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Synthesis and characterization of scandium(III) complexes with *p*-tert-butylcalix[*n*]arenes ($n=4,6,8$)

Yoshitaka Masuda[a,*], Yawen Zhang[a], Chunhua Yan[b], Biaoguo Li[b]

[a]*Division of Science of Materials, The Graduate School of Science and Technology, Kobe University, Rokkodai, Nada-ku, Kobe 657, Japan*
[b]*State Key Laboratory of Rare Earth Materials, Chemistry and Application, Peking University, Beijing 100871, People's Republic of China*

Abstract

Three new Sc^{3+}–calix[*n*]arene ($n=4,6,8$) complexes (**1**) [Sc(*p*-tert-butylcalix[4]arene-3H)$_2$(DMF)$_x$](2−*x*)DMF·ClO_4, (**2**) [Sc(*p*-tert-butylcalix[6]arene-4H)(DMF)$_x$](3−*x*)DMF·ClO_4 and (**3**) [Sc(*p*-tert-butylcalix[8]aren-7H)(DMF)$_6$]·$(ClO_4)_2$ were synthesized in a DMF solution of $Sc(ClO_4)_3$. The properties and coordination characteristics of the three calixarene compounds were determined by elemental analyses, TG-DTA, electric conductance measurements, UV, FT-IR and ^{1}H-NMR spectroscopy. According to FT-IR analysis, in the three complexes the scandium ion is coordinated by oxygen donor atoms from calixarene ligands and DMF molecules. The complexes behave as 1:1 and 1:2 electrolytes in the case of calix[*n*]arene ($n=4,6$) and calix[8]arene, respectively, and the limiting molar conductances of **1**, **2** and **3** are 105.9, 32.3 and 74.5 S cm^2 mol^{-1}, respectively. ^{1}H-NMR studies demonstrate that **2** is more stable than **1** and **3** in $CDCl_3$, and are indicative of partial cone conformation of the calix[6]arene ligand. © 1998 Elsevier Science S.A.

Keywords: *p*-t-Butylcalix[*n*]arenes ($n=4,6,8$); Conductivity measurements; FT-IR; ^{1}H-NMR spectroscopy; Scandium; Thermal analysis

1. Introduction

In the past decade, calixarene complexability and extraction selectivity towards rare earths has been demonstrated to be highly correlated with the fit between the cation and the cavity size and the conformational functional groups [1–4]. In contrast to studies of lanthanide–calixarene complexes [5–13], Sc^{3+}–calixarene complexes have rarely been synthesized and characterized, therefore calixarene complexability with Sc^{3+} and the coordination features of Sc^{3+}–calixarene complexes are unknown. In 1995, the first X-ray structure of an oxa-calix[3]arene Sc^{3+} complex was reported [14]. It showed that the Sc^{3+} complex has a structure with coordination number 6 and, according to NMR studies, displays temperature-dependent dynamic behavior. Despite the trivalency of Sc^{3+} and Ln^{3+}, the ionic radius of the former is smaller than that of the latter, however the radius of the former is closer to that of the smallest lanthanide Lu^{3+}. In 1991, the crystal structure of Lu^{3+}–*p*-t-butylcalix[8]arene was published by Harrowfield et al. [15], demonstrating that Lu^{3+} was 8-coordinate. In this work, we concentrate on the complexation between Sc^{3+} and *p*-tert-butylcalix[*n*]arenes in order to extend the calixarene complexing reactions to Sc^{3+}, in an attempt to understand the important properties of Sc^{3+}–calixarene compounds.

2. Experimental

2.1. Reagents and preparation

Scandium oxide (99.5%) was used to prepare scandium perchlorate DMF solution. *p*-tert-butylcalix[4]arene, *p*-tert-butylcalix[6]arene and *p*-tert-butylcalix[8]arene (purity >95%) were purchased from Aldrich and used without further purification. Other reagents were all of extra purity.

A slurry of 1.0 mmol *p*-tert-butylcalix[*n*]arene in 15 ml DMF was heated to 60°C and triethylamine (0.3 g) was added dropwise until a clear and colorless solution was formed in nitrogen atmosphere. $Sc(ClO_4)_3$·6DMF (1.0 mmol) solution was quickly mixed with the ligand solution. A white precipitate formed quickly or after a few days at room temperature. The product was filtered, washed twice with 2 ml DMF, and dried by vacuum desiccation.

