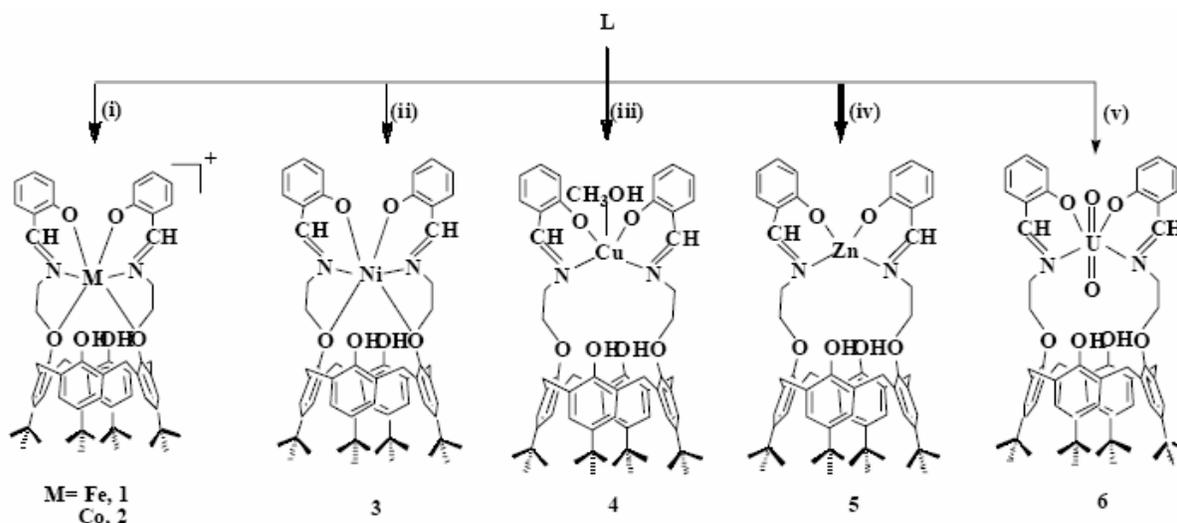
Results and Discussion

The 1,3-di-calix[4]arene-imine conjugate, (L) was synthesized in three steps starting from *p*-tert-butylcalix[4]arene via 1,3-dinitrile and 1,3-diamine and then coupling the 1,3-diamine with salicylaldehyde (Scheme 1)⁷. Reactions of (L) with the corresponding salts of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and UO_2^{2+} yielded complexes having molecular formulae, $[\text{Fe}(\text{H}_2\text{L})](\text{ClO}_4)$, (1), $[\text{Co}(\text{H}_2\text{L})](\text{CH}_3\text{COO}) \cdot 2\text{CH}_2\text{Cl}_2$, (2), $[\text{Ni}(\text{H}_2\text{L})] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{CH}_3\text{OH}$, (3), $[\text{Cu}(\text{H}_2\text{L})]\text{CH}_3\text{OH}$ (4), $[\text{Zn}(\text{H}_2\text{L})]$ (5) and $[\text{UO}_2(\text{H}_2\text{L})]$ (6) respectively as shown in Scheme 2.



Synthesis of calix[4]arene-schiff base conjugate. [(i) ClCH_2CN , NaI, K_2CO_3 , acetone, reflux, 7h; (ii) LiAlH_4 , THF, reflux, 5h; (iii) salicylaldehyde, EtOH, reflux, 12h].

Scheme 1



Complexes of calix-imine conjugates. [(i) $\text{Fe}(\text{ClO}_4)_2 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; (ii) $\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$; (iii) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$; (iv) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and (v) $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. All reactions were carried out in $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (1:5) (except in the case of Fe(III) where ethanol was used instead of methanol) and stirred at room temperature for 24 h].

