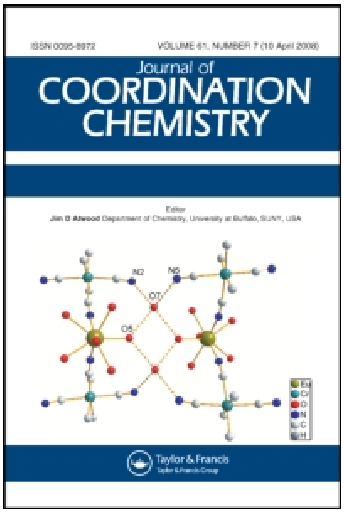

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Structural analysis of calix[*n*]arene-iron(III) complexes (*n*=4, 6, 8) and thermal decomposition of the parent calix[*n*]arenes

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Structural analysis of calix[*n*]arene-iron(III) complexes ($n = 4, 6, 8$) and thermal decomposition of the parent calix[*n*]arenes

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In this study, six new calix[*n*]arene-Fe^{3+} complexes ($n = 4, 6, 8$) were synthesized with parent calix[*n*]arenes in a DMF solution of $FeCl_3 \cdot H_2O$. The properties and coordination characteristics of the six parent calix[*n*]arene-Fe^{3+} complexes were determined by elemental analyses, TG-DTA, UV-vis, FT-IR and ^1H NMR spectroscopy. According to UV-vis analysis, in the six complexes the iron(III) coordinated by oxygen donor atoms from calix[*n*]arene ligands and DMF molecules. The complexes behave as 1 : 1 and 1 : 2 electrolytes in the case of calix[*n*]arenes ($n = 4, 6$) (**1**–**4**) and calix[8]arene (**5**, **6**), respectively. ^1H NMR studies demonstrate that **1** and **2** are more stable than **3, 4, 5** and **6** in DMF, and indicate *cone* conformation of the calix[4]arene ligands (**1** and **2**).

Keywords: Calix[*n*]arene; Iron(III) complexes; TG/DTA; Thermal analysis; FT-IR, ^1H NMR spectroscopy

1. Introduction

Calix[*n*]arenes are macrocyclic molecules made of *n*-phenol units connected by *ortho* methylene groups [1, 2]. Calix[4]arenes are the simplest and the most common compounds of this family with four phenolic residues in the macrocyclic ring. These molecules and their derivatives have been extensively studied for their interesting properties, for example being host to cations, anions and neutral molecules, and for the formation of supramolecular assemblies [3].

In the past decades, calix[*n*]arene complexation and extraction selectivity towards rare earths has been demonstrated to correlate with the fit between the cation and the cavity size and the conformational functional groups [4, 5]. In contrast calix[*n*]arene-iron(III) complexes have rarely been synthesized and characterized, therefore calix[*n*]arene complexation with Fe^{3+} and the coordination features of calix[*n*]arene-Fe^{3+} complexes are unknown.

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Because of the four phenoxy groups in calix[4]arenes, reactions with transition metal cations can produce metal phenolate complexes by substitution of one to four hydrogen atoms [6]. Thus, these ligands may serve as models for polyoxo surfaces. In such a role, calix[4]arenes have some geometrical peculiarities. In 1994, the first selective ionophore for a calix[4]arene-Fe^{3+} complex was reported [7]. It showed that the Fe^{3+} complex has a structure with coordination number six. The ionic radius of the Fe^{3+} is smaller than that of Sc^{3+} and La^{3+}, however the radius of Sc^{3+} is closer to that of Fe^{3+}. In 1991, the crystal structure of *p*-*tert*-butylcalix[4]arene-Lu^{3+} was published by Harrowfield *et al.* [8], demonstrating that Lu^{3+} was eight coordinate.

The *p*-*tert*-butylcalix[*n*]arenes ($n = 4, 6, 8$) were synthesized and characterized with scandium(III) complexes [9]. Zeller *et al.* [10] also prepared a calix[4]arene-supported iron(III) complex which was structurally analyzed.

In our recent work [11–16], the preparations of parent calix[*n*]arenes, calix[*n*]arene derivatives, and polymer-supported calix[4]arenes were described from reacting an oligomer or polyacryloylchloride with tetraethylcalix[4]arene tetraacetate. We used the prepared ligands for selective extraction of Fe^{3+} in transition metal cation mixtures such as Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+}. Furthermore, the coordination chemistry of calix[*n*]arenes has stimulated polymer chemists to design calixarenes as carriers for the selective extraction of Fe^{3+} cation from the aqueous into the organic phase.

