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Alkali-Metalated Forms of Thiacalix[4]arenes

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The alkali metal salts [TCALi_4] (**1**), [TCANa_4] (**2**), and [TCAK_4] (**3**) of fully deprotonated *p-tert*-butyltetrathiacalix[4]arene (H_4TCA) are readily available from the reactions of thiacalix[4]arene and *n*-BuLi, NaH, or KH as deprotonating reagents. Crystals of the sodium salts **2** and the potassium salt **3** suitable for X-ray diffraction were obtained in the form of the pyridine solvates [$(TCA)_2Na_8$·8py] (**2**·8py) and [$(TCA)_2K_8$·8py] (**3**·8py). These molecules are dimers in the solid state but are structurally not related. In addition, the reaction of H_4TCA and lithium hydroxide afforded the structurally characterized complex [(TCA)Li_5(OH)·4THF] (**4**). The molecular structure of **4** as well as the structures of **2**·8py and **3**·8py reveal a close relationship to the corresponding alkali metal salts of the calix[4]arenes.

Introduction

One reason for the interest in the chemistry of calix[*n*]arenes is the utility of these polyphenols and derivatives as metal-ion-complexing agents. These molecules have a number of attractive properties, which leads to their application in supramolecular chemistry, in selective metal coordination, as catalysts and sensors, or as models for simulating catalytic oxide surfaces.[1−3] One of the simplest variations that have already been made on the basic calixarene structure to control and enhance metal-ion binding has been the substitution of sulfur atoms for the bridging methylene groups, as in *p-tert*-butyltetrathiacalix[4]arene (H_4TCA),[4] for example. Compared to the related *p-tert*-butylcalix[4]arene (H_4Calix), the chemistry of thiacalixarenes is recent, as the synthesis of thiacalixarenes and their sulfinyl and sulfonyl derivatives has been known only since the late 1990s.[5] Recent publications provide evidence that the thiaether units of H_4TCA take part in metal-ion coordination, which leads to a stronger interaction with transition metals compared to that found in H_4-Calix. This was structurally demonstrated, for example, for the TCA complexes of Co,[6g,h] Ni,[6g] Cu,[6e] Zn,[6h,i], Rh,[6j] Ir,[6j] U,[6k] and Nd.[6l]

The introduction of calix[*n*]arenes as ancillary ligands into organometallic chemistry is often achieved through the reaction of alkali metal calix[*n*]arenes with anhydrous metal halides in a metathesis-type reaction. Therefore, interactions with alkali metal ions have been intensively investigated for the calix[4]arene systems. The first alkali metal (cesium) complex of the monoanion of H_4Calix was published by Harrowfield and co-workers in 1991,[7a] and a number of other alkali metal complexes with partially deprotonated calix[4]arenes have been synthesized.[7] Alkali metal complexes with fully deprotonated calix[4]arenes are also known. The first compound of this type, a lithium complex, was described

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by Davidson et al. in 1997.[8a] In subsequent works, Floriani and co-workers[8b] and Fromm and co-workers[8c] achieved the preparation and structural characterization of polymetalated alkali metal complexes with Li, Na, and K. Furthermore, the syntheses and structures of alkali metal complexes of fully deprotonated calix[4]arene mono- and dialkyl ethers have been published.[9]

Surprisingly little is known about alkali metal salts of thiacalix[4]arenes. Harrowfield et al. described partially deprotonated thiacalixarene complexes of the metals lithium to cesium.[10a] They succeeded in determining the crystal structures of complexes of the alkali metal ions with, in the case of Li, the dianion and, in the cases of Na to Cs, the monoanion of *p-tert*-butyltetrathiacalix[4]arene. For these complexes, both the sulfur atoms, which form part of the macrocyclic ring, and the pendent phenolic/phenoxide oxygen donor atoms are involved in coordination to the metal atoms. Just recently, Walther et al. reported on reactions of H_4Calix and H_4TCA with sodium hydride in the presence of 18-crown-6. In the case of the thiacalix[4]arene, the complex $[Na(18\text{-crown-6})(dmf)_{1.5}]_2[(TCA)_2Na_6(dmf)_2]$ was structurally characterized, which contains a highly symmetrical dianion $[(TCA)_2Na_6(dmf)_2]^{2-}$ and two crown-ether-stabilized cations $[Na(18\text{-crown-6})(dmf)_{1.5}]^+$.[10b]

Herein, we report the synthesis and molecular structures of new polymetalated lithium, sodium, and potassium thiacalix[4]arene complexes, which might be useful starting materials for the synthesis of organometallic thiacalix[4]arene complexes.