Scheme 2

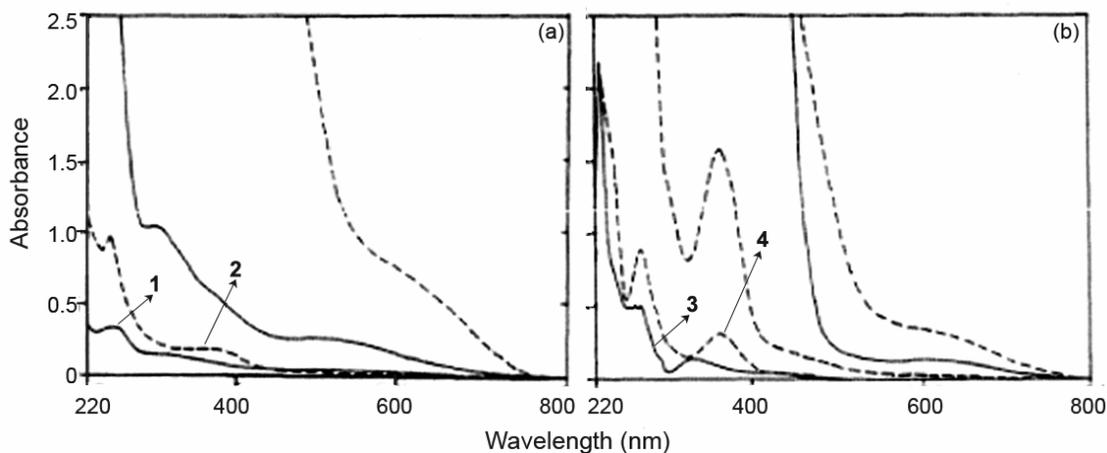


Fig. 1—UV-visible spectra of the metal ion complexes. [(a) **1** (—) and **2** (---); (b) **3** (—) and **4** (---) in chloroform-methanol solvent mixture at different concentrations].

All the compounds were synthesized in good to high yields. The complexes were analyzed for their composition and were characterized by FTIR, UV-vis, FAB mass spectra, conductivity, EPR and magnetic susceptibility measurements and also by Mossbauer spectroscopy in the case of Fe(III) complex. Further, the Zn(II) complex has been studied for its ester hydrolysis property.

Spectral studies

Binding of imine moiety to the metal ion centers has been identified from lowering of the $\nu_{\text{C}=\text{N}}$ vibrational frequency from 1634 cm^{-1} to $1617\text{--}1624 \text{ cm}^{-1}$ in FTIR spectra of the complexes. The FTIR spectrum of

iron complex, (**1**) shows a strong peak at 1091 cm^{-1} due to the vibrations of the perchlorate moiety. Characteristic vibrational band observed at 896 cm^{-1} for (**6**) is assignable to the asymmetric stretching vibration⁸ of trans-UO_2^{2+} . This value is comparable to the uranium-azomethine complexes reported by us earlier⁹ wherein the corresponding $\nu_{\text{U}=\text{O}}$ vibration was found in the region $897\text{--}912 \text{ cm}^{-1}$.

The electronic absorption spectra of (**L**) and the complexes were recorded in freshly prepared $\text{CHCl}_3/\text{CH}_3\text{OH}$ solvent mixture in the range $220\text{--}800 \text{ nm}$ (Fig. 1). The (**L**) as well as the complexes exhibited at least two intense absorption

bands in the range of 256-385 nm associated with the phenolate and azomethine $\pi \rightarrow \pi^*$ transitions and were red shifted by 20 and 50 nm respectively upon complexation. All this indicates the involvement of these groups in the metal ion binding. The band observed at 505 nm with a shoulder at 390 nm in (1) is characteristic of the high spin Fe(III) complex and a charge transfer from phenolate¹⁰.

The Co(III), Ni(II) and Cu(II) complexes additionally exhibited one distinct band in the visible region around 610 nm with molar absorptivity of $130\text{-}336 \text{ L cm}^{-1} \text{ mol}^{-1}$ that can be assigned to a $d \leftrightarrow d$ transition. The spectral feature observed with (4) is characteristic of a five coordinated Cu(II) with square-pyramidal geometry¹¹. Thus, comparison of the absorption data of the complexes with that of (L), clearly indicates the formation of the complex in each case.