In this work, in order to extend the calixarene complexing reactions to Fe^{3+}, we concentrate on complexation between calix[*n*]arenes ($n = 4, 6, 8$) and Fe^{3+}, in an attempt to understand the important properties of calix[*n*]arene-Fe^{3+} complexes.

2. Experimental

2.1. *Chemicals and reagents*

Chemicals used in all ligands synthesis were chemically pure and were used in all ligand syntheses and were purchased from Merck or Carlo–Erba companies. *p*-*tert*-Butylcalix[4]arene, calix[4]arene, *p*-*tert*-butylcalix[6]arene, calix[6]arene, *p*-*tert*-butylcalix[8]arene and calix[8]arene (purity 95%) were prepared according to established methods [17, 18]. All other reagents were purchased from commercial sources and purified by standard techniques. $FeCl_3 \cdot H_2O$ (99.5%) solution was used to prepare iron trichloride in DMF.

2.2. Apparatus

All melting points were determinated with an Electrothermal IA9100 digital melting point apparatus and are uncorrected. pH measurements were carried out with a GLP22 Crison Model pH-ionmeter. All experimental work was carried out at $20 \pm 1°C$ and the pH values were determined using a combined glass-pH electrode (DI ph52-01). ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as internal standard and were recorded on a Bruker 400 MHz spectrometer in DMSO-d_6 at room temperature. IR spectra were recorded on a Matson 1000 FT-IR Spectrometer as KBr pellets. UV-vis spectra were obtained with a Shimadzu UV-1601 UV-visible recording spectrophotometer. All data were quoted in wavenumbers (cm^{-1}). Elemental analyses were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

Thermo-analytical TG, DTG and DTA curves were obtained simultaneously by using a Shimadzu DTG-60H thermogravimetric analyzer. The measurements were carried out in flowing nitrogen with a flow rate of $25\,mL\,min^{-1}$ and the temperature range of 25–850°C in platinum crucible. The heating rate was $10°C\,min^{-1}$ and the sample masses were in the range of 3–5 mg. Highly sintered α-Al_2O_3 was used as the reference material.

2.3. *Preparation of calix[*n*]arene-Fe^{3+} complexes*

A slurry of 1.0 mmol calix[*n*]arene in 15 mL DMF was heated to 60°C in a water bath and colorless solution was formed in nitrogen. $FeCl_3 \cdot 6DMF$ (1.0 mmol) solution was quickly mixed with the ligand solution. The color of the solution changed immediately, and the dark green solution was kept on a water bath at 60°C for about 1 h. The solvent (DMF) was removed until 1–2 mL remained under vacuum and precipitation of complex was completed. The precipitate was filtered, washed with water, ethanol and ether, and dried in a vacuum dessicator.

The percentage of iron(III) in the complex was determined by complexometry after decomposition.

2.3.1. [(*p*-tert-Butylcalix[4]arene-3H)F • 2(DMF)] • 2H$_2$O (1). Yield 63%. Found: C, 71.07%; H, 7.83%; N, 3.04%; Fe, 6.79%. Calcd: for $C_{50}H_{71}N_2O_8Fe$ (MW: 883.97): C, 67.94%; H, 8.10%; N, 3.17%; Fe, 6.32%. IR (KBr pellet): υ(O–H) 3221 (s, br); υ_{as}(C–H) 2960 (s, sh); υ_s(C–H) 2842 (m); υ(C=O) 1653 (vs); υ_s(C=C) 1528 (m); δ_{as}(C–H) 1479 (vs, sh); δ(C–H) 1328 (s); υ(C–N) 1379 (s); υ_s(C–OH) 1203 (s); υ(M–O) 882 (w); υ(M–N) 778 cm^{-1} (s).

2.3.2. [(Calix[4]arene-3H)Fe • 2(DMF)] • 2H$_2$O (2). Yield 78%. Found: C, 65.62%; H, 5.62%; N, 4.07%; Fe, 9.17%. Calcd: for $C_{34}H_{41}N_2O_8Fe$ (MW: 661.56): C, 61.72%; H, 6.25%; N, 4.23%; Fe, 8.44%. IR (KBr pellet): υ(O–H) 3234 (s, br); υ_{as}(C–H) 2964 (s, sh); υ_s(C–H) 2859 (m); υ(C=O) 1652 (vs); υ_s(C=C) 1518 (m); δ_{as}(C–H) 1459 (vs, sh); δ(C–H) 1333 (s); υ(C–N) 1382 (s); υ_s(C–OH) 1197 (s); υ(M–O) 879 (w); υ(M–N) 749 cm^{-1} (s).