Results

As mentioned above, Harrowfield et al. succeeded in the partial deprotonation of thiacalix[4]arene H_4TCA using triethylamine or potassium hydroxide as a base. The acidities of the phenolic OH groups in macrocycles such as calix[*n*]-arenes in their differently deprotonated forms, which are of importance for selective and full deprotonations, are determined by the system of intramolecular hydrogen bonds.[1] Determinations of the acidity constants performed on different calixarenes have shown a systematic increase of the pK_a value with increasing degree of deprotonation, as expected. For future work on the preparation of TCA transition-metal complexes, we were interested in achieving and verifying a full deprotonation of H_4TCA with commonly used strong bases and in characterizing the resulting materials. In our hands, H_4TCA was most easily converted to its tetraanion using *n*-BuLi, NaH, or KH in toluene or THF solution to afford the compounds $[TCALi_4]$ (1), $[TCANa_4]$ (**2**), or $[TCAK_4]$ (**3**) as colorless solids. The solubility of the alkali metal salts in THF increases significantly in the series from the lithium to the sodium and then the potassium salt. Whereas the lithium salt is insoluble in THF (as well as in halogenated and nonpolar solvents), the solubility of complex **2** in THF is sufficient to obtain a proton NMR spectrum, and that of compound **3** is sufficient to obtain proton as well as carbon NMR spectra. Additional solvent molecules (see below), either coordinated at the alkali metal or not, can be removed in vacuo at higher temperatures, and the compositions of solvent-free **1**−**3** were confirmed by elemental analyses. In the IR spectra of these complexes, no resonances for O−H vibrations were observed, indicating a complete deprotonation of the thiacalix[4]arene. The ^{1}H NMR spectra of compounds **2** and **3** in THF-d_8 are similar to the spectrum of H_4TCA, with a resonance for the protons of the *tert*-butyl groups at 1.30 ppm (**2**) or 1.17 ppm (**3**) and a singlet for the protons in the meta position of the aromatic rings at 7.54 ppm (**2**) or 7.30 ppm (**3**). A resonance for OH protons was not detected. The ^{13}C NMR spectrum of **3** also reveals the signal pattern typically found for a molecule of pseudo-C_{4v} symmetry: a resonance at 31.2 ppm for the *tert*-butyl methyl carbon atoms; a resonance at 34.21 ppm for the *tert*-butyl quartery carbon atoms; and a set of signals for the phenolate ring carbon atoms at 126.49, 131.61, 133.07, and 169.00 ppm.

Despite several attempts to crystallize complex **1** in donor solvents, we could not obtain good-quality crystals of solvate complexes of this compound. In one case, however, we isolated crystals of the complex $[(TCA)Li_5(OH)\cdot 4THF]$ (**4**) (see Figure 1), which is apparently the reaction product of H_4TCA with decomposition products of *n*-butyllithium employed for the deprotonation reaction. Compound **4** was then prepared independently from the reaction of H_4TCA with lithium hydroxide hydrate in THF. In the IR spectrum of this complex, a weak but sharp resonance for the O−H vibration was detected at 3622 cm^{-1}, indicating an isolated hydroxyl group. Crystals suitable for X-ray diffraction of this complex were obtained from saturated THF solutions.

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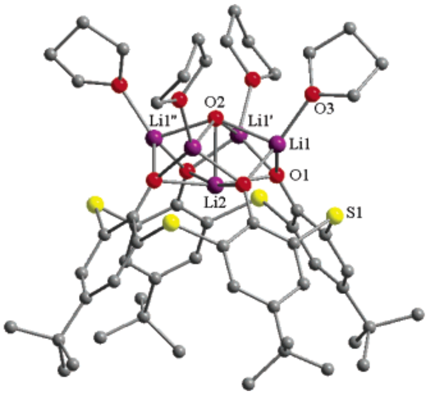

Figure 1. Molecular structure of [(TCA)Li$_5$(OH)·4THF] (**4**) in the solid state. Additional solvent molecules and H atoms have been omitted for clarity. Selected bond lengths (pm) and angles (deg): Li(1)−Li(1′), 285.0(7); Li(1′)−S(1), 285.5(5); Li(1)−Li(2), 242.6(7); Li(1′)−O(1), 193.0(5); Li(1)−O(1), 192.2(5); Li(2)−O(1), 208.0(2); Li(1)−O(2), 213.5(5); Li(2)−O(2), 205.5(10); Li(1)−O(3), 196.7(5); Li(1′)−Li(1)−Li(1‴), 90.0; O(1)−Li(2)−O(1″), 167.6(5); O(1)−Li(1)−O(2), 85.6(2); Li(1)−O(1)−Li(1′), 95.4(3); O(1)−Li(1)−O(3), 129.5(3); Li(1)−O(1)−Li(2), 74.5(2); O(3)−Li(1)−O(2), 106.7(2); Li(1′)−O(1)−Li(2), 74.3(2); Li(1)−Li(2)−Li(1′), 71.9(2); Li(1)−O(2)−Li(1′), 83.74(9); Li(1)−Li(2)−Li(1″), 112.3(4); Li(1)−O(2)−Li(1″), 141.4(3); O(1)−Li(2)−O(1′), 89.33(5); Li(1)−O(2)−Li(2), 70.72(15).

