



Communication

Formation of a novel hexanuclear Zr^{IV} cage compound with bridging chelating ligand: [(CpZr)₆(μ-O₂C-C₆H₂Cl₂-2-O)₉(OH₂)₃]·H₂O

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ABSTRACT

The reaction of Cp₂ZrCl₂ with 3,5-dichlorosalicylic acid in a CH₂Cl₂–Et₂O system containing HCl (1.0 mol L⁻¹), gives a cage half-sandwich cyclopentadienyl–zirconocene compound, [(CpZr)₆(μ-O₂C-C₆H₂Cl₂-2-O)₉(OH₂)₃]·H₂O (**1**). The crystal structure of **1** shows a twisted tripyramidal prism cage structure with one water molecule in the cage's cavity. In the cage, the dianionic, substituted salicylate ligands adopt a bridging chelate μ₂-(O, O', O'') coordination mode.

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1. Introduction

Organometallic cage compounds have received considerable attention because of their special structures and properties such as host–guest inclusion and catalysis [1]. We are particularly interested in organozirconium compounds that are known as catalysts in polymerization, hydrogenation, isomerization and selective oxidation reactions [2]. Generally, the synthesis of organozirconium cage compounds is carried out with anhydrous organic solvents and under anaerobic conditions or hydrolysis of zirconocene compounds, and a variety of interesting frameworks, in which Zr^{IV} is known to exist in the forms of trinuclear, tetranuclear, hexanuclear, non-nuclear and decanuclear species, have been prepared by these ways [3]. In addition, because of a great range of coordination modes of substituted salicylate acids, the metal–salicylate compounds have been found to display a great deal of diversity in their structural nature [4]. In this paper, one such new organozirconium cage compound (**1**) has been prepared in a two-phase media, using the multifunctional substituted salicylic acid as the ligand (Scheme 1).

2. Results and discussion

In the presence of hydrochloric acid solution (1.0 mol L⁻¹), which inhibited the deephydrolysis of “Cp₂Zr” species in aqueous system

[5], compound **1** was obtained by the reaction of Cp₂ZrCl₂ with 3,5-dichlorosalicylic acid in the CH₂Cl₂–Et₂O system at room temperature and in good yield. Compound **1**, the pale yellow needle-shaped crystals were found stable when exposed to air and suitable single crystals for X-ray diffraction were obtained from CH₂Cl₂–Et₂O/hexane solution. The IR spectrum shows the broad bands around 3430 cm⁻¹ due to the O–H stretching mode and suggests the presence of water molecules in the compound. Typical absorptions for cyclopentadienyl rings are seen in **1** at 3082 cm⁻¹, 1453 cm⁻¹, 1020 cm⁻¹ and 808 cm⁻¹ [6]. The breathing modes seen at 1597 cm⁻¹ and 1502 cm⁻¹ are phenyl rings. The carboxylate modes in **1** present two strong bands assigned to ν_{asym}(CO₂⁻) (1561 cm⁻¹) and ν_{sym}(CO₂⁻) (1381 cm⁻¹). The Δν_{asym–sym} value (180 cm⁻¹) is less than 200 cm⁻¹ suggests bidentate carboxylate coordinate mode with Zr atoms [7,8], which is further confirmed by the X-ray analysis.

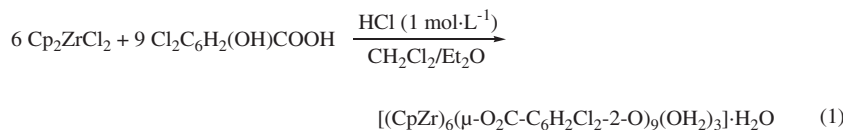
The ¹H NMR spectrum of compound **1** exhibits two sets of resonance signals for the Cp ring and the phenyl ring protons (the integrate of which is a ratio of 5:3), which are also consistent with its solid-state structure.

Compound **1** crystallizes in the Monoclinic space group C2/c; the structure with the atom numbering scheme is shown in Fig. 1 and a view down the c axis in Fig. 2. In **1**, the 3,5-dichlorosalicylate ligand shows the flexibility, as previously observed with other salicylate ligands. Salicylic acid and its derivatives are versatile ligands exhibiting a number of coordination modes, such as chelate (O,O'), bridging μ₂-(O',O''), bridging chelate μ₂-(O,O',O''), doubly bridging chelate μ₃-(O,O,O',O''), triply bridging chelate μ₃-(O,O,O',O',O'') [4a]. The deprotonated, dianionic 3,5-dichlorosalicylic acid adopts a less common bridging chelate μ₂-(O,O',O'')

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Scheme 1.

coordination mode in **1**, which is particularly rare in Group 4 compounds [4a]. In addition, compound **1** contains six cyclopentadienyl–zirconium fragments, held together by nine 3,5-dichlorosalicylate bridging ligands to form a “nanoscopic” cage, and the six metal atoms adopt a trigonal antiprismatic geometry.