2.3.3. [(*p-tert*-Butylcalix[6]arene-5H)Fe • 2(DMF)] (3). Yield 58%. Found: C, 73.27%; H, 8.67%; N, 2.13%; Fe, 4.59%. Calcd: for $C_{72}H_{101}N_2O_{10}Fe$ (MW: 1174.45): C, 71.44%; H, 8.41%; N, 2.31%; Fe, 4.61%. IR (KBr pellet): υ(O–H) 3332 (s, br); υ_{as}(C–H) 2962 (s, sh); υ_s(C–H) 2859 (m); υ(C=O) 1652 (vs); υ_s(C=C) 1518 (m); δ_{as}(C–H) 1459 (vs, sh); δ(C–H) 1333 (s); υ(C–N) 1382 (s); υ_s(C–OH) 1197 (s); υ(M–O) 869 (w); υ(M–N) 872 cm^{-1} (s).

2.3.4. [(Calix[6]arene-5H)Fe • 2(DMF)] (4). Yield 86%. Found: C, 68.46%; H, 6.29%; N, 3.02%; Fe, 6.13%. Calcd: for $C_{48}H_{53}N_2O_{10}Fe$ (MW: 837.88): C, 65.98%;

H, 6.11%; N, 3.21%; Fe, 6.39%. IR (KBr pellet): υ(O–H) 3236 (s, br); υ_{as}(C–H) 2956 (s, sh); υ_s(C–H) 2873 (m); υ(C=O) 1654 (vs); υ_s(C=C) 1560 (m); δ_{as}(C–H) 1478 (vs, sh); δ(C–H) 1318 (s); υ(C–N) 1366 (s); υ_s(C–OH) 1197 (s); υ(M–O) 869 (w); υ(M–N) 872 cm^{-1} (s).

2.3.5. [(*p-tert*-Butylcalix[8]arene-6H)2Fe • 4(DMF)] (5). Yield 67%. Found: C, 75.09%; H, 8.85%; N, 1.63%; Fe, 3.85%. Calcd: for $C_{100}H_{146}N_4O_{16}Fe_2$ (MW: 1699.97): C, 67.78%; H, 8.31%; N, 3.16%; Fe, 6.30%. IR (KBr pellet): υ(O–H) 3237 (s, br); υ_{as}(C–H) 2962 (s, sh); υ_s(C–H) 2881 (m); υ(C=O) 1653 (vs); υ_s(C=C) 1528 (m); δ_{as}(C–H) 1478 (vs, sh); δ(C–H) 1332 (s); υ(C–N) 1381 (s); υ_s(C–OH) 1197 (s); υ(M–O) 782 (w); υ(M–N) 695 cm^{-1} (s).

2.3.6. [(Calix[8]arene-6H)2Fe · 4(DMF)] (6). Yield 89%. Found: C, 65.12%; H, 6.28%; N, 4.17%; Fe, 9.27%. Calcd: for $C_{68}H_{82}N_4O_{16}Fe_2$ (MW: 1251.11): C, 61.73%; H, 6.25%; N, 4.23%; Fe, 8.44%. IR (KBr pellet): υ(O–H) 3318 (s, br); υ_{as}(C–H) 2963 (s, sh); υ_s(C–H) 2867 (m); υ(C=O) 1652 (vs); υ_s(C=C) 1534 (m); δ_{as}(C–H) 1467 (vs, sh); δ(C–H) 1334 (s); υ(C–N) 1380 (s); υ_s(C–OH) 1197 (s); υ(M–O) 869 (w); υ(M–N) 698 cm^{-1} (s).

3. Results and discussion

Much work has been reported related to functionalized calix[*n*]arenes and a number of complexes containing functional groups have been synthesized. Reports on complexes with iron(III) of calix[*n*]arenes are scarce; however selective extraction of Fe^{3+} cation from aqueous to organic phase was achieved with calix[4]arene and some of its derivatives [13, 16].

3.1. *Solubility*

Both parent calix[*n*]arenes and their Fe^{3+}-complexes are soluble in acetone, carbon disulfide dimethylformamide (DMF) and dimethylsulfoxide (DMSO), but the Fe^{3+}-complexes are slightly soluble in chloroform and insoluble in toluene, while the calix[*n*]arenes are soluble in these solvents. On the contrary, both parent calix[*n*]arenes and their Fe^{3+}-complexes are soluble.