The FAB mass spectra of all the complexes, (1)-(6) showed molecular ion peaks with m/z values as follows: L (943 $[\text{M}+\text{H}]^+$); 1 (998 $[\text{M}+2]^+$); 2 (1000 $[\text{M}+1]^+$); 3 (999 $[\text{M}]^+$); 4 (1005 $[\text{M}+1]^+$); 5 (1005 $[\text{M}]^+$); 6 (1211 $[\text{M}+1]^+$). Besides the molecular ion (M) peak, most of the spectra also exhibited fragments corresponding to the species, (a) with the loss of metal ion (T), (b) with the loss of metal ion plus one pendant arm (T+1P) and (c) with the loss of metal ion plus both the pendant arms (T+2P) (Fig. 2). The isotopic peak pattern observed in each case corresponds to the presence of metal ion in that complex.

Conductivity studies

The complexes were studied for their neutral versus ionic behavior in solution by measuring the conductivity. The conductivity measurements of (3), (4), (5) and (6) in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$ (1:9) revealed that these four complexes are neutral while (1) and (2) exhibited specific conductance values of 94.5 and 105.6 mho, suggesting their 1:1 electrolyte behaviour.

Magnetic susceptibility studies

The magnetic susceptibility data at 298 K reveal that (1), (2), (3) and (4) have magnetic moments of 3.59, 5.41, 3.84 and 2.27 BM respectively. The value observed for (1) is too low for a high-spin ($S = 5/2$) or too high for a low-spin ($S = 1/2$) Fe(III) complexes which are generally found in the range of 2.3-5.9 BM. For Fe(III) compounds of intermediate spin ($S = 3/2$), the expected μ_{eff} value is about 4.00 BM, which may arise from a spin equilibrium existing between low and high-spin states. Equilibria of the type ($S=1/2$) \leftrightarrow ($S=5/2$) are well characterized for several Fe(III) complexes, such as bis(tridentate)Fe(III) Schiff base complexes^{12(a)}, tris (dithiocarbamate) iron(III) compound^{12(b)}, tris (monothiocarbamate) Fe(III) complexes^{12(c),(d)}, tri(monothio- β -diketonato) iron(III) complexes^{12(e),(f)}, $[\text{Fe}(\text{X-Sal})_2\text{trien}]^+$ and $[\text{Fe}(\text{acac})_2\text{trien}]^+$ complexes^{12(g),(h)}, $[\text{Fe}(\text{X-Sal-meen})_2]^+$ (ref. 12i), $[\text{Fe}(\text{SalAPA})_2]\text{ClO}_4$ (ref. 12j), and $[\text{Fe}(\text{3-X-Salbenz})_2]^+$ complexes^{12k}. Similar observations have also been made for some six-coordinate Fe(III)