The molecule has approximate C_3 symmetry. The triangles formed by the zirconium atoms Zr1Zr2Zr3 and Zr4Zr5Zr6 are nearly equilateral and a pseudo C_3 axis penetrates these two triangles. Furthermore, the CpZr4, CpZr5 and CpZr6 fragments form a propeller-like arrangement and the other cyclopentadienyl groups bound to Zr1, Zr2 and Zr3 are near coplanar, and parallel to the plane that formed by three Zr atoms to which they are bounded. The angles in the quadrangles formed by the Zr atoms in **1** vary from 73.05° to 99.72° . The Zr...Zr lengths, which are not bonded, range from 5.759 Å to 6.141 Å (av 5.947 Å), almost twice as long as those exhibited in $\{[(\text{EtMe}_4\text{C}_5)\text{Zr}]_6(\mu_6\text{-O})(\mu_3\text{-O})_8\} \cdot (\text{C}_7\text{H}_8)$ (3.1542 (9)–3.1709 (11) Å, av 3.1635 Å) [3f], amido-imidonitrido zirconium compounds [9] and the zirconium halide clusters [10–12].

Selected bond lengths and angles for **1** are listed in Table 1. All of the salicylate ligands chelate one Zr atom with one carboxyl O atom and a phenoxy O atom, and bind a different Zr atom with the remaining carboxylate oxygen. The Zr– $\mu\text{-OOC}$ distances range from 2.076(6) Å to 2.255(6) Å, because of the different coordination sphere of the metal atoms. The Zr–OPh bond lengths are in the range of 2.018(5)–2.074(6) Å and the average Zr–OH₂ bond lengths in

compound **1** is 2.243(6) Å (Table 1), is marginally longer than those in $[(\text{LOEt})_4\text{Zr}_4(\mu_3\text{-O})_2(\mu\text{-OH})_4(\text{H}_2\text{O})_2][\text{NO}_3]_4$ (av. 2.207(7) Å) [3e].

Of the nine substituted salicylate ligands, six of which form bridges within each triangle of the trigonal antiprism and another three, link the two triangles. The three bridging Zr1, Zr2 and Zr3 have their phenyl groups (C2–C7, C9–C14 and C23–C28) nearly parallel to the plane defined by those zirconium atoms. In contrast, the three linking to Zr4, Zr5 and Zr6 have their rings (C44–C49, C51–C56 and C58–C63) oriented nearly perpendicular to the plane of the Zr atoms. Those three ligands containing C16–C21, C30–C35 and C37–C42 bridge the two triangles, and the planes of those phenyl rings are nearly parallel to the pseudo C_3 axis.

Molecule **1** contains four water molecules, three coordinated to Zr4, Zr5 and Zr6 and pointing to the interior of the cage (Fig. 1), the fourth water molecule is encapsulated in the cavity of the cage. To the best of our knowledge, inclusion of molecules in the cavity of the polynuclear zirconium compounds has not yet been encountered. The cavity of **1** is about 21×13 Å along the direction of c axis; the water molecule in this cavity is stabilized by the hydrogen bonding of the guest water and the three water molecules coordinated to Zr4, Zr5 and Zr6, and as one oxygen atoms of each carboxylate groups bridging each two of other three metal centers (Fig. 3).

Thermogravimetric analysis (TG/DTA) of **1** (in N₂) shows a weight loss of 2.61% in the temperature range of $50^\circ\text{--}185^\circ\text{C}$, corresponding to the removal of four H₂O molecules (expected