The solvent (DMF) has a very important role in the formation of calix[*n*]arene complexes with Fe^{3+}, since parent calix[4]arene cannot make complexes with Fe^{3+} in $CHCl_3$.

The six Fe^{3+} complexes **1**–**6** are soluble in DMF and appear as amorphous dark green solutions. In DMF at room temperature, the solubility order of the calix[*n*]arenes are *p*-*tert*-butylcalix[4]arene > *p*-*tert*-butylcalix[6]arene > *p*-*tert*-butylcalix[8]arene and calix[*n*]arene > *p*-*tert*-butylcalix[*n*]arene. Furthermore, Fe^{3+} complexes of calix[*n*]arenes (**1**–**6**) are more soluble than parent calix[*n*]arenes.

Table 1. pH values of parent calix[*n*]arene, Fe^{3+} and complexes in DMF.[a]

Complex no.	Complex	Fe^{3+}	Parent calix
1	4.96	2.65	4.99
2	3.99	2.65	4.20
3	4.63	2.65	4.93
4	2.88	2.65	4.17
5	3.70	2.65	5.05
6	3.17	2.65	4.13

[a] 1×10^{-2} M solutions.

3.2. *pH values*

The present work was focused on calix[*n*]arene-Fe^{3+} complex measurements with the parent calix[*n*]arenes ($n = 4, 6, 8$) and Fe^{3+} studied. Results of the pH measurements of Fe^{3+} complexes with the parent calix[*n*]arenes are summarized in table 1.

The pH value of complex **2** in DMF is 3.99, while the pH of the 10^{-2} M calix[4]arene solution in DMF is 4.20 and the pH of 10^{-2} M Fe^{3+} solution in DMF is 2.65. The increase of pH is due to H^+ liberated after the complex formed between calix[*n*]arene and Fe^{3+} in DMF.

$$Fe^{3+} + H_nL ==== [H_{n-1}L]Fe^{2+} + H^+$$

The plot of the ratio between the amount of Fe^{3+} in aqueous phase to that in organic phase against pH was linear with a slope of one, which indicates that one proton was separated from the ligand [7].

3.3. *UV-vis and IR spectra*

The UV spectra of the complexes show that the wavelengths of maximum absorbance lie at 280 and 288 nm, which are also observable for the corresponding ligands. At 280 and 288 nm, the molar absorption coefficients $\varepsilon_{\max}$ of complexes **1**–**6** are approximately $1.0 \times 10^5\,\mathrm{mol^{-1}\,dm^2}$. The relative intensities of the peaks keep the same order as that of the ligands. Sc(III) Eu^{3+} and Tb^{3+} complexes with calix[*n*]arenes have a low energy ligand-to-metal charge-transfer (LMCT) absorption besides those at 280 and 288 nm [19].

We determined the ratio of calix[4]arene and Fe^{3+} ion in the complex by the continuous variation plots method. The complex of calix[4]arene and Fe^{3+} has its maximum absorbance at $[(FeCl_3/calix{+}FeCl_3)] = 0.50$. The results show that calix[*n*]arene-Fe^{3+} complexes **1**, **2**, **3** and **4** form a 1 : 1 complex with Fe^{3+} [7].

The UV spectrum of calix[8]arene in DMF did not exhibit an absorption maximum above 300 nm, while the absorption maximum of its Fe^{3+} complexes **5** and **6** appeared at 534 nm. The ligand/metal ratio determined at this wavelength by the Job method was 1 : 2.

IR spectra of the complexes show changing intensities or wavenumbers of the stretching vibration of the OH groups from breaking of the especially strong

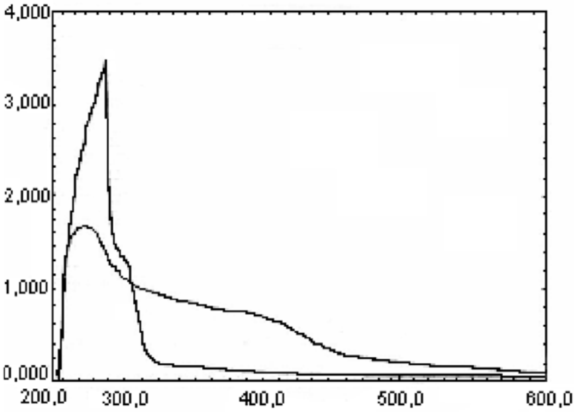

Figure 1. The UV-vis absorption spectra of calix[4]arene and its complex **2**.