The percentage of scandium in the complex was determined by complexometry after decomposition.

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*Corresponding author.

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*2.1.1. [Sc(p-tert-butylcalix[4]arene-3H)$_2$·(DMF)$_x$]·(2−x)DMF·ClO$_4$ (**1**)*

Found: C, 72.00%; H, 8.25%; N, 1.87%; Sc, 2.57%. Calc.: for $C_{94}ClH_{124}N_2O_{14}Sc$: C, 71.17%; H, 7.88%; N, 1.77%; Sc, 2.84%. Yield 74%. IR (KBr pellet): ν(O–H) 3143 (s, br); ν_{as}(C–H) 2952 (s, sh); ν_s(C–H) 2869 (m); ν(C=O) 1675 (vs); ν_s(C=C) 1604 (m); δ_{as}(C–H) 1480 (vs, sh); δ(C–H) 1356 (s); ν(C–N) 1380 (s), 1256 (m); ν_s(C–OH) 1197 (s); ν(Cl–O) 1156 (w), 1121(w), 1091 (w); δ(C–H) 872 (m), 813 (s), 778 cm^{-1} (s).

*2.1.2. [Sc(p-tert-butylcalix[6]arene-4H)·(DMF)$_x$]·(3−x)DMF·ClO$_4$ (**2**)*

Found: C, 67.83%; H, 7.91%; N, 3.59%; Sc, 3.08%. Calc.: for $C_{75}ClH_{103}N_3O_{13}Sc$: C, 67.48%; H, 7.78%; N, 3.15%; Sc, 3.37%. Yield 51%. IR (KBr pellet): ν(O–H) 3155 (s, sh); ν_{as}(C–H) 2952 (s, sh); ν_s(C–H) 2857 (m); ν(C=O) 1675 (vs, br), 1652 (vs); ν_s(C=C) 1622 (w); δ_{as}(C–H) 1480 (vs, sh); δ(C–H) 1362 (s); ν(C–N) 1386 (s), 1250 (m); ν_s(C–OH) 1197 (s); ν(Cl–O) 1114 (m), 1091(m); δ(C–H) 872 (m), 813 (s), 778 cm^{-1} (s).

*2.1.3. [Sc(p-tert-butylcalix[8]arene-7H)·(DMF)$_6$]·(ClO$_4$)$_2$ (**3**)*

Found: C, 64.70%; H, 7.90%; N, 4.06%; Sc, 2.52%. Calc.: for $C_{106}Cl_2H_{153}N_6O_{22}Sc$: C, 64.33%; H, 7.79%; N, 4.24%; Sc, 2.27%. Yield 48%. IR (KBr pellet): ν(O–H) 3221 (m, vbr); ν_{as}(C–H) 2946 (s, sh); ν_s(C–H) 2862 (m); ν(C=O) 1649 (vs, br); ν_s(C=C) 1613 (m); δ_{as}(C–H) 1483 (vs, sh); δ(C–H) 1358 (s), 1381 (s); ν(C–N) 1362 (m), 1203 (s); ν_s(C–OH) 1114 (s); ν(Cl–O) 1090 (s); δ(C–H) 870 (s), 816 (m), 781 cm^{-1} (w).

2.2. Instruments

IR spectra were recorded with a Perkin-Elmer FT-IR spectrometer (Spectrum 1000). Thermo-analytical TG-DTA curves were obtained with a Rigaku Thermo Plus DTA and TG 8120 analyzer, under air from room temperature to 700°C. Al_2O_3 was used as reference, and the temperature was increased at a rate of 10°C min^{-1}. Ultraviolet and visible absorption spectra in $CHCl_3$ were recorded using a Shimadzu self recording spectrophotometer (Model 240) with 10 mm optical path quartz cells. ^{1}H-NMR spectra were recorded on a JEOL JNM-GX 61D FT-NMR spectrometer at 400 MHz in $CDCl_3$, using TMS as internal standard. Molar conductivity in DMF was measured at a frequency of 1 kHz using a 4291A LCR meter (Yokogawa–Hewlett-Packard Co., Ltd) and a Yanagimoto cell. The cell constant was determined as 0.443 using 0.1 M and 0.01 M KCl solutions as standards at room temperature. The molar conductivities Λ of **1**, **2** and **3** in DMF at a concentration of 1.0×10^{-4} M are 71.9, 55.8, 118 S cm^2 mol^{-1}, respectively. (At 0.001 M in DMF, Λ of 1:1, 2:1, and 3:1 electrolytes is 85–100, 140–170 and 200–260 S cm^2 mol^{-1}, respectively [16]; at 1.0×10^{-4} M, Λ of 1:1 electrolytes of quaternary ammonium bromides and iodides is 75–95 S cm^2 mol^{-1} [17].)