The molecular structure of **4**, including important bond lengths and angles, is depicted in Figure 1.

[(TCA)Li$_5$(OH)·4THF] (**4**) crystallizes in the tetragonal space group *P*4/*n* with two molecular units and four THF molecules in the elemental cell. A crystallographically imposed 4-fold axis runs through the molecule along the Li(2)−O(2) vector, i.e., the thiacalix[4]arene crystallizes in a perfect cone conformation adopting C_{4v} symmetry. The lithium atom Li(2) lies 22.8 pm below the plane spanned by the phenolate oxygen atoms O(1) and symmetry equivalents; 112.2 pm above this plane are the lithium atoms Li(1) to Li(1‴). These four coplanar metal atoms form a square with sides of length 285.0(7) pm. Each of these lithium atoms is coordinated to an additional THF ligand. Together, the lithium atoms Li(1) and Li(2) form a square pyramid, which is bridged at each triangular side with the phenolate oxygen atom O(1) and at the square with a hydroxyl group containing O(2). The observed lithium−oxygen distances in **4** range from 192.2(5) pm observed for Li(1)−O(1) to 213.5(5) pm observed for Li(1)−O(2). Interestingly, the distance Li(2)−O(2) of 205.5(10) pm is significantly shorter than the Li(1)−O(2) bond length, which implies a bonding interaction of the oxygen atom O(2) with all lithium atoms of the molecule. Thus, the structure of **4** can be regarded as a result of the incorporation of LiOH into the Li$_4$TCA moiety. The same structural motif has been found for the calix[4]arene lithium salt [(Calix)Li$_5$(OH)·4HMPTA],[8a] in which HMPTA ligands (HMPTA = hexamethyl phosphoric acid trisamide) act as neutral donors to saturate the lithium atoms. The distance of the endohedrally coordinated lithium atom [Li(2)] to the oxygen atom of the hydroxyl group [O(2)], however, is approximately 20 pm (10%) larger in the calix[4]arene complex [225(1) pm] than in **4** [205.5(10) pm].

Crystals of the sodium salt [TCANa$_4$] (**2**) suitable for X-ray diffraction were obtained in the form of the pyridine solvate [(TCA)$_2$Na$_8$·8py] (**2**·8py) from hot saturated solutions of **2** in pyridine. The molecular structure of **2**·8py, including important bond lengths and angles, is depicted in Figure 2.

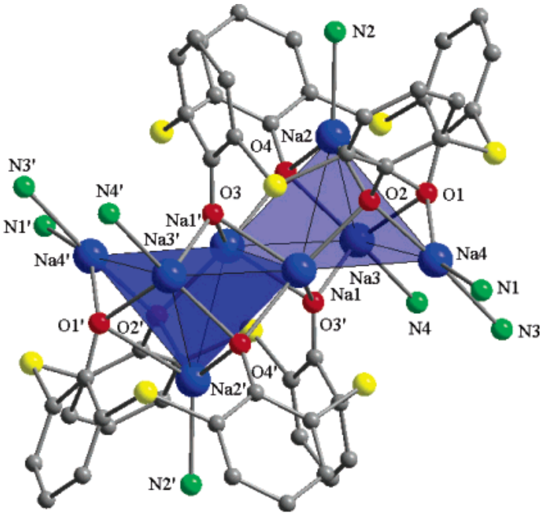

Figure 2. Molecular structure of [(TCA)$_2$Na$_8$·8py] (**2**·8py) in the solid state. The pyridine ligands are represented by the coordinating nitrogen atoms (green). Additional solvent molecules, H atoms, and TCA *tert*-butyl groups have been omitted for clarity. Selected bond lengths (pm) and angles (deg): Na(1)−O(2), 225.2(3); Na(2)−C(40′), 282.5(4); Na(1)−O(3), 238.0(3); Na(2)−N(2), 242.2(4); Na(1)−O(3′), 232.3(3); Na(3)−O(1), 223.9(3); Na(1)−O(4), 223.8(3); Na(3)−O(3′), 239.0(3); Na(2)−O(1), 277.8(3); Na(3)−O(4′), 230.4(3); Na(2)−C(10), 273.1(3); Na(3)−N(4), 245.5(3); Na(2)−O(2), 226.2(3); Na(4)−O(1), 229.5(3); Na(2)−C(20), 285.0(3); Na(4)−O(2), 228.5(3); Na(2)−C(30), 308.9(4); Na(4)−N(1), 251.3(4); Na(2)−O(4′), 228.5(3); Na(4)−N(3), 243.4(4); Na(1′)−Na(1)−Na(4), 103.44(6); Na(3)−Na(2)−Na(1), 73.59(5); Na(1′)−Na(1)−Na(3′), 81.03(6); Na(3)−Na(2)−Na(1′), 53.36(5); Na(3′)−Na(1)−Na(2), 113.56(6); Na(1′)−Na(2)−Na(4), 86.30(6); Na(3′)−Na(1)−Na(4), 174.83(6); O(2)−Na(2)−N(2), 120.66(12); Na(1)−Na(2)−Na(1′), 52.36(5); O(4′)−Na(2)−N(2), 120.07(12); Na(1)−Na(2)−Na(4), 54.14(4); O(2)−Na(2)−O(4′), 118.98(11).