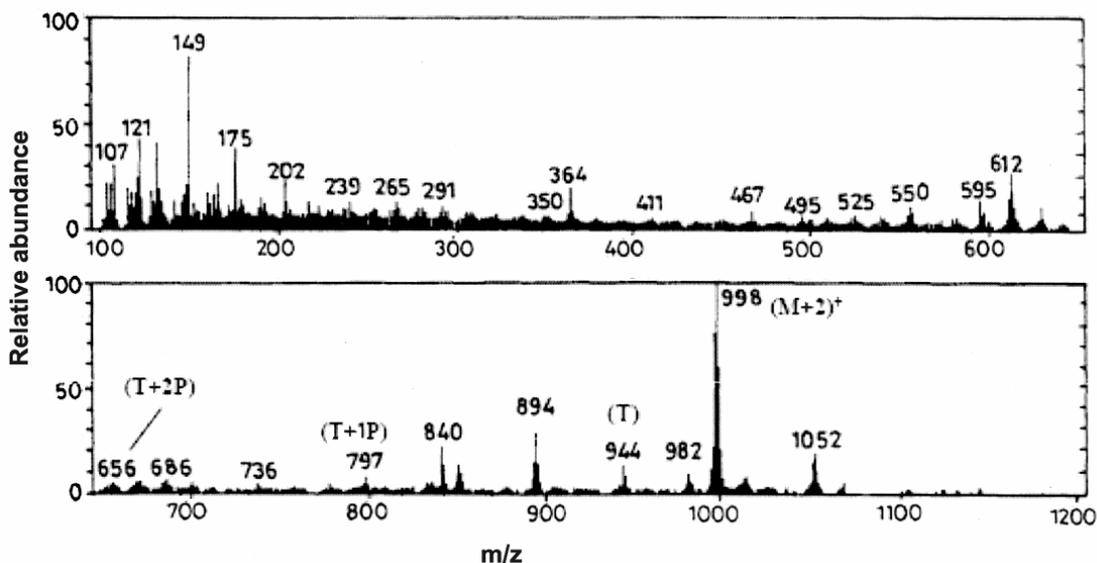


Fig. 2—FAB mass spectra for (1). 'M' represents the molecular ion. (T), (T+1P) and (T+2P) respectively denote the peaks corresponding to the loss of metal ion, metal ion plus one pendant arm and metal ion plus two pendant arms.

Schiff base complexes with tetradentate ligands^{12(l),(m)}. The μ_{eff} observed for (2) and (3) are characteristic of high spin Co(III) and Ni(II) respectively. The rather higher μ_{eff} observed for (4) is attributable to the incomplete quenching of the orbital magnetic moment by the surrounding ligands. The $X_M T$ versus T plot for (1) has a maximum at about $1.59 \text{ cm}^3 \text{ K mol}^{-1}$ and then decreases until the value comes down to $0.42 \text{ cm}^3 \text{ K mol}^{-1}$ for the iron complex (1). Complex (1) has a moment of 3.56 BM at 290 K, which decreases to 2.76 BM at 77 K and is further lowered to 1.84 BM at 5 K. This indicates that at room temperature it exists as a mixture of high and low-spin state species, whereas at 5 K, it exists predominantly in the low-spin form.

Electron paramagnetic resonance (EPR) spectra

The EPR spectra of the complexes of (1), (2), (3) and (4) were recorded in polycrystalline state and in solution both at room as well as low (77 K) temperatures. The spectra recorded at room temperature were isotropic. The X-band EPR spectra of powder samples of the complex (1), both at room and liquid nitrogen temperatures display a strong signal near $g = 4.2$ which is typical of that predicted for a transition between the middle Kramer's doublet of rhombically distorted, high spin monomeric Fe(III) complexes.

The spectra of (1) in solid and in chloroform solution also show a wide signal near $g = 2.3$ that is typical of Fe(III) in low-spin state. Existence of both high-spin and low-spin states has been reported for Fe(III) complexes with tetradentate Schiff base ligands by Kennedy and coworkers^{12(l,m)}. The EPR spectrum of the Co(III) complex, (2), in 1:1 $\text{CHCl}_3/\text{toluene}$ at 77 K, displays a signal at $g = 2.002$ with eight equally spaced hyperfine lines due to hyperfine splitting by the cobalt nucleus (^{57}Co 100% natural abundance, $I = 7/2$) with a hyperfine splitting constant of, $A_{\text{av}} = 20 \text{ G}$ along with an additional signal observed at $g = 3.769$. The EPR spectra of Ni(II) complex, (3) at 77 K displays signals at $g = 1.999$

