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Synthesis and structural characterization of a binuclear zirconium complex of tetraanionic *p*-tert-butylthiacalix[4]arene bridged by methanol

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A BINUCLEAR ZIRCONIUM COMPLEX OF TETRAANIONIC *p*-tert-BUTYLTHIACALIX[4]ARENE BRIDGED BY METHANOL

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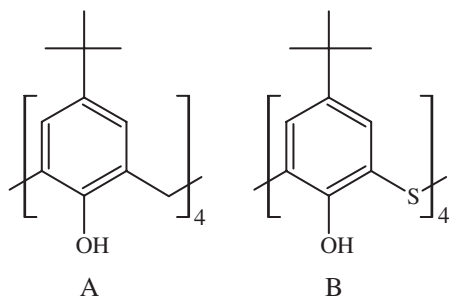
A zirconium complex with the *p*-tert-butylthiacalix[4]arene anion was synthesized and its crystal structure was determined by single-crystal X-ray analysis. The complex $[\text{Zr}(\mu_2\text{-CH}_3\text{OH})(p\text{-tert-butylthiacalix[4]arene})_2 \cdot 9\text{H}_2\text{O}$ (**1**) belongs to the orthorhombic system, space group *Pnmm*, with $a = 20.436(16)$, $b = 12.160(8)$, $c = 20.305(12)$ Å, $V = 6774(7)$ Å³ and $Z = 2$. In Complex **1** zirconium coordinates to four phenolic anions of the deprotonated *p*-tert-butylthiacalix[4]arene and is bridged by two methanol molecules; the *p*-tert-butylthiacalix[4]arene adopts a cone conformation.

Keywords: Calixarene; Binuclear; Zirconium complex; Crystal structure

INTRODUCTION

Calix[*n*]arenes are bowl-shaped macrocycles formed by phenolic oligomerization, which can be used both as building blocks and as platforms, and have a wide range of applications [1,2]. Calix[4]arenes (Scheme 1A) are the simplest and most common family, with four phenolic binding sites. Since the Atwood group reported the first structure of titanium-calixarene [3] in 1986, calixarenes have been widely used as metal ion complexing ligands because they can provide unique polyphenoxy binding sites for ions [4–7]. Many metallocalixarenes have been reported that include mononuclear and polynuclear coordination metal cores: Ti, Zr, V, Nb, Ta, Cr, Mo, W, etc. [8–31]. Recently, a new calixarene analogue, thiacalix[4]arene (Scheme 1B) was reported, in which the methylene linkage of calix[4]arene was replaced by sulfur atom bridges [32,33]. Thiacalix[4]arene shares common features with the “classical”

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SCHEME 1

calix[4]arene and has additional ligating atoms. Our attention has been focused on designing polynuclear metal complexes of thiacalix[4]arene. Here, we report a new binuclear Zr complex of tetraanionic *p*-*tert*-butylthiacalix[4]arene bridged by two methanol molecules with the *p*-*tert*-butylthiacalix[4]arene adopting a cone conformation.

EXPERIMENTAL

Materials and Methods

p-*tert*-Butylthiacalix[4]arene was prepared according to the literature method [32,33]. All commercially available chemicals were of reagent grade and were used without further purification.

C, H and N were determined using a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer using KBr pellets in the 400–4000 cm^{-1} region. ^1H NMR spectra were recorded on an Avance 500 Brüker spectrometer in CDCl_3 .

Preparation of $[\text{Zr}(\mu_2\text{-CH}_3\text{OH})(p\text{-tert-butylthiacalix[4]arene})_2 \cdot 9\text{H}_2\text{O}$ (1)

To a stirred solution of *p*-*tert*-butylthiacalix[4]arene $\cdot \text{CHCl}_3$ (0.084 g, 0.10 mmol) in 20 mL of CHCl_3 was added three drops of $\text{N}(\text{C}_2\text{H}_5)_3$. The mixture was stirred for 2 h before a solution of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.027 g, 0.10 mmol) in 20 mL of CH_3OH was added. The reaction mixture was stirred at room temperature for 4 h and under reflux for 6 h. The resulting mixture was cooled to room temperature, and the residue removed by filtration. Large colorless crystals were obtained from the solution by slow evaporation for several days. Elemental analysis was carried out on this compound ($M_r = 1842.65$). Anal. Calcd. for $\text{C}_{82}\text{H}_{114}\text{O}_{19}\text{S}_8\text{Zr}_2$ (%): C, 55.06; H, 6.09. Found: C, 55.06; H, 6.38. ^1H NMR, δ (ppm): 7.63 (8H, s, Ar-H), 5.39 (1H, q, CH_3OH), 3.55–3.56 (3H, d, CH_3OH), 1.23 (36H, s, CH_3). IR (KBr) ν_{max} 3442($\nu\text{-H}_2\text{O}$), 2962($\nu\text{-CH}_3$), 1262($\pi\text{-H}_2\text{O}$), 1559, 1476, 1442, 1393, 1360, 856, 832, 761, 736 cm^{-1} .