Compound **2** is a dimeric molecule in the solid state. It crystallizes as **2**·8py in the triclinic space group $P\bar{1}$ with four additional pyridine molecules in the elemental cell. The sodium atoms of this compound form two edge-sharing distorted square pyramids, the apexes of which point inside the cavity of each thiacalix[4]arene ligand (see polyhedral representation in Figure 2). The square planes of the pyramids containing the atoms Na(1), Na(1)′, Na(3), and Na(4) as well as Na(1), Na(1)′, Na(3′), and Na(4′) share the edge Na(1)−Na(1)′ and are connected at an angle of 2.45(2)°. The internuclear distances of the sodium atoms are in the range between 314.4(3) pm [Na(1)−Na(1′)] and 340.8(2) pm [Na(3)−Na(4)]. Three of the triangular faces and three sodium atoms of the square plane are capped by the oxygen atoms O(1) to O(4) with sodium oxygen bond lengths in a range between 223.9(3) and 239.0(2) pm. Additionally, each of the sodium atoms Na(1), Na(2), and Na(4) have two contacts to the sulfur atoms of the thiacalix[4]arene with distances between 296.1(2) and 339.2 pm. Furthermore, Na(3) is coordinated to one and Na(4) to two pyridine ligands to reach 6-fold, distorted octahedral coordination. Sodium atom Na(2) is located within the thiacalix[4]arene cavity and coordinated to O(1), O(2), and O(4) with distances of 277.8(3), 226.3(2), and 228.5(3) pm, respectively, and to the nitrogen atom N(2) of an endohedrally positioned pyridine molecule. This atom is also involved in an interaction with the π-system of the phenolate rings, as indicated by the

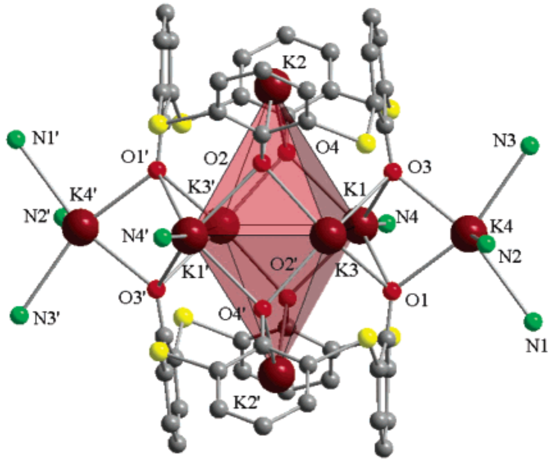

Figure 3. Molecular structure of [(TCA)$_2$K$_8$·8py] (**3**·8py) in the solid state. The pyridine ligands are represented by the coordinating nitrogen atoms (green). Additional solvent molecules, H atoms, and TCA *tert*-butyl groups have been omitted for clarity. Selected bond lengths (pm) and angles (deg): K(1)−O, 273.4(3)−282.4(3); K(4)−O(3), 264.6(3); K(1)−N(4), 298.4(4); K(4)−N(2), 282.7(4); K(2)−O(2), 267.0(3); K(4)−N(3′), 289.1(5); K(2)−O(4′), 269.5(3); K(4)−N(1), 290.8(6); K(2)−C, 308.8(4)−320.7(4); K(4)−C(62), 384.6(1); K(3)−O, 264.6(3)−270.2(3); K(4)−C(63), 366.4(1); K(4)−O(1), 263.1(3); K(4)−C(64), 377.2(1); N(4)−K(1)−K(3′), 113.25(9); O(2)−K(2)−O(4′), 90.05(7); N(4)−K(1)−K(4), 118.46(9); K(1)−K(3)−K(4), 64.73(3); K(3′)−K(1)−K(4), 128.22(3); K(1′)−K(3)−K(4), 177.54(4); N(4)−K(1)−K(3), 176.44(9); O(1)−K(4)−O(3), 74.37(8); K(3)−K(1)−K(3′), 67.12(3).

Na−C distances in the range between 273.1(3) and 363.4(1) pm, The structure obtained for **2**·8py is thus similar to the molecular structure of [(Calix)$_2$Li$_8$·4HMPTA],[8a] but different from the structure observed for the analogous calix[4]arene compound [(Calix)$_2$Na$_8$·8Py][8b] (see below).