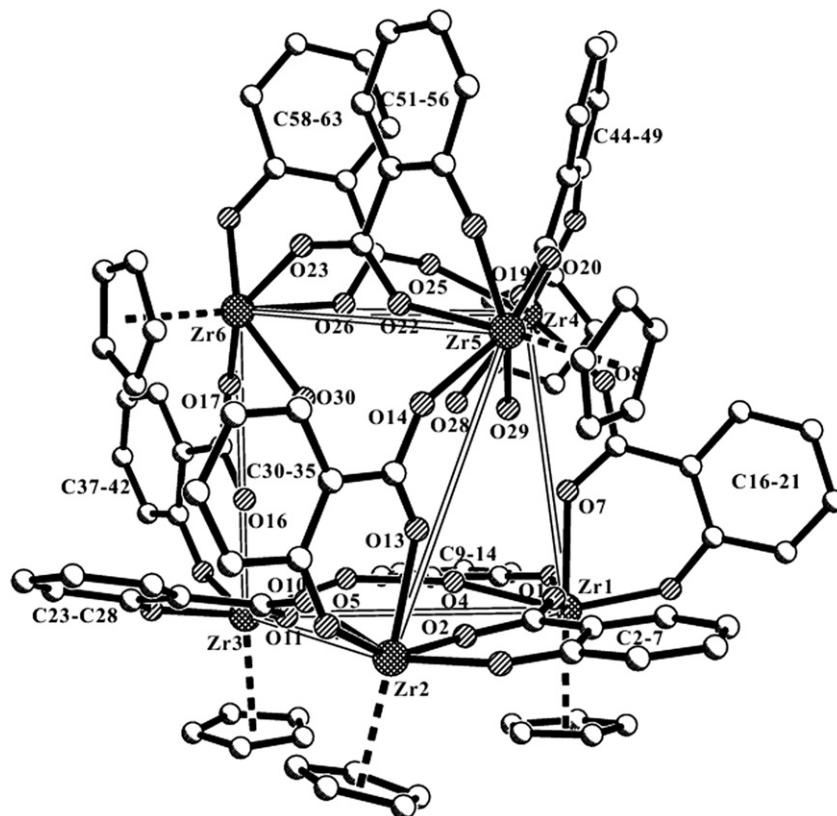


Fig. 1. The structure of $[(\text{CpZr})_6(\mu\text{-O}_2\text{C-C}_6\text{H}_2\text{Cl}_2\text{-2-O})_9(\text{OH}_2)_3]\cdot\text{H}_2\text{O}$ (**1**), the hydrogen atoms and chlorine atoms bonded to phenyl rings are omitted for clarity. Thermal ellipsoids represent 30% probability.

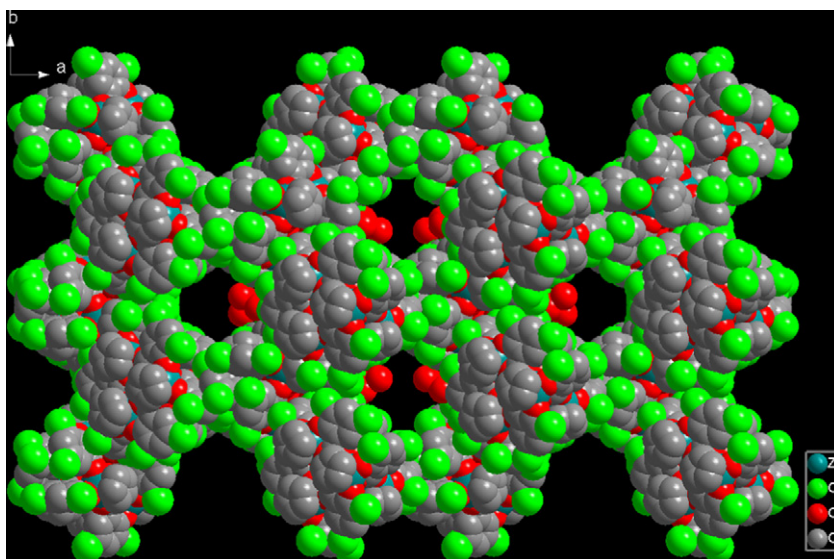


Fig. 2. Caption packing diagrams of compound **1** with channels as viewed along *c* axis, and the H₂O molecules are encapsulated in the channels (21 × 13 Å).

2.52%) per formula unit. Then, the following decomposition step in the range of 185–240 °C, shows a loss weight of 6.82% (expected 6.79%), corresponding to the loss of three Cp rings. In addition, the residual percentage weight at the end of the decomposition of **1**, from 240° to 800 °C, which may correspond to four ZrO₂ molecules (observed, 17.22%; calcd, 17.16%), not six ZrO₂ molecules as expected. The presence of Cl atoms in **1** could lead to the formation of zirconium tetrachloride which sublimes at these higher temperatures, leading to a lower fraction of mass present after treatment.

In summary, by using a ligand with flexible coordination modes, a novel cage organozirconium compound was synthesized in CH₂Cl₂–Et₂O–HCl solution, which can accommodate water molecules from the mixed solvent. We believe that the diameter of the cavity could be adjusted by selection of a suitable ligand.

3. Experimental

3.1. Synthesis of compound **1**

A solution of Cp₂ZrCl₂ (0.292 g, 1 mmol) in 1 mol L⁻¹ hydrochloric acid (10 mL) was added to a