and $g = 3.79$, which is characteristic of paramagnetic centers with even number of unpaired electron spins as expected for Ni(II). In 1:1 $\text{CHCl}_3/\text{toluene}$ at 77 K, (4) displays a four line spectrum ($g_{\parallel} = 2.25$; $g_{\perp} = 2.00$) with hyperfine coupling constant $A_{\parallel(\text{av})} = 143.3 \text{ G}$, characteristic of distorted square pyramidal mononuclear copper(II) complex. The larger g_{\parallel} and smaller A_{\parallel} values are associated with an off-planar distortion occurring in Cu(II) square-planar basal plane, leading to the pyramidal geometry¹⁶. It has been known that the hyperfine tensor components A_{\parallel} of some Cu(II) complexes decrease upon axial coordination due to a reduction in the d -orbital spin density and/or admixing of $4s$ character the into anti-bonding orbital of singly occupied $3d^9$ system¹⁷.

Mossbauer spectra

The Mossbauer spectra measured at 78 K can be fitted either as one doublet or as two doublets as shown in Fig. 3. The best-fit values of the isomer shift, δ and quadrupole splitting, ΔE_Q , at 78 K for (1) are given in Table 1. Thus based on the Mossbauer spectral data including the hyperfine parameters, the complex (1) corresponds to a high-spin Fe(III) in a

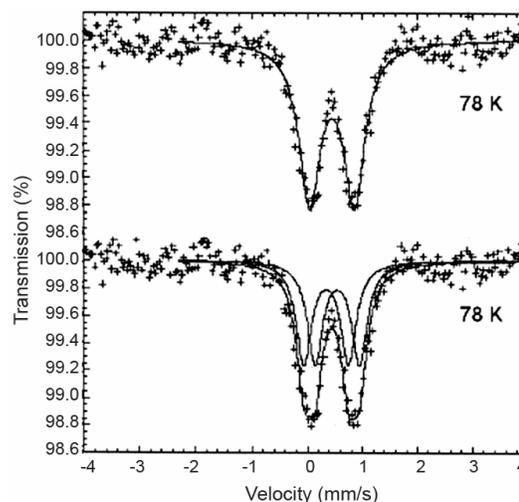


Fig. 3—Mossbauer spectrum of the iron complex (1) at 78 K. The experimental data points ('+') have been fitted (full line).

Table 1—Mössbauer spectral hyperfine parameters for (1)

Comp.	T (K)	δ^a (mm/s)	ΔE_Q (mm/s)	δ (mm/s)	Area (%)	Assignment
$\text{FeC}_{62}\text{H}_{72}\text{N}_2\text{O}_6$	78	0.445	0.81	0.47	100	
Two doublet fit	78	0.339	0.81	0.34	50	Higher s-density iron
As shown		0.541	0.81	0.34	50	Lower s-density iron
Two doublet fit	78	0.438	1.01	0.34	50	More distorted iron
not shown		0.441	0.61	0.34	50	Less distorted iron

^aThe isomer shifts are given relative to room temperature α -iron foil.

distorted environment with no possibility of the presence of Fe(II) centers. The isomer shift and quadrupole splitting values are also typical for high-spin Fe(III)-Schiff base systems.

pH Titration

The potentiometric pH titration curves of (**L**) exhibit one sharp inflection point at pK_a 9.26, while in the presence of one equivalent of zinc acetate, two inflections, one at 6.54 and the other at 8.97 are seen. The first inflection observed at $pK_a = 6.54$ corresponds to deprotonation of the phenolic-OH followed by formation of stable complex at $pH > 6$. The pK_a value for phenolate agrees well with that reported in the literature wherein deprotonation of the phenol was promoted by Zn(II) coordination, with the pK_a shifting from 9.2 (without zinc) to 6.5 (with zinc)¹⁸. The second inflection point observed at $pK_a = 8.97$ corresponds to the deprotonation of Zn(II)-bound water in the complex. A potentiometric pH titration experiment carried out under similar conditions with the isolated complex, (**5**), also indicated an inflection point at $pK_a = 8.63$, corresponding to the deprotonation of Zn(II)-bound aquo species.