Crystals of [TCAK$_4$] (**3**) suitable for X-ray diffraction were obtained in the form of the pyridine solvate [(TCA)$_2$K$_8$·8py] (**3**·8py) from hot saturated solutions of **3** in pyridine or in the form of [(TCA)$_2$K$_8$·10THF] (**3**·10THF) from hot saturated solutions of **3** in THF. Unfortunately, **3**·10THF readily loses solvent molecules even at low temperatures, so we have currently obtained only a limited data set of this complex. These preliminary X-ray analyses reveal that the arrangement of the central [(TCA)$_2$K$_8$] entity is the same in the THF adduct as observed for **3**·8py.

Compound **3**·8py also crystallizes as a dimeric molecule in the centrosymmetric space group $P\bar{1}$ with one formula unit and three additional pyridine solvent molecules in the elemental cell. The crystallographically imposed center of inversion lies in the center of the dimer. The molecular structure, including selected bond lengths and angles, is depicted in Figure 3. Eight potassium atoms in **3**·8py are coordinated to two TCA ligands, which adopt a cone conformation. The atoms K(1), K(3), K(1′), and K(3′) form a square, which is completed to a distorted octahedron by the endohedrally coordinated metal atoms K(2) and K(2′) (see polyhedral representation in Figure 3). The remaining potassium atoms K(4) and K(4′) are located within the plane of the square and are in an almost ideal linear alignment with the atoms K(1′) and K(3) [angle K(1′)−K(3)−K(4) = 177.54(4)°].

The polyhedron at K(1) is best described as a square pyramid, spanned by the four oxygen donor atoms O(1) to O(4) of two thiacalix[4]arene ligands and the pyridine nitrogen atom N(4), whereas K(3) is square-planar coordinated with four oxygen atoms of two thiacalix[4]arene ligands. The environment at K(2) can be regarded as distorted tetrahedral, coordinated by the oxygen atoms O(2) and O(4) and the π-systems of the phenolate units at O(1) and O(3′). The distances of K(2) to the carbon atoms of these rings lie in a range between 308.8(4) pm [K(2)−C(11)] and 348.15(4) pm [K(2)−C(15)]. The angle at K(2) to the centers of these rings is 161.4(1)°. The coordination polyhedron at K(4) is also a distorted square pyramid, in which the basal positions are occupied by O(3), O(1), N(3), and N(1) and the apical position by N(2). The sum of the angles within the basal plane is 359.6°, which allows a description of the coordination polyhedron at K(4) as an octahedron minus one ligand. A closer inspection of the packing of the molecules reveals that this coordination site is occupied by the π-system of a neighboring pyridine ligand (see Figure 4). The intermolecular distances observed for the pyridine carbon atoms C(62), C(64), and C(63) to K(4) are 384.58(5), 377.14(5), and 366.37(4) pm, respectively, and are in accordance with a weak interaction of the pyridine ligand with the potassium atom.

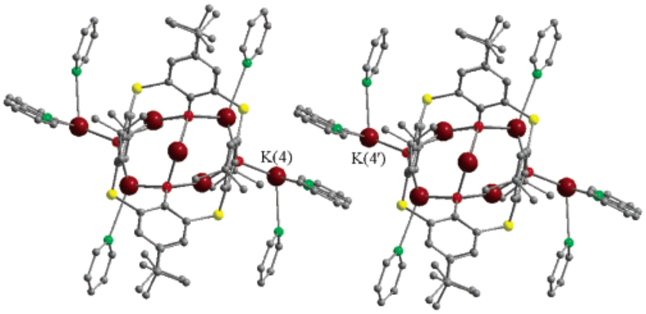

Figure 4. Arrangement of two molecules of [(TCA)$_2$K$_8$·8py] in the solid state.

Discussion

The thiacalix[4]arene alkali metal salts synthesized in this work have a structural relationship with the alkali metal salts of the corresponding calix[4]arenes. The structure found for [(TCA)Li$_5$(OH)·4THF] (**4**) closely resembles the structure of [(Calix)Li$_5$(OH)·4HMPTA] published by Davidson and co-workers.[8a] In this compound, the lithium atoms also build a capped square pyramid at the lower rim of a calix[4]arene ligand, but the lithium atoms are coordinatively saturated by HMPTA ligands.