intramolecular hydrogen bonding existing in the free ligands [1]. For instance, in the case of **1**, υ(OH) is shifted by $13\,\mathrm{cm^{-1}}$ from 3221 to $3234\,\mathrm{cm^{-1}}$. The changes in the υ(OH) absorbance indicate that some hydroxy groups are deprotonated and coordinated to Fe^{3+} ions. The shift of the carbonyl band υ(C=O) from $1652\,\mathrm{cm^{-1}}$ for the free amide to $1654\,\mathrm{cm^{-1}}$ for the complex [20] indicates the bonding interactions between Fe^{3+} and DMF molecules can be identified by the wavenumber shift of υ(OH). For the six complexes, $\upsilon(\mathrm{OH}) = 3221\,\mathrm{cm^{-1}}$ (**1**), $\upsilon(\mathrm{OH}) = 3234\,\mathrm{cm^{-1}}$ (**2**); $\upsilon(\mathrm{OH}) = 3332\,\mathrm{cm^{-1}}$ (**3**), $\upsilon(\mathrm{OH}) = 3236\,\mathrm{cm^{-1}}$ (**4**), $\upsilon(\mathrm{OH}) = 3237\,\mathrm{cm^{-1}}$ (**5**); $\upsilon(\mathrm{OH}) = 3318\,\mathrm{cm^{-1}}$ (**6**). The medium or weak peaks at ca $3318–3237\,\mathrm{cm^{-1}}$ are assigned to un-coordinate H_2O molecules [21].

Analysis of FTIR spectrum of complexes **2, 4** and **6** (figure 2) provide information on the molecular form of building units in complexes **2, 4** and **6**. The characteristic absorption bands of carbonyl groups of DMF have been observed at lower wavenumbers (1686 and $1631\,\mathrm{cm^{-1}}$) than in pure DMF (1717 and $1667\,\mathrm{cm^{-1}}$), a strong indication of N(7) deprotonated calix[*n*]arene participating in hydrogen bonds, i.e. calix[*n*]arene anion is present in the crystal lattice as previously observed in calix[*n*]arene-complexes [22] and complexes of calix[*n*]arene ion [23]. The characteristic absorption band of amide groups (–CON–) occurs at $3430\,\mathrm{cm^{-1}}$ showing that both hydroxyl groups of calix[*n*]arene are deprotonated and these amide groups take part in quite strong H-bonds as found for *N*,*N*-dimethylamide with calix[*n*]arene [24].

3.4. ^{1}H-NMR spectra

The solution behavior of the complexes was determined by ^{1}H-NMR spectroscopy in DMSO at room temperature. In the spectra of **1**, **3** and **5**, one singlet for protons of $-C(CH_3)_3$ and two pairs of doublets for methylene protons are observed at chemical shifts of $\delta = 3.50$ and 4.30 ppm, respectively; singlet resonances of Ar–H are observed at $\delta = 6.70$ and 7.15 ppm. For Ar–OH these resonances are at $\delta = 8.10$ and 8.90 ppm, respectively. The ^{1}H-NMR spectra of **1**, **3** and **5** are similar to the corresponding ligands, indicating that the complexes may dissociate into free ligands in DMF;

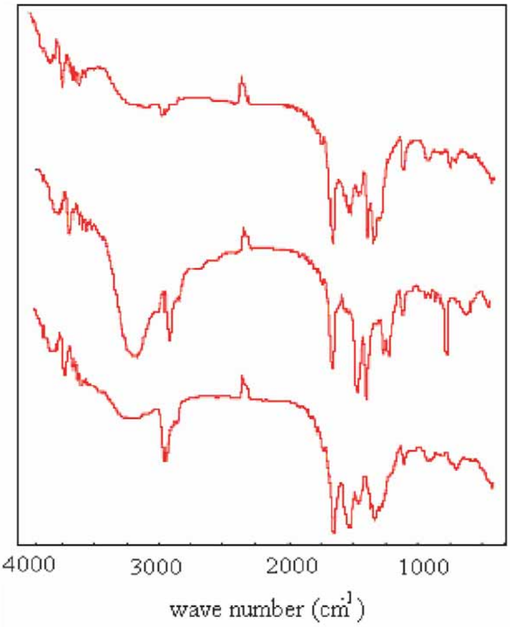

Figure 2. The FTIR spectra of complexes **2**, **4** and **6**.