Kinetics of the hydrolysis of *p*-nitrophenyl acetate (*p*-NPA)

The kinetics of *p*-NPA hydrolysis in the presence and in the absence of zinc complex (**5**) has been studied. The initial rate of the reaction was determined from the slope of the linear plot of absorbance of *p*-nitrophenolate versus time. The slope was calculated for first 10% conversion from which the initial rate of the reaction was determined. The reactions yielded initial rates of 0.87×10^{-4} , 3.22×10^{-4} , 8.28×10^{-4} and $26.38 \times 10^{-4} M s^{-1}$ at pH values of 8.27, 9.08, 9.42 and 10.16, respectively at 25°C. The initial rate of hydrolysis was found to increase with increasing pH of the reaction medium, which is due to the increase in the concentration of Zn-OH species in the medium. The experimental results were compared with the results of the corresponding control experiments. Four- or five-coordinated mononuclear Zn(II) complexes containing water have been used in the literature as models for zinc hydrolytic enzymes¹⁹.

Conclusions

Though the coordination chemistry of simple Schiff bases is rich in literature, that of Schiff bases attached to calix[4]arene is rather less explored.

In the metal ion complexes reported herein, the azomethine is tethered to the lower rim of calix[4]arene as 1,3-pendants. In all these complexes, the ligand acts as dianionic and tetradentate. While the spectral data strongly support five-coordination in the case of Cu(II) with the involvement of pyridine moiety as supported by crystal structure²⁰, the spectral data strongly support six coordination in the case of the complexes of Fe(III), Co(III) and Ni(II) where the additional coordination may arise from the ether oxygen of the pendant arm. Hence, the conjugate acts as hexadentate ligand. The Mossbauer spectrum of the iron complex (**1**) and the hyperfine parameters are typical of high-spin iron(III) in a distorted octahedral environment. In the case of the Co(III) complex, the acetate acts as counteranion. Proposed structures of these complexes are shown in Scheme 2. Precedence for variability in coordination number and geometry is well demonstrated in the case of mono-, di-, tri- and tetra-amide derivatives of calix[4]arene with alkali^{21a}, transition^{21(b,c)} and lanthanide^{21(d,e,f)} ions where the metal center forms 5-membered chelate arising from the pendants including the ether oxygen. Some of these complexes possess pseudo coordination geometries as well. Thus, the present ligand, calix[4]arene-imine conjugate exhibits diverse coordination with different metal ions, Fe(III), Co(III) and Ni(II) (dianionic, hexadentate, N_2O_4), Cu(II), Zn(II) and UO_2^{2+} (dianionic, tetradentate, N_2O_2). The Zn(II) complex has been shown to hydrolyze *p*-nitrophenylacetate ester through the formation of Zn-hydroxo species.

Acknowledgement

CPR acknowledges the financial support from the DST and CSIR. MD and CJP acknowledge their SRF fellowship from CSIR. We thank CDRI, Lucknow for FAB mass and SAIF, IIT Bombay, for some spectral measurements.

References

- 1 Gutsche C D, in *Calixarenes Revisited, Monographs in Supramolecular Chemistry*, edited by J F Stoddart, (Royal Society of Chemistry, Cambridge) 1998.
- 2 Wieser C, Dieleman C B & Matt D, *Coord Chem Rev*, 165 (1997) 93.
- 3 (a) Chang K C, Su I H, Lee G H & Chung W S, *Tetrahedron Lett*, 48 (2007) 7274; (b) Liang Z, Liu Z, & Gao Y, *Tetrahedron Lett*, 48 (2007) 3587; (c) Othman A B, Lee J W, Wu J S, Kim J S, Abidi R, Thury P, Strub J M, Dorsselaer A V & Vicens J J, *Org Chem*, 72 (2007) 7634; (d) Song K C, Choi M G, Ryu D H, Kim K N & Chang S K, *Tetrahedron Lett*, 48 (2007) 5397; (e) Métivier R, Leray I & Valeur B,