The structural motifs found for the rest of the TCA metal salts are similar to the structures determined for the corresponding calix[4]arene complexes, but analogous structures were observed for the corresponding higher congener of the alkali metal in the case of the TCA complexes. The pyridine-stabilized thiacalix[4]arene sodium salt **2**·8py, for example, is structurally related to the known lithium salt [(Calix)$_2$Li$_8$·4HMPTA].[8a] In these compounds, the metal atoms arrange in the form of two trans-configured, edge-sharing distorted square pyramids embedded between two calix[4]arene tetra-anions (see Figure 5). The number of additional neutral

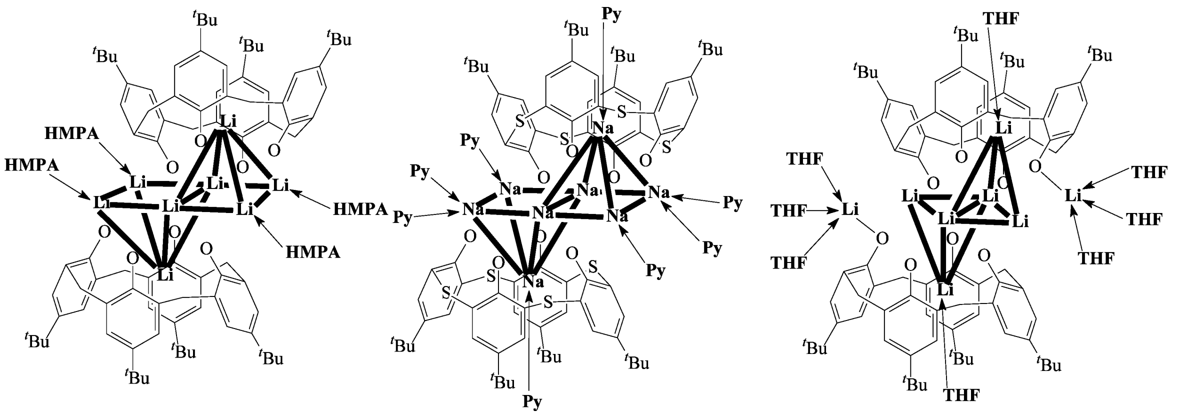

Figure 5. Comparison of the central cluster cores in [(Calix)$_2$Li$_8$·4HMPTA] (left), [(TCA)$_2$Na$_8$·8py] (**2**·8py) (middle), and [(Calix)$_2$Li$_8$·8THF] (right).

donor ligands is different according to the different sizes of the ionic radii of the metal atoms employed. Furthermore, an additional donor molecule is coordinated in **2**·8py to the endohedrally located sodium atom, which is presumably prevented in the case of the calix[4]arene lithium compound by the smaller ring size of the calix[4]arene ring and the bulkiness of the HMPTA ligand.

The connectivity of the metal atoms in molecular structures of lithium salts of calix[4]arenes reported so far depends, however, on the nature of the neutral donor ligand. Fromm et al. published the X-ray crystal structure of [(Calix)$_2$Li$_8$·8THF]·6THF, in which eight lithium atoms are also coordinated by two fully deprotonated calix[4]arene ligands. In this case, the metal core consists of two edge-sharing, trans-connected tetrahedrons, the apexes of which point into the centers of the two calix[4]arene ligands (see Figure 5, right side). These lithium atoms in apical positions are endohedrally coordinated by THF ligands. Two lithium atoms that are not involved in this central cluster unit are bound to one oxygen donor atom of the calix[4]arene ligand and to three THF ligands. With respect to the arrangement of the metal atoms and the ligands, complex **2**·8py might be regarded as an intermediate structure between the complexes [(Calix)$_2$Li$_8$·4HMPTA] and [(Calix)$_2$Li$_8$·8THF]. The structural motif found for the potassium salt [(TCA)$_2$K$_8$·8py] closely resembles the arrangements observed for [(Calix)$_2$Na$_8$·8py][8b] and [Calix$_2$K$_8$·10THF].[8c] A similar structural motif was published only recently by Walther and co-workers for a thiacalix[4]arene-based system.[10b] In the ionic compound [(TCA)$_2$Na$_6$]$^{2-}$2[(dmf)$_{1.5}$Na(18-Krone-6)]$^+$, six sodium atoms form an octahedron that is sandwiched by two TCA ligands. In these cases, however, no interaction between the endohedrally coordinated metal atoms and the π-system of the phenolate rings was observed.

Conclusion

The reaction of *p*-*tert*-butyltetrathiacalix[4]arene H$_4$TCA and *n*-BuLi, NaH, or KH as a deprotonating reagent affords the alkali metal salts [TCALi$_4$] (**1**), [TCANa$_4$] (**2**), and [TCAK$_4$] (**3**) of the fully deprotonated thiacalix[4]arene. In addition, the reaction of H$_4$TCA and lithium hydroxide gives the structurally characterized complex [(TCA)Li$_5$(OH)·4THF] (**4**) in good yields. The molecular structure of **4** as well as the structures of the pyridine adducts of **2** and **3**, [(TCA)$_2$Na$_8$·8py] and [(TCA)$_2$K$_8$·8py] reveal a close relationship to the corresponding alkali metal salts of the calix[4]arenes.