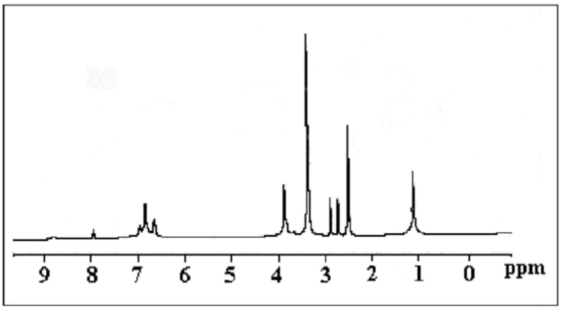

Figure 3. ^{1}H-NMR spectra of complex **3**.

however, **1** and **2** are more stable than **3**, **4**, **5** and **6**. Dissociation for Fe^{3+}-calix[*n*]arene ($n = 4, 6, 8$) complexes in different solvents [2] was observed. The ^{1}H-NMR spectra of **3** (figure 2) show that the resonances for protons of –$C(CH_3)_3$, Ar–H and Ar–OH split into doublets at $\delta = 1.10$ and 1.20 ppm, $\delta = 6.70$ and 7.15 ppm, $\delta = 8.10$ and 8.90 ppm, respectively. Further splitting of the resonances of doublets for methylene protons, which are located at $\delta = 2.80$ and 3.10 ppm, respectively, are uncertain. Such splitting, which also occured in the ^{1}H-NMR spectrum of [(calix[8]arene-6H)2Fe · 4(DMF)] in C_6D_6 [2], is characteristic of the symmetry of calix[8]arenes from free to bonded. From the resonance for methylene protons it appears that a partial *cone* conformation is adopted by the calix[6]arene ligand [25, 26]. For all six complexes, three chemical shifts related to DMF molecules are observed at $\delta = 3.90$ and 4.15 ppm, respectively,

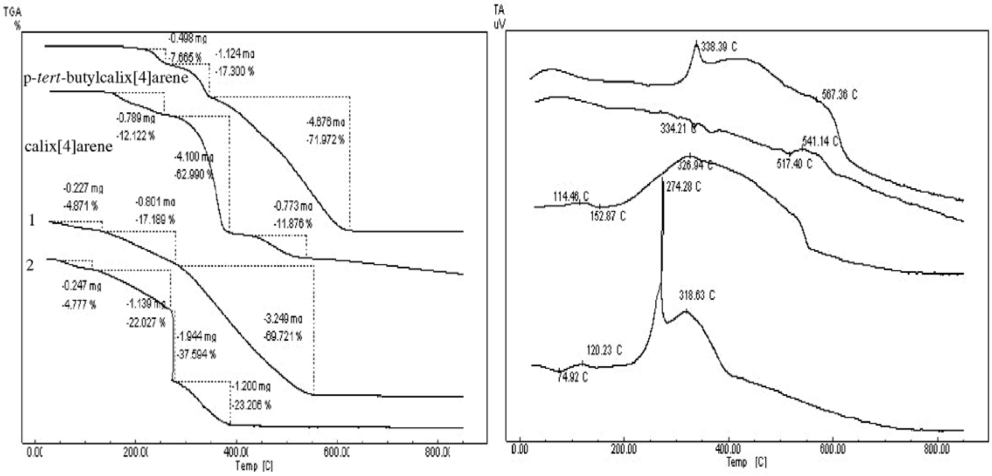

Figure 4. The TG and DTA curves of parent calix[4]arenes and their complexes **1**, **2** in nitrogen atmosphere.

indicating DMF in these complexes. Furthermore, the proton NMR spectrum of complex **3** shows weak, paramagnetically shifted signals at $\delta = 2.40$ and 3.30 ppm, which are assigned to the protons of DMSO and H_2O.

After careful comparison with the stoichiometry and properties of the calix[*n*]arene-Fe^{3+} complexes, it is concluded that calix[*n*]arenes do not exhibit the same complexation tendency toward Ln^{3+} as toward Fe^{3+}.

3.5. *Thermogravimetric analyses*

The prepared complexes were placed into dried Schlenk tubes under nitrogen and heated to the desired temperature. As in previous studies [19–21], no degradation takes place until 200°C. Above this temperature thermal degradation of the complex occurs.