3. Results and discussion

3.1. Solubility

The three Sc^{3+} complexes appear as amorphous white powders. Compound **1** is soluble in DMF and $CHCl_3$, **2** is soluble in hot $CHCl_3$ and DMSO, and **3** is soluble in DMSO, $CHCl_3$ and hot DMF. In DMF at room temperature, the solubility order of the three complexes is **1**>**3**≫**2**.

3.2. TG-DTA analyses

From the TG-DTA curves of **1**, it was found that it loses two DMF molecules (9.2%) in the range 199.0–221.6°C, accompanied by a weak endothermic reaction; it then begins to decompose. In the decomposition process, a medium to strong exothermic peak (232.0–405.8°C), a large multiple peak (405.8–525.3°C) and, finally, a very strong peak (525.3–660.0°C) could be observed successively. In the case of **2**, dehydration occurred between 48.1 and 72.4°C and three DMF molecules (16.42%) were lost in the range 175.4–224.3°C, at the beginning of a very large and complicated exothermic reaction. The decomposition process ends at 588.8°C. Compound **3** dehydrates in the range 49.3–95.5°C, and then gradually loses six DMF molecules (22.2%, 195.2–280.7°C), giving a medium strong exothermic peak. Decomposition is then completed through a very strong exothermic reaction within 283.7–535.0°C. After complete decomposition, all three complexes result in a white Sc_2O_3 residue.

3.3. Molar conductance measurements

The molar conductance measurements show that **1** and **2** can be regarded as 1:1 electrolytes and **3** as a 1:2 electrolyte. This suggests that the perchlorate ions should be free and located in the outer sphere of the complexes. Fig. 1 shows that the limiting conductances Λ^0 of **1**, **2** and **3** were calculated as 147.8, 74.2 and 158.3 S cm^2 mol^{-1}, respectively, by extrapolating the three straight lines plotted as Λ vs. the root of the concentration $C^{1/2}$, based on the modified Onsager limiting equation $\Lambda = \Lambda^0 - SC^{1/2}$ for low concentrations (here, S is the slope) [18]. Additionally, using the equation $\lambda_+^0 = \Lambda^0 - \lambda_-^0$, the limiting molar conductances λ_+^0 of cations of **1**, **2** and **3** were obtained to be 105.9, 32.3 and 74.5 S cm^2 mol^{-1}, respectively. For calculations in DMF solution, the value of λ_-^0 for ClO_4^- is 41.9 S cm^2 mol^{-1} at 25°C, which was computed using a dielectric constant of $\varepsilon=38.25$ and a viscosity of $\eta=0.794$ cP.

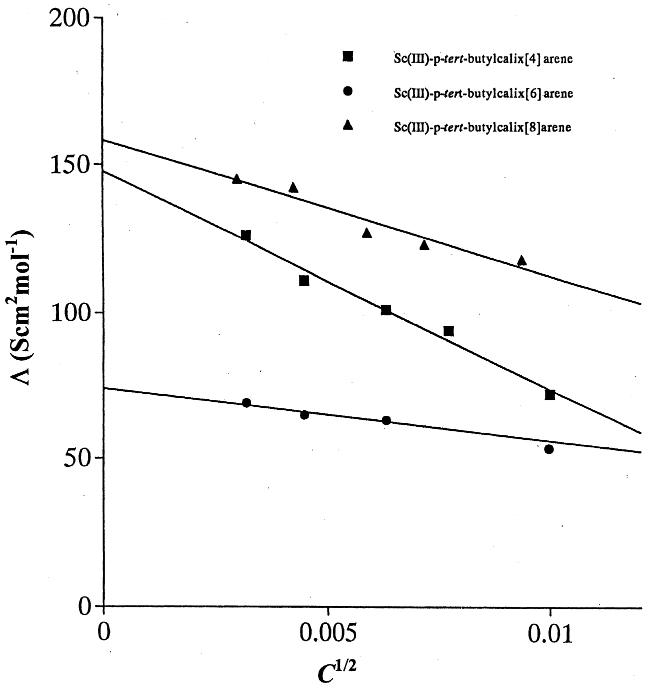

Fig. 1. Plots of molar conductance Λ (S cm^2 mol^{-1}) vs. the root of concentration $C^{1/2}$.

