A first report of the complexes of 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarboxymethoxy-26,28-dihydroxycalix[4]arene with Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)

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Abstract

Totally six dinuclear complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) of calix[4]arene derivatized with two pendants possessing terminal –COOH functions at two of its alternate phenolic –OH groups were synthesized for the first time and were well characterized.

Keywords: p-tert-Butyl-calix[4]arene-1,3-diacid; Dinuclear complexes; Distorted octahedral; Antiferromagnetic coupling

Calixarenes are intrinsically interesting due to their complexing abilities and conformational flexibility and often considered as important as cyclodextrins [1]. The chemistry of calixarenes has been applied in diverse areas, such as, enzyme mimics [2], host–guest chemistry [3] and selective ion transport and sensors [4]. Reports on the isolated and characterized products of metal ion interactions of calix[4]arene derivative systems are quite limited in the literature [5]. Derivatives based on calix[4]arene-di- and tetraacids have been used for the extraction of metal ions from H2O to CH2Cl2 [6]. Beer et al. [7] reported a crystal structure of UO2+ where the calix[4]arene has two strands while one of it is possessing a –COOH, the other possesses a –N(C2H5)2 function. Further, to our knowledge there has been no metal ion complex of p-tert-butyl-calix[4]arene-1,3-diacid (H4L, Fig. 1) reported in the literature, however, this ligand has been used in literature for the solution studies of a few f-block elements [8]. In this communication, we report for the first time the synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of p-tert-butyl-calix[4]arene-1,3-diacid.

The precursor ligand, p-tert-butyl-calix[4]arene-1,3-diacid (H4L) was synthesized by us as reported earlier [9]. Reaction of this derivative (H4L) with M(II) perchlorates in the ratio 1:1 in MeOH followed by the addition of pyridine as co-ligand yielded the corresponding metal ion complexes, viz., Mn(II), 1, Fe(III), 2, Co(II), 3, Ni(II), 4, Cu(II), 5 and Zn(II), 6. Characterization of these complexes [10–15] was carried out by measuring the elemental analysis, conductivity, magnetic susceptibility, TGA, FAB mass, FT-IR, UV–Vis, 1H NMR and EPR spectra. The elemental analysis including that of the metal ion contents fits well with a composition of metal to ligand to pyridine ratio as 1:1:1 in case of 1, 2, 3 and 5, and as 1:1:2 in case of 4 and 6. The molecular ion peaks observed in the FAB mass spectra are consistent with dinuclear complexes and the spectra exhibit several
other interpretable fragments [10–15]. The presence of bound pyridine in all the six complexes has been quantitatively demonstrated based on the weight loss observed in TGA under N2 atmosphere in the temperature range 60–200°C. These complexes were found to be neutral based on the conductivity studies. Thus the analytical along with the mass spectral data fits well with the formula, \[ \text{[M(H}_2\text{L)Py}]_2 \] for Mn(II), Co(II), and Cu(II), \[ \text{[Fe(HL)Py}]_2 \] for Fe(III) and \[ \text{[M(H}_2\text{L)Py}_2]_2 \] for Zn(II) and Ni(II) and these complexes have no precedence in the literature.

FT-IR spectra of all the complexes exhibited bands at 1600–1620, \(~1480\) and \(~1380\) cm\(^{-1}\) corresponding to the \(\nu_{\text{carboxylate}}\) vibrations. The difference between these frequencies, viz., \(~120\) and \(~220\) cm\(^{-1}\), indicate that the coordinations arise from monodentate as well as bidentate including bridging mode for the carboxylate groups in these complexes and the results agree well with the literature reports [16]. A trinuclear Ni(II) complex where the acetates are bridged both as mono-dentate as well as bi-dentate exhibited the stretching vibrations at around 1585, 1400 and 1460 cm\(^{-1}\) [17]. Absorption spectra of these complexes [10–15] clearly indicated d → d transitions besides the ligand based bands in the UV–Vis spectra, except for the Zn(II) and Mn(II) owing to the d\(^{10}\) and d\(^{3}\) configurations, respectively, in these cases. The d → d region of the spectra are largely reminiscent of octahedral complexes.

\(^1\)H NMR spectra measured in CDCl\(_3\) exhibited paramagnetically broadened and down-field shifted peaks in case of Cu(II) complex, 5. The spectrum exhibited two signals for OCH\(_2\) protons of the pendants, one at 17.5 and the other at 35.8 ppm, in comparison to 4.66 ppm in the free ligand (Fig. 2), indicating that both the pendants were involved in binding to the metal ion to different extents where the ether oxygen is involved in binding at least from one of the pendants. Generally the non-equivalent protons on a –CH\(_2\) do not differ by a large value in their chemical shifts (viz., diastereotopic coupling). The large difference observed between the two peaks in the present case, viz., \(~17\) ppm, excludes any possibility for the presence of two non-equivalent hydrogens on a methylene group.