- Chem Commun*, (2003) 996; (f) Talanov V S, Roper E D, Buie N M & Talanova G G, *Tetrahedron Lett*, 48 (2007) 8022; (g) Chen Q Y & Chen C F, *Tetrahedron Lett*, 46 (2005) 165; (h) Kim J H, Hwang A R & Chang S K, *Tetrahedron Lett*, 45 (2004) 7557; (i) Métivier R, Leray I & Valeur B, *Chem Eur J*, 10 (2004) 4480; (j) Creaven B S, Deasy M, Flood P M, McGinley J & Murray B A, *Inorg Chem Commun*, 11 (2008) 1215.
- 4 (a) Valeur B & Leray I, *Inorg Chim Acta*, 360 (2007) 765; (b) Ikeda A & Shinkai S, *Chem Rev*, 97 (1997) 1713; (c) Valeur B & Leray I, *Coord Chem Rev*, 205 (2000) 3; (d) Kim J S & Quang D T, *Chem Rev*, 107 (2007) 3780; (e) Creaven B S, Donlona D F & McGinley J, *Coord Chem Rev*, 253 (2009) 893.
- 5 (a) Dessingou J, Joseph R & Rao C P, *Tetrahedron Lett*, 46 (2005) 7967; (b) Pathak R K, Ibrahim Sk Md & Rao C P, *Tetrahedron Lett*, 50 (2009) 2730; (c) Joseph R, Ramanujam B, Pal H & Rao C P, *Tetrahedron Lett*, 49 (2008) 6257; (d) Joseph R, Ramanujam B, Acharya A & Rao C P, *Tetrahedron Lett*, 50 (2009) 2735; (e) Joseph R, Ramanujam B, Acharya A, Khutia A. & Rao C P, *J Org Chem*, 73 (2008) 5745.
- 6 (a) Kumar M, Mahajan R K, Sharma V, Singh H, Sharma N & Kaur I, *Tetrahedron Lett*, 42 (2001) 5315; (b) Asfari Z, Wenger S, & Vicens J, *J Incl Phenom Mol Recog Chem*, 19 (1994) 137; (c) Guo T D, Zheng Q Y, Yang L M & Huang Z T, *J Incl Phenom Macrocycl Chem*, 36 (2000) 32; (d) Liu Y, Zhao B T, Zhang H Y, Wada T & Inoue Y, *J Chem Soc, Perkin Trans*, 2 (2001) 1219; (e) Tamburini S, Tomasin P, Vigato P A, Casnati A & Domiano L, *Inorg Chim Acta*, 254 (1997) 209.
- 7 Zhang W C & Huang Z T, *Synthesis*, (1997) 1073.
- 8 Singnorini O, Dockal E R, Castellano G & Oliva G, *Polyhedron*, 15 (1996) 245.
- 9 Rao P V, Rao C P, Sreedhara A, Wegelius E K, Kolehmainen E & Rissanen K, *J Chem Soc, Dalton Trans*, (2000) 1213.
- 10 Timkin M D, Hendrickson D N & Sinn E, *Inorg Chem*, 24 (1985) 3947.
- 11 (a) Sacconi L, *Coord Chem Rev*, 1 (1966) 192; (b) Yamada S, *Coord Chem Rev*, 1 (1966) 415; (c) Inada Y, Sugimoto K, Ozutsumi K & Funahashi S, *Inorg Chem*, 33 (1994) 1875; (d) Hathaway B J, Dudley R J & Nicholls P, *J Chem Soc A*, (1969) 1845; (e) Kimura E, Kurosaki H, Kurogi Y, Shionoya M & Shiro M, *Inorg Chem*, 31 (1992) 4314.