3.4. *UV and FT-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 nm, the molar absorption coefficients $\varepsilon_{\max}$ of **1**, **2** and **3** are 1.4×10^5, 1.3×10^5 and 1.0×10^5 mol^{-1} dm^2, respectively; at 288 nm, the $\varepsilon_{\max}$ of **1**, **2** and **3** are 1.1×10^5, 1.2×10^5 and 1.3×10^5 mol^{-1} dm^2, respectively. For **1** and **3**, the relative intensities of the two peaks keep the same order as that of the ligands. However, it is interesting and unclear why the intensity of the two peaks for **2** are reversed with respect to those of the free ligand. Compared with the Sc(III) complexes, Ln^{3+} such as Eu^{3+} and Tb^{3+} complexes with calixarenes have a low energy ligand-to-metal charge-transfer state (LMCT) absorption band [19] besides those at 280 and 288 nm.

In the IR spectra of the complexes, the intensities or wave numbers of the stretching vibration of the OH groups change drastically with complexation by breakage of the especially strong intramolecular hydrogen bonding existing in the free ligands [20]. For instance, in the case of **1**, ν(OH) is shifted by 12 cm^{-1} from 3155 to 3143 cm^{-1}. So, the changes in the ν(O–H) absorbance indicate that some hydroxide groups are deprotonated and coordinated to Sc^{3+} ions. Secondly, from the criterion of the shift of the carbonyl band ν(C=O) from 1685 cm^{-1} for the free amide to 1660 cm^{-1} for the complex [21], the bonding interactions between Sc^{3+} and DMF molecules can be identified by the wavenumber shift of ν(C=O). For the three complexes, ν(C=O) = 1675 cm^{-1} (**1**); ν(C=O) = 1675, 1652 cm^{-1} (**2**); ν(C=O) = 1649 cm^{-1} (**3**). Lastly, the medium or weak peaks which lie at ca. 1160–1090 cm^{-1} are assigned as triplets of ν_1 of perchlorate ions, revealing the existence of un-coordinate ClO_4^- in the complexes [22].

3.5. *^{1}H-NMR spectra*

The solution behavior of the complexes was determined by ^{1}H-NMR spectroscopy in $CDCl_3$ at room temperature. In the spectra of both **1** and **3**, one singlet resonance for protons of $-C(CH_3)_3$ and two pairs of doublets for methylene protons are observed at chemical shifts of δ = 1.25, 3.5 and 4.3 ppm, respectively. For **1** and **3**, singlet resonances of Ar–H are observed at δ = 7.05 and 7.18 ppm, respectively; for Ar–OH these resonances are at δ = 10.3 and 9.6 ppm, respectively. Indeed, the ^{1}H-NMR spectra of **1** and **3** are similar to the those of the corresponding ligands, which reveals that the complexes probably dissociate into free ligands in $CDCl_3$. However, **2** is more stable than **1** and **3** in this polar solvent. The above dissociation phenomenon was ever observed for Ln^{III}–calix[*n*]arene (n = 4,6,8) complexes in different solvents [23]. The ^{1}H-NMR spectra of **2** (Fig. 2) shows that the resonances for protons of $-C(CH_3)_3$, Ar–H and Ar–OH split into two peaks at δ = 1.25 and 1.21 ppm, δ = 7.05 and 7.14 ppm, and δ = 10.3 and 10.5 ppm, respectively. Further splitting of the resonances of doublets for methylene protons, which are located at δ = 3.5 and 4.3 ppm, respectively, are uncertain. Peak splitting, which also occurred in the ^{1}H-NMR spectrum of [Y_2(calix[8]arene-6H)·$(DMF)_n$] in C_6D_6 [23], is characteristic of the variation of the symmetry of calix[6]arene ligands from free to bonded. Additionally, from the features of the peak for methylene protons it appears that a partial cone conformation is adopted by the calix[6]arene ligand [24,25]. Lastly, for the three complexes, three chemical shifts related to DMF molecules are observed at δ = 2.88, 2.95 and 8.01 ppm, respectively, suggestive of the involvement of DMF molecules in these complexes.