All the other resonances were found at the expected positions with some line broadening and the spectral pattern including that of tertiary butyl region indicated a rather symmetric dinuclear complex for 5. However, the Zn(II) complex, 6 exhibited a characteristic diamagnetic spectrum.

Room temperature magnetic moments per metal ion, 5.73, 3.86, 4.16, 3.21, 1.62 BM were observed respectively for 1, 2, 3, 4 and 5. The data is well within the acceptable range for the corresponding metal centers [18] and agree well with the octahedral complexes of high spin Mn(II), high spin Co(II), Ni(II) and Cu(II).

For the Cu(II) complex, 5, the \(\chi_m \cdot T\) was found to be 0.66 emu K mol\(^{-1}\) at 300 K which is less than that observed for two non-coupled Cu(II) centers. The \(\chi_m \cdot T\) continuously decreases on cooling up to 75 K and exhibits a well defined local maximum in the temperature range 75–45 K. A further decrease was observed in \(\chi_m \cdot T\) up to 5 K where the value is 0.10 emu K mol\(^{-1}\).

The observed \(\mu_{\text{eff}}\) varies from 2.28 to 0.92 BM on going from 300 to 5 K. The magnetic behaviour observed in 5 accounts for the antiferromagnetic coupling between the copper (II) centers, extending to both intra- as well as inter-molecular types as also reported in the literature [19]. The EPR spectra of Cu(II) complex, 5 shows

![Fig. 1](image1.png)

**Fig. 1.** 1,5,11,17,23-tetra-tert-butyl-25,27-diehoxycarboxymethoxy-26,28-dihydroxy-4,8-calix[4]arene (p-tert-butyl-calix[4]arene-1,3-diacid, H\(_4\)L); [R = tert-butyl].

![Fig. 2](image2.png)

**Fig. 2.** \(^1\)H NMR spectra of, (a) \(H_4\)L; (b) 5.
rhombic signal ($g_{iso} = 2.13$) with resolved hyperfine splitting.

This communication clearly demonstrates for the first time the synthesis and characterization of the complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) of $p$-tert-butyl-calix[4]arene derivatized with two pendants possessing terminal –COOH functions at two of its alternate phenolic –OH groups as shown in Fig. 1. All the characterization data strongly support the octahedral geometry and dinuclear as well as neutral behaviour. The ligand acts as dinegative in all the cases, and in case of Fe(III) complex it acts as tri-negative, implying that in 2, the ligand uses its one of the lower rim phenolic O$^-$ in the binding. The mass spectra in all the cases and variable temperature magnetic study in case of 5, strongly support the presence of dinuclear complexes. The FTIR spectra in all the cases are indicative of the presence of mono and bidentate as well as bridging nature of the carboxylate function. $^1$H NMR in 5, while indicated a difference in the binding of the two strands, the overall pattern supported the presence of a symmetric dinuclear complex. While the structural establishment of one or more of these complexes is essential to understand the nature of this new category of metal ion bound calixarene derivatives, all attempts made to isolate the single crystals were futile so far. Therefore, based on the present characterization data, a proposed structure is shown in Fig. 3 for 5.

The present studies clearly evoked an interest to ascertain whether these dinuclear species are basic structural units or otherwise. We plan to address this by going through a synthetic exercise where the solvent and/or co-ligand used will be varied. Variable temperature magnetic and EPR studies will eventually be a part of our on-going efforts in this direction in order to further demonstrate the dinuclear nature of these complexes beyond doubt.