X-ray Crystallography

X-ray measurements were performed at 293(2) K on a SMART 1000CCD single-crystal diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Crystallographic data and details of the structure refinement are listed in Table I.

TABLE I Summary of data collection and crystal parameters

Empirical formula	C ₈₂ H ₁₁₄ O ₁₉ S ₈ Zr ₂
Formula weight	1842.65
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, <i>Pnmm</i>
Unit cell dimensions	$a = 27.436(16)$ Å, $\alpha = 90^\circ$ $b = 12.160(8)$ Å, $\beta = 90^\circ$ $c = 20.305(12)$ Å, $\gamma = 90^\circ$
Volume	6774(7) Å ³
Z, Calculated density	2, 0.903 g cm ⁻³
Absorption coefficient	0.320 mm ⁻¹
<i>F</i> (000)	1932
Crystal size	0.30 × 0.25 × 0.20 mm
θ range for data collection	3.10–23.37°
Limiting indices	$-22 \leq h \leq 30$, $-13 \leq k \leq 13$, $-21 \leq l \leq 22$
Reflections collected/unique	21 452/4827 [<i>R</i> (int) = 0.1018]
Max. and min. transmission	0.9288 and 0.9102
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	0.998
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0734, <i>wR</i> 2 = 0.1857
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1310, <i>wR</i> 2 = 0.2356

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Zr(1)–O(1)	1.989(4)	O(1C)–Zr(1)–O(1)	104.7(3)
Zr(1)–O(2)	2.112(4)	O(1C)–Zr(1)–O(2)	84.77(17)
Zr(1)–O(3)	2.156(3)	O(1)–Zr(1)–O(2)	85.89(17)
Zr(1)–Zr(1A)	3.539(3)	O(2)–Zr(1)–O(2C)	164.7(2)
S(1)–C(2)	1.790(7)	O(1C)–Zr(1)–O(3)	92.83(18)
S(1)–C(16C)	1.793(7)	O(1)–Zr(1)–O(3)	162.47(18)
S(2)–C(6)	1.776(8)	O(2)–Zr(1)–O(3)	95.4(2)
S(2)–C(12)	1.796(7)	O(2C)–Zr(1)–O(3)	97.2(2)
O(1)–C(1)	1.335(7)	O(1C)–Zr(1)–O(3A)	162.47(18)
O(2)–C(11)	1.345(7)	O(3)–Zr(1)–O(3A)	69.7(2)
O(3)–C(21)	1.448(12)	O(1)–Zr(1)–Zr(1A)	127.66(14)
		O(2)–Zr(1)–Zr(1A)	97.65(11)
		O(3)–Zr(1)–Zr(1A)	34.83(12)
		C(2)–S(1)–C(16C)	105.4(3)
		C(6)–S(2)–C(12)	105.7(3)
		C(21)–O(3)–Zr(1)	124.83(12)
		Zr(1)–O(3)–Zr(1A)	110.3(2)

Symmetry transformations used to generate equivalent atoms are A: $-x, -y, -z$; C: $-x, -y, z$.

The structure was solved by direct methods and refined by full-matrix least-square techniques on *F*² using the SHELXL-97 program [34]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms of *p*-*tert*-thiacalix[4]arene were located on calculated positions and assigned isotropic displacement parameters; other hydrogen atoms were not located. Selected bond lengths and angles are listed in Table II. Other crystallographic data are available as supplementary material.

RESULTS AND DISCUSSION

X-ray crystallographic analysis shows that the title complex consists of two coordinated zirconium ions, two *p*-*tert*-butylthiacalix[4]arene anions (L⁴), two bridging methanol

molecules and some crystal water molecules. The molecular structure of the binuclear complex **1** with D_{2h} symmetry is shown in Fig. 1.