After careful comparison with the stoichiometry and properties of the previously studied Ln^{3+}–calixarene complexes, it is concluded that the above calixarenes do not exhibit the same complexation tendency toward Sc^{3+} as toward Ln^{3+}.

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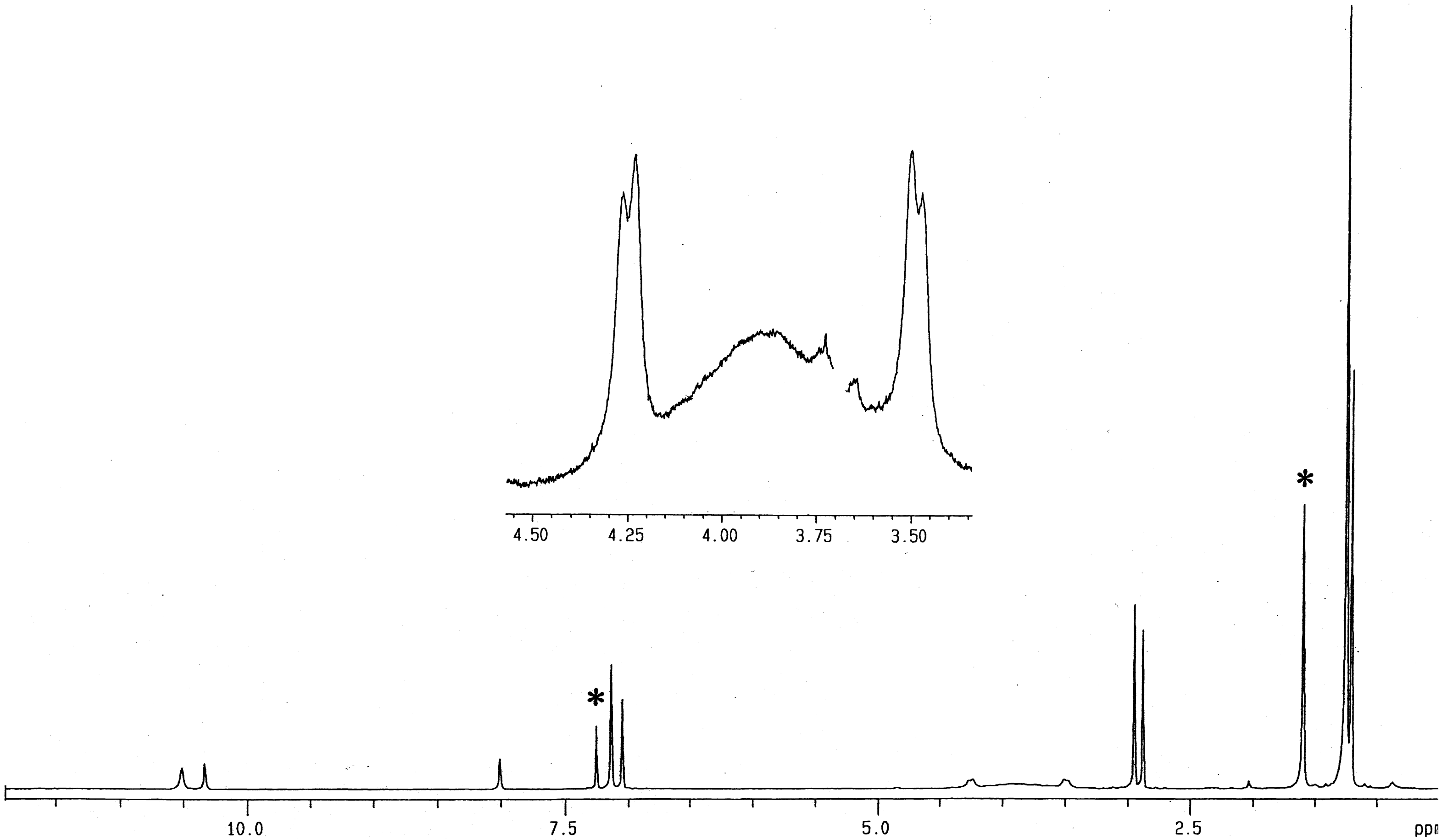

Fig. 2. ^{1}H-NMR spectrum of [Sc(*p*-tert-butylcalix[6]arene-4H)·$(DMF)_x$]·$(3-x)$DMF·ClO_4 at 25°C in $CDCl_3$ (TMS as internal standard). Asterisks indicate protio solvent and water.

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