- 12 (a) Haddad M S, Lynch M W, Federer W D & Hendrickson D N, *Inorg Chem*, 20 (1981) 123; (b) Hall G R & Hendrickson D N, *Inorg Chem*, 12 (1973) 2269; (c) Kunze K R, Perry D L & Wilson L J, *Inorg Chem*, 16 (1977) 594; (d) Nakajima H, Tanaka T, Kobayashi H & Tsujikawa I, *Inorg Nucl Chem Lett*, 12 (1976) 689; (e) Cox M, Darken J, Fitzsimmons B W, Smith A W, Larkworthy L F & Rogers K A, *J Chem Soc, Dalton Trans*, (1972) 1192; (f) Hoskin B F & Panna C D, *Inorg Nucl Chem Lett*, 11 (1975) 409; (g) Dose E V, Murphy K M M & Wilson L J, *Inorg Chem*, 15 (1976) 2622; (h) Tweedle M F & Wilson L J, *J Am Chem Soc*, 98 (1976) 4824; (i) Petty R H, Dose E V, Tweedle M F & Wilson L J, *Inorg Chem*, 17 (1978) 1064; (j) Federer W D & Hendrickson D N, *Inorg Chem*, 23 (1984) 3861; (k) Timkin M D, Hendrickson D N & Sinn E, *Inorg Chem*, 24 (1985) 3947; (l) Kennedy B J, Gavin B, Ernst H, Murray K S & Snow M R, *Inorg Chem*, 24 (1985) 1647; (m) Kennedy B J, McGrath A C, Murray K S, Skelton B W & White A H, *Inorg Chem*, 26 (1987) 483.
- 13 Ainscough E W, Brodie A M, Plowman J E, Bloor S J, Sanders-Loehr J & Loehr T M, *Biochemistry*, 19 (1980) 4072.
- 14 (a) Oosterhuis W T, *Struct Bond (Berlin)*, 20 (1974) 59; (b) Aasa R, *J Chem Phys*, 52 (1970) 3919; (c) Nanni E J Jr, Stallings M D & Sawyer D T, *J Am Chem Soc*, 102 (1980) 4481; (d) Scullane M I, White L K & Chasteen N O, *J Magn Reson*, 47 (1982) 383.
- 15 Ishizu K, Haruta T, Kohno Y, Mukai K, Miyoshi K & Sigiura Y, *Bull Chem Soc Japan*, 53 (1980) 3513.
- 16 Miyoshi K, Tanaka H, Kimura E, Tsuboyama S, Murata S, Shimizu H & Ishizu K, *Inorg Chim Acta*, 78 (1983) 23.
- 17 (a) Garito A F & Wagland B B, *J Am Chem Soc*, 91 (1969) 866; (b) Sugiura Y, *Inorg Chem*, 17 (1978) 2176.
- 18 Kimura E, *Acc Chem Res*, 34 (2001) 171.
- 19 (a) Koike T & Kimura E, *J Am Chem Soc*, 113 (1991) 8935; (b) Kimura E, Nakamura I, Koike T, Shionoya M, Kodama Y, Ikeda T & Shiro M, *J Am Chem Soc*, 116 (1994) 4764.
- 20 Dey M, Rao C P & Guionneau P, *Inorg Chem Commun*, 8 (2005) 998.
- 21 (a) Queslati I, Abidi R, Amri H, Thuery P, Nierlich M, Asfari Z, Harrowfield J M & Vicens J, *Tetrahedron Lett*, 41 (2000) 8439; (b) Beer P D, Drew M G B, Leeson P B & Ogden M I, *J Chem Soc, Dalton Trans*, (1995) 1273; (c) Ogden M I, Skelton B W & White A H, *J Chem Soc, Dalton Trans*, (2001) 3073; (d) Beer P D, Drew M G B, Grieve A, Kan M, Leeson P B, Nicholson G, Ogden M I & Williams G, *J Chem Soc, Chem Commun*, (1996) 1117; (e) Beer P D, Drew M G B, Kan M, Leeson P B, Ogden M I & Williams G, *Inorg Chem*, 35 (1996), 2202; (f) Beer P D, Drew M G B, Leeson P B & Ogden M I, *Inorg Chim Acta*, 246 (1996) 133.