In the complex, the tetradentate ligand L^{4-} adopted a cone conformation and coordinated to zirconium via the four phenoxy oxygen atoms. The four aromatic rings A [C(1)–C(6)], B [C(7)–C(12)], C [C(1C)–C(6C)] and D [C(7C)–C(12C)] constitute the walls of the cavity (Fig. 2), with the A and C rings pushed outward and the B and D

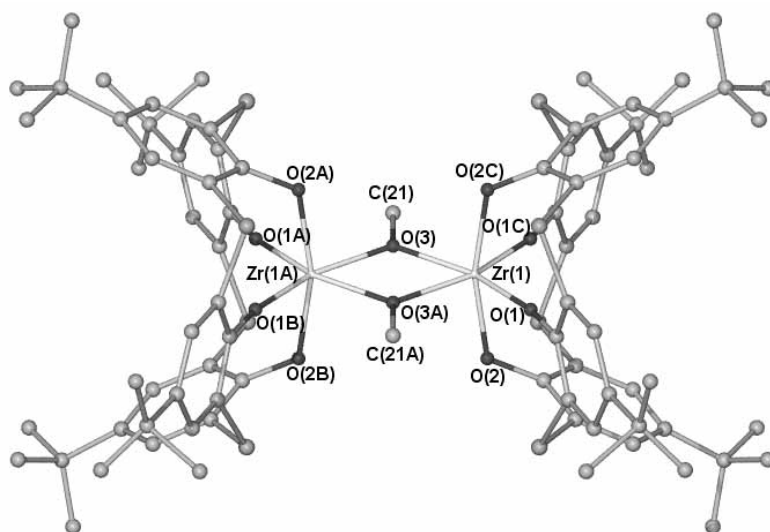


FIGURE 1 Molecular structure of **1**. H atoms and water molecules are omitted for clarity. Primed atoms were generated using the symmetry transformations A: $-x, -y, -z$; B: $x, y, -z$; C: $-x, -y, z$.

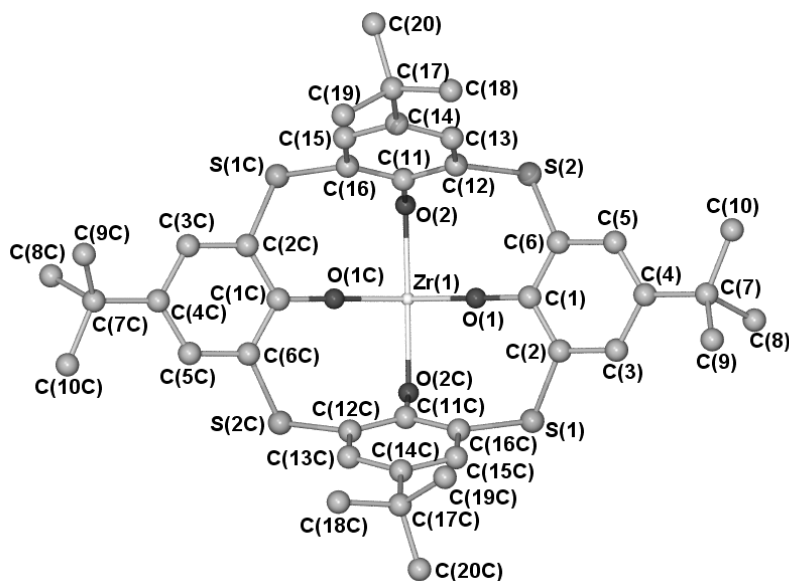


FIGURE 2 Top view of **1**. The calix unit adopts the cone conformation. H atoms are omitted for clarity. Primed atoms were generated using the symmetry transformation C: $-x, -y, z$.

TABLE III Conformational parameters within the thiacalix[4]arene

Dihedral angles ($^{\circ}$) between planar moieties	
$E\omega A$	156.4
$E\omega B$	115.0
$E\omega C$	156.4
$E\omega D$	115.0
$A\omega C$	132.8
$B\omega D$	49.9
$A\omega B$	112.9
Contact distances (\AA) between <i>para</i> -carbon atoms of opposite aromatic rings	
$C(4)\cdots C(4C)$	10.795
$C(14)\cdots C(14C)$	7.705

E: reference plane refers to the least-squares mean plan defined by the S(1), S(2), S(1C), S(2C) bridging sulfur atoms.