Experimental Section

General Considerations. All reactions and subsequent manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. Elemental analyses were performed in the microanalytical laboratory of the authors' department. NMR spectra were recorded on Bruker AMX 300 and Bruker AV 400 spectrometers at 298 K. ^{13}C NMR spectra are broad-band proton-decoupled (^{13}C{^{1}H}). NMR data are listed in parts per million (ppm) and are reported relative to tetramethylsilane. Spectra are referenced internally to residual protio-solvent resonances (^{1}H: CDCl$_3$, 7.24 ppm; C$_6$D$_6$, 7.15 ppm; C$_4$D$_8$O, 1.72 and 3.77 ppm) or natural-abundance carbon resonances (^{13}C: CDCl$_3$, 77.0 ppm; C$_6$D$_6$, 128.0 ppm; C$_4$D$_8$O, 24.50 ppm). Infrared spectra were recorded as KBr pellets on a Bruker IFS 28 instrument and are reported in wavenumbers (cm^{-1}). H$_4$TCA was prepared according to a published procedure.[4]

Synthesis of [TCALi$_4$] (1). *n*-Butyllithium (2.50 mL of a 1.60 m solution in hexane) was added slowly at room temperature to a solution of 721 mg (1.00 mmol) H$_4$TCA. A white product precipitated immediately after addition of the first drops of *n*-BuLi. The reaction mixture was stirred for an additional 2 h at 40 °C. Afterward, the product was filtered off, washed with two portions of 5 mL of hexane, and dried vigorously in vacuo. Yield: 699 mg (0.94 mmol, 94%), colorless solid. C$_{40}$H$_{44}$S$_4$O$_4$Li$_4$ (744.8): Calcd. (found) (%): C 64.51 (64.03), H 5.95 (6.34). IR (KBr, cm^{-1}): 2960 vs br, 2873 m, 1588 w, 1462 vs br, 1386 m, 1361 m, 1311 w, 1248 vs, 1009 s br, 889 m, 833 m, 790 s, 733 m, 621 m, 548 m, 471 m.

Synthesis of [TCANa$_4$] (2). THF (200 mL) was added to a mixture of sodium hydride (520 mg, 22.0 mmol) and H$_4$TCA (3.60 g, 5.00 mmol) at room temperature. The resulting suspension was stirred at room temperature until no gas bubbles evolved and then for 4 h at 60 °C. The reaction mixture was filtered through a pad of Celite, and the resulting yellow solution was concentrated under precipitation of the product to a volume of approximately 30 mL. The colorless solid was filtered off, washed three times with THF (5 mL), and dried in vacuo at 40 °C. Yield: 3.60 g (4,45 mmol, 89%) colorless solid. Crystals suitable for X-ray diffraction were obtained in the form of the pyridine solvate [(TCA)$_2$Na$_8$·8py] (**2**·8py) from hot saturated solutions of **2** in pyridine. C$_{40}$H$_{44}$O$_4$S$_4$Na$_4$ (809.0): Calcd. (found) (%): C 59.68 (60.01), H 5.48 (6.05). IR

(KBr, cm^{-1}): 2958 vs br, 2868 s, 1776 w, 1582 m, 1433 vs br, 1387 s, 1360 s, 1298 vs, 1252 vs br, 1184 m, 1051 s, 883 s, 831 vs, 766 vs, 728 s, 634 w, 611 w, 542 m, 525 m, 398 s, 344 m. ^{1}H NMR (THF-d_8): δ 1.30 [s, 36H, C(CH_3)$_3$], 7.54 (s, 8H, aryl-H).

Synthesis of [TCAK$_4$] (3). THF (40 mL) was added to a mixture of potassium hydride (560 mg, 14.0 mmol) and H$_4$TCA (2.16 g, 3.00 mmol) at room temperature. The resulting suspension was stirred at room temperature until no gas bubbles evolved and then for 4 h at 60 °C. The reaction mixture was filtered through a pad of Celite while hot, and the resulting yellow solution was concentrated to approximately 15 mL. After the solution had been allowed to stand at room temperature for 12 h, colorless crystals precipitated that were then isolated and dried in vacuo at 60 °C. Yield: 1.43 g (1.64 mmol, 54%), colorless solid. Crystals suitable for X-ray diffraction were obtained in the form of the pyridine solvate [(TCA)$_2$K$_8$·8py] (**3**·8py) from hot saturated solutions of **3** in pyridine or in the form of [(TCA)$_2$K$_8$·10THF] (**3**·10THF) from hot saturated solutions of **3** in THF. $C_{40}H_{44}O_4S_4K_4$ (873.4): Calcd. (found) (%): C 55.0 (54.99), H 5.08 (5.08). IR (KBr, cm^{-1}): 2958 vs br, 2866 s, 1579 s, 1446 vs br, 1386 s, 1359 s, 1319 vs, 1245 vs, 1174 m, 1133 w, 1048 w br, 881 s, 830 s, 764 s, 727 s, 631 w, 546 w, 525 w, 392 w, 334 m. ^{1}H NMR (THF-d_8): δ 1.17 [s, 36H, C(CH_3)$_3$], 7.30 (s, 8H, aryl-H). ^{13}C NMR (THF-d_8): δ 31.20 [s, C(CH$_3$)$_3$], 32.99 [s, C(CH$_3$)$_3$], 126.49 (s, aryl-C_o), 131.61 (s, aryl-C_m), 133.07 (s, aryl-C_p), 169.00 (s, aryl-C_i).