The TG and DTA curves of the calix[4]arenes and their complexes **1**, **2** in flowing nitrogen atmosphere are shown in figure 4. The oxidative degradation for the complexes occurs at lower temperature than for the calix[4]arene. Decomposition of these compounds occurs in three steps. First, H_2O was released from the lattice compounds in an endothermic step which begins decomposition of complex. Second, DMF was released from the lattice and this step was also endothermic; in order to confirm this result, the complexes have been analysed by TGA analysis. The DTG curve shows decomposition of complex is at 420°C. Then the biggest decomposition occurs. Complex residues are Fe_2O_3 but the ligands did not have a residue product. For complexes this step was exothermic due to calix[4]arene · Fe which is intermediate product is not stable. From figure 4 we can say ligands thermal stabilities are higher than the complexes.

The TG-DTA curves of complex **1**, show two DMF molecules (17.2%) in the range 137–279°C, accompanied by a weak endothermic reaction; initiating decomposition. In the decomposition process, a medium strong exothermic peak occurs between

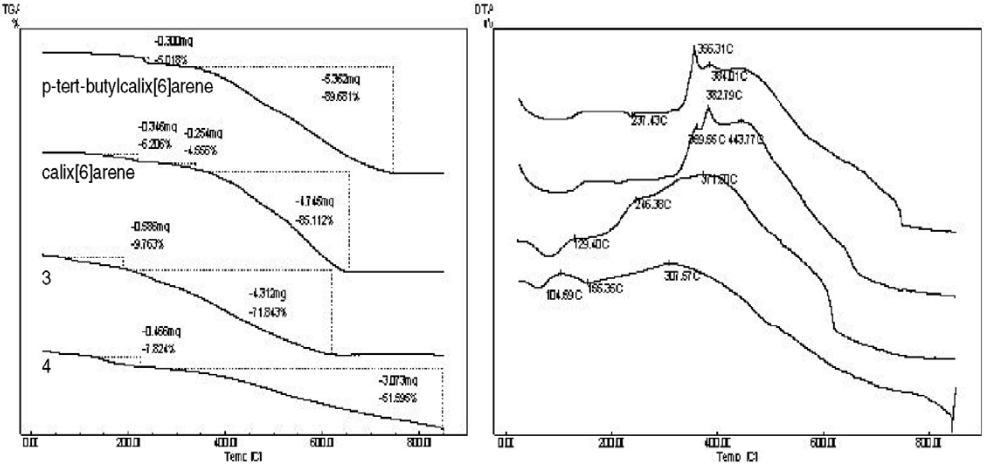

Figure 5. The TG and DTA curves of parent calix[6]arenes and their complexes **3**, **4** in nitrogen atmosphere.

285–554°C. For complex **2**, dehydration occurred between 48 and 114°C and two DMF molecules (22.0%) were lost in the range 118–270°C. The decomposition process ends at 588.8°C.

Figure 5 shows TG and DTA curves of calix[6]arenes and their complexes **3**, **4** in flowing nitrogen. These complexes lose two DMF molecules in the range 57–224°C and then gradually lose two more DMF molecules. For this decomposition step $\mathrm{DTA}_{\max}$ values are 129.4–155.4°C (8.8%), respectively. After this stage the unstable calix[6]arene $\cdot$ Fe decomposes to Fe_2O_3 in a medium strong exothermic peak. Complete decomposition of all complexes result in Fe_2O_3.

The fully deprotonated form of the parent calix[*n*]arenes act as tetra-, hexa- and octa anionic ligands and almost exclusively assume the conformation in metalla-calix[*n*]arenes, which keeps the set of the oxygen donor atoms quasi-planar. The charge of the O_n set can be tuned by etherification or esterification of the *lower rim* of the calix[*n*]arene.

Figure 6 shows TG and DTA curves of **5** and **6** measured simultaneously in flowing nitrogen atmosphere. Decomposition of calix[*n*]arene-Fe^{3+} occurs in two steps. The last decomposition gives a medium strong exothermic peak. For this peak, $\mathrm{DTA}_{\max}$ values are 302.78–313.40°C. Between 35 and 150°C, DMF is released from the lattice and a two-fold molar amount of DMF is left behind. The studies reported here give insight into the structural changes occurring as calix[*n*]arene-Fe^{3+} complexes **1**–**6** are decomposed with DMF.

Thermoanalytical results from TG-DTA and DTG curves of all complexes were illustrated in table 2.