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References

[10] Mn(II) complex, 1: Yield 66%, m.p. 200–210 °C (decomp.); IR (KBr disc) $\nu_{max}$ (cm$^{-1}$) 3430 ($\nu_{OH}$), 1596 ($\nu_{CO}$); $\lambda_{max}$, nm (CHCl$_3$, $\mu$mol$^{-1}$ L cm$^{-1}$): 281 (6150), 242 (10,310); FABMS: $m/z$: 1636 ([M$_2$(H$_2$L)$_2$]$,^+$, 10%), 1581 ([M(H$_2$L)$_3$]$^+$, 10%), 818 ([M(H$_2$L)]$^+$, 25%), 801 ([K + H$_2$L]$^+$, 80%); Anal. Calc. for C$_{53}$H$_{63}$N$_2$O$_8$: C, 70.96; H, 7.07; N, 1.50; Mn, 6.13. Found: C, 70.40; H, 7.35; N, 1.06; Mn, 5.54%.
[11] Fe(II) complex, 2: Yield 70%, m.p. 200–215 °C (decomp.); IR (KBr disc) $\nu_{max}$ (cm$^{-1}$) 1596 ($\nu_{CO}$); 2044 (4040) ($\lambda_{max}$, nm (CHCl$_3$, $\mu$mol$^{-1}$ L cm$^{-1}$)): 281 (21900), 249 (24,540), 465 (398); FABMS: $m/z$: 1639 ([Fe$_2$(H$_2$L)$_2$]$^+$, 10%), 819 ([Fe(H$_2$L)$_3$]$^+$, 60%), 780 ([Fe(H$_2$L)]$^+$, 100%); Anal. Calc. for C$_{53}$H$_{63}$N$_2$O$_8$: C, 71.53; H, 6.92; N, 2.87; Fe, 5.31%.
[12] Co(II) complex, 3: Yield 72%, m.p. 240–250 °C (decomp.); IR (KBr disc) $\nu_{max}$ (cm$^{-1}$) 1603 (3390) ($\nu_{CO}$); 1580 ($\lambda_{max}$, nm (CHCl$_3$, $\mu$mol$^{-1}$ L cm$^{-1}$)): 282 (13,670), 244 (17,690), 520 (165); FABMS: $m/z$: 1644 ([Co$_2$(H$_2$L)$_2$]$^+$, 22%), 1586 ([Co(H$_2$L)$_3$]$^+$, 12%), 822 ([Co(H$_2$L)]$^+$, 300%); Anal. Calc. for C$_{53}$H$_{63}$N$_2$O$_8$: C, 70.65; H, 7.05; N, 1.55; Co, 6.92%.
[13] Ni(II) complex, 4: Yield 70%, m.p. 220–240 °C (decomp); IR (KBr disc) $\nu_{max}$ (cm$^{-1}$) 1596 ($\nu_{CO}$); 3404 (4040) ($\lambda_{max}$, nm (CHCl$_3$, $\mu$mol$^{-1}$ L cm$^{-1}$)): 282 (11,720), 245 (17,030), 398 (14); FABMS: $m/z$: 1645 ([Ni$_2$(H$_2$L)$_2$]$^+$, 32%), 1586 ([Ni(H$_2$L)$_3$]$^+$, 10%), 822 ([Ni(H$_2$L)]$^+$, 100%), 780 ([Ni$_2$(H$_2$L)$_2$]$^+$, 60%); Anal. Calc. for C$_{53}$H$_{63}$N$_2$O$_8$: C, 70.03; H, 7.17; N, 2.72; Ni, 5.19%.
[14] Cu(II) complex, 5: Yield 65%, m.p. 220–232 °C (decomp); IR (KBr disc) $\nu_{max}$ (cm$^{-1}$) 1608, 1638 ($\nu_{CO}$); 3403 (4040) ($\lambda_{max}$, nm (CHCl$_3$, $\mu$mol$^{-1}$ L cm$^{-1}$)): 282 (32,860), 249 (28,960), 491 (76); $^1$H NMR (300 MHz, CDCl$_3$, $\delta_{ppm}$): 1.06, 1.25 (s, 36H, $t$-but-H), 3.42
(br, 8H, CH₃), 6.95, 7.03 (s, 8H, Ar–H), 17.56, 35.83 (s, OCH₂, 4H); FABMS: \( m/z \): 1652 ([Cu₂(H₂L)₂]⁺, 4 %); 827 ([Cu(H₂L)]⁺, 20%), 764 (H₂L + 2] +, 100%); Anal. Calc. for C₁₅H₁₅NO₉Cu.: C, 69.17; H, 7.20; N, 1.49; Cu, 6.77. Found: C, 68.74; H, 6.63; N, 1.15, Cu, 6.92%.

[15] Zn(II) complex, 6: Yield 65 %; m.p. 210–225 °C (decomp); IR (KBr disc) \( \nu_{\text{max}} \) (cm⁻¹) 1613, 1631 (vC=O), 3407 (vOH); \( \lambda_{\text{max}}/nm \), (CHCl₃, \( \mu \text{mol}^{-1} \text{L cm}^{-1} \)): 282 (7760), 242 (12,030): \(^1\)H NMR (300 MHz, CDCl₃, \( \delta \) ppm): 0.88, 1.30 (s, 36H, \( t-\text{but-H} \)), 3.25 (d, \( J = 11.7 \), 4H, CH₂), 4.13 (d, \( J = 10.2 \), 4H, CH₂), 6.69, 7.31 (s, 8H, Ar–H), 7.02, 7.69, 8.73 (s,10H, Py–H); FABMS: \( m/z \): 1659 ([Zn₂(H₂L)₂]⁺, 20%), 828 ([Zn(H₂L)]⁺, 28%), 765([H₂L + 2] +, 30 %); Anal. Calc. for C₁₆H₁₆N₂O₁₀Zn: C, 68.59; H, 7.29; N, 2.66; Zn, 6.22. Found: C, 68.57; H, 6.73; N, 2.75; Zn, 6.24%.


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