Synthesis of [(TCA)Li$_5$(OH)·4THF] (4). THF (40 mL) was added at room temperature to a mixture of H$_4$TCA (1.44 g, 2.00 mmol) and LiOH·H$_2$O (0.42 g, 10.0 mmol), and the resulting suspension was stirred for 10 h at 60 °C. After addition of a further 60 mL of THF, the resulting yellowish suspension was filtered at 60 °C and cooled to room temperature. Standing for a longer period of time afforded **4** in the form of almost colorless crystals, which were separated and dried in vacuo. Yield: 1.16 g (1.10 mmol, 54.9%); light yellow powder. $C_{56}H_{77}Li_5O_9S_4$ (1057.2): Calcd. (found) (%): C 63.62 (63.18), H 7.34 (7.49). IR (KBr, cm^{-1}): 3622 w ν(O−H), 2963 vs ν(C−H), 1786 w, 1588 m, 1483 vs, 1387 s, 1360 s, 1312 s, 1246 vs, 1189 s, 1043 s ν(C−O), 888 s, 836 m, 766 m, 734 m, 672 m, 622 m, 477 vs. ^{1}H NMR (THF-d_8): δ 1.14 [s, 36H, C(CH_3)$_3$], 7.44 (s, 8H, aryl-H). No resonance for the OH proton was detected.

Crystal Structure Determination of [(TCA)Li$_5$(OH)·4THF] (4), [(TCA)$_2$Na$_8$·8py] (2·8py), and [(TCA)$_2$K8·8py] (3·8py). The Supporting Information and CCDC−623501 to CCDC−623503 contain crystallographic data for the complexes prepared in this work. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax (+44) 1223-336-033 or deposit@ccdc.cam.uk].

Table 1. X-ray Data Collection and Processing Parameters

	4	**2**·8py	**3**·8py
formula	$C_{64}H_{77}Li_5O_{11}S_4$	$C_{140}H_{144}N_{12}Na_8O_8S_8$	$C_{134}H_{143}K_8N_{11}O_8S_8$
formula weight	1185.20	2563.07	2604.87
crystal system	tetragonal	triclinic	triclinic
space group	$P4/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.4487(19)	14.513(3)	13.2614(12)
b (Å)	13.4487(19)	15.335(3)	15.2201(11)
c (Å)	18.570(4)	17.759(4)	18.8693(17)
α (deg)		104.62(3)	81.046(10)
β (deg)		101.38(3)	77.249(11)
γ (deg)		110.04(3)	69.810(9)
V (Å^3)	3358.6(9)	3413.1(12)	3473.2(5)
Z	2	1	1
μ (mm^{-1})	0.107	0.216	0.223
total/indep reflns	27169/3444	16183/10554	24386/11400
observed reflns[a]	2362	7842	7441
parameters	207	766	769
final R^b, wR2^c	0.0595, 0.1480	0.0772, 0.1855	0.0552, 0.1262

[a] Reflections with $I > 2\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [d] For data with $I > 2\sigma(I)$.

Crystal data collection and processing parameters are listed in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Stoe-IPDS I image plate diffractometer (Ag Kα radiation) equipped with an FTS AirJet low-temperature device (4, **3**·8py) or to a Stoe-IPDS II image plate diffractometer (Mo Kα radiation) equipped with an Oxford Cryosystems low-temperature device (**2**·8py). Data were collected at 160 K (**2**·8py) or 203 K (**4**, **3**·8py); equivalent reflections were merged, and the images were processed with the STOE IPDS software package. Corrections for Lorentz polarization effects and absorption were performed, and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Extinction corrections were applied as required. Crystallographic calculations were performed using SHELXS-97 and SHELXL-97.[11]

For the compound **2**·8py, the calix[4]arene *tert*-butyl groups containing C(27) to C(29), were positionally disordered and were refined in an isotropic approximation with occupancy factors of 50% each. For the compound **3**·8py, the calix[4]arene *tert*-butyl groups containing C(27) to C(29) and C(37) to C(39) were positionally disordered, and the carbons were refined in an isotropic approximation with occupancy factors of 50% each. In addition, the *tert*-butyl group containing C(47) to C(49) was positionally disordered over three sites and refined in an isotropic approximation with occupancy factors of 33% each. For compound **4**, the carbon atoms C(24) to C(27) of the THF solvent molecules were positionally disordered over two sites and refined in an isotropic approximation with equal occupation factors.

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Supporting Information Available: X-ray crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC numbers for these CIFs are 623501−623503.

IC0613311

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(11) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Universität Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen, Göttingen, Germany, 1997.