4. Conclusion

Thermal analyses suggest that the decompositions of [calix[*n*]areneFe $\cdot$ 2(DMF)] $\cdot$ H_2O occur in several steps before reaching stable intermediate species (figures 4, 5 and 6,

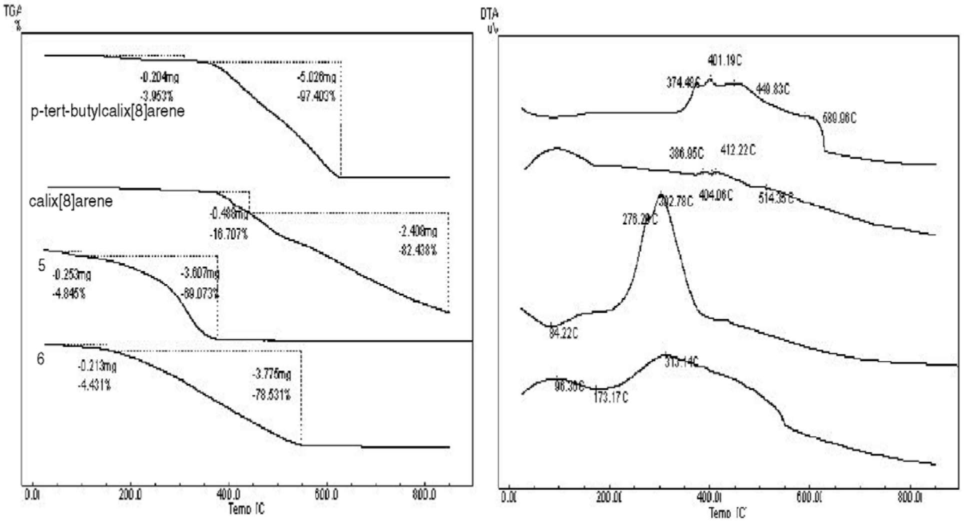

Figure 6. The TG and DTA curves of parent calix[8]arenes and their complexes **5**, **6** in nitrogen atmosphere.

Table 2. The thermoanalytical results obtained from TG, DTA and DTG curves.

Complex	Stage	Temperature range (°C)	DTA_{max} (°C)
1	1	32–134	114.48
$C_{50}H_{69}N_2O_6Fe$	2	137–279	152.87
	3	285–554	326.94
2	1	48–114	74.92
$C_{34}H_{37}N_2O_6Fe$	2	118–270	120.33
	3	272–277	274.28
3	1	57–188	129.40
$C_{72}H_{97}N_2O_8Fe$	2	205–618	371.50
4	1	133–224	155.36
$C_{48}H_{49}N_2O_8Fe$	2	272–846	307.57
5	1	35–98	84.22
$C_{100}H_{138}N_4O_{12}Fe_2$	2	100–376	302.78
6	1	46–150	96.30
$C_{68}H_{74}N_4O_{12}Fe_2$	2	161–548	313.14

table 2). Therefore, the mechanism of decomposition of the iron(III) complex can be proposed to occur as follows: the first stage is the formation of [calix[*n*]areneFe $\cdot$ *n*(DMF)] by the loss of H_2O, followed by complete loss of DMF, to form the intermediate [calix[*n*]areneFe]. Finally the formation of iron(III) oxide is reached by the elimination of calix[*n*]arene. The mechanism for the thermal pyrolysis of calix[*n*]areneFe $\cdot$ 2(DMF) complex can therefore be represented as follows:

For **1** and **2**;

$$[\text{calix}[n]\text{areneFe}\cdot 2(\text{DMF})]\cdot 2H_2O \underset{-H_2O}{\overset{\Delta}{=\!=\!=}} \text{calix}[n]\text{areneFe}\cdot 2(\text{DMF})$$

$$\underset{-\text{DMF}}{\overset{\Delta}{=\!=\!=}} \text{calix}[n]\text{areneFe} \overset{\Delta}{=\!=\!=} Fe_2O_3$$

For **3** and **4**;

$$[\text{calix}[n]\text{areneFe}\cdot 2(\text{DMF})] \underset{-\text{DMF}}{\overset{\Delta}{=\!=\!=}} \text{calix}[n]\text{areneFe} \overset{\Delta}{=\!=\!=} \text{Fe}_2\text{O}_3$$

For **5** and **6**;

$$[\text{calix}[n]\text{arene2Fe}\cdot 4(\text{DMF})] \underset{-\text{DMF}}{\overset{\Delta}{=\!=\!=}} \text{calix}[n]\text{arene2Fe} \overset{\Delta}{=\!=\!=} \text{Fe}_2\text{O}_3$$

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