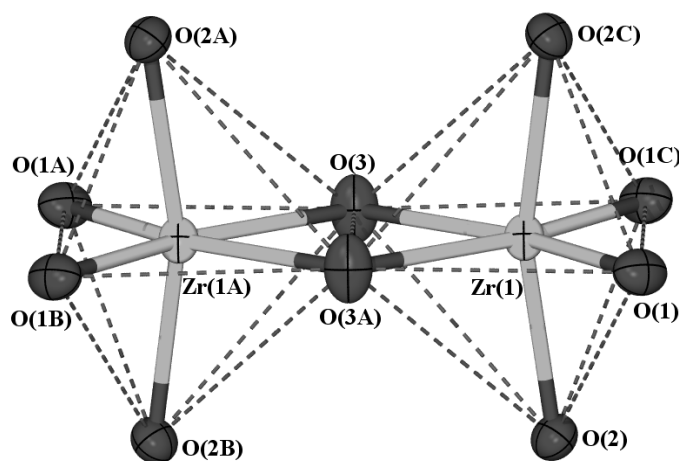


FIGURE 3 An ORTEP view of the coordination polyhedron of Zr^{4+} , showing the atom labeling scheme and thermal ellipsoids drawn at the 35% probability level. Primed atoms were generated using the symmetry transformations A: $-x, -y, -z$; B: $x, y, -z$; C: $-x, -y, z$.

rings inward to the cavity, as indicated by the dihedral angles they form with the “reference plane” (Table III) [12,13].

Figure 3 shows the distorted octahedral coordination around each zirconium ion, formed by the four phenoxy oxygen atoms of the ligand L^{4-} and two μ_2 -bridging methanolic oxygen atoms. As a consequence of six-coordination of the metal, the planarity of the O_4 core is completely removed, and the best coordination plane is defined by O(1), O(1C), O(3) and O(3A) atoms. The bond distances in the metal coordination sphere are almost symmetrical, with values of 1.989(4) \AA for Zr(1)–O(1) and Zr(1)–O(1C), 2.156(3) \AA for Zr(1)–O(3) and Zr(1)–O(3A), and 2.112(4) \AA for Zr(1)–O(2) and Zr(1)–O(2C). The two zirconium ions lie on the C_2 symmetry axis, and the Zr(1)–Zr(1A) distance is 3.539(3) \AA .

Figure 4 is a molecular packing diagram for Complex 1. In the crystal, the adjacent calixarene molecules are arranged parallel along the c axis and also head-to-head and tail-to-tail along the b axis. The calixarene molecules are stacked in this way so that

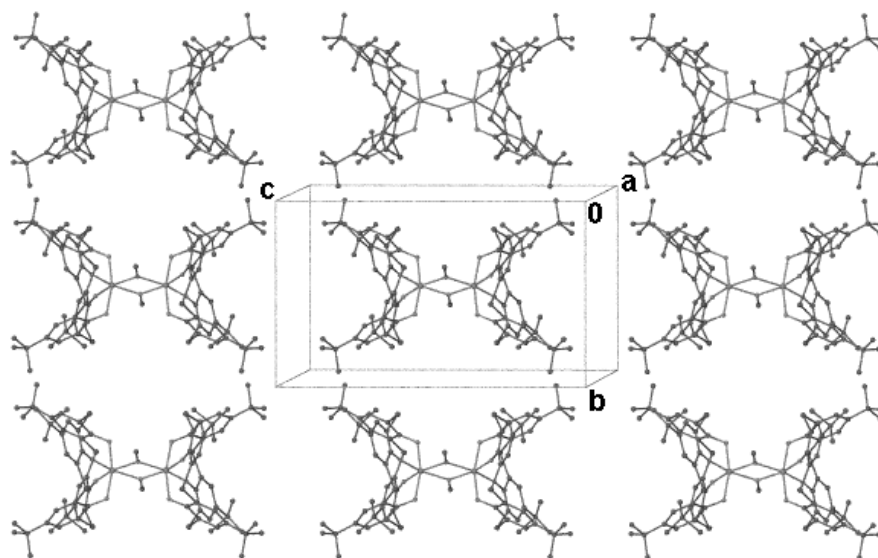


FIGURE 4 Crystal packing of **1** viewed along *a* axis. H atoms and water molecules were omitted for clarity.

channels can be constructed along the *a* axis. There is a $13 \times 10 \text{ \AA}$ cavity formed by two facing *p*-*tert*-butylthiacalix[4]arene molecules and it unexpectedly remained totally unoccupied. Although many neutral molecules including chloroform and methanol can be included in the cavity of *p*-*tert*-butylthiacalix[4]arene, the inclusion ability of *p*-*tert*-butylthiacalix[4]arene for the neutral molecule guests is not strong enough for a stable inclusion compound to be formed under the reaction conditions. The title compound was formed at reflux and the volatile methanol and chloroform solvent molecules must have escaped from the *p*-*tert*-butylthiacalix[4]arene cavity during formation of the title complex.

Acknowledgments

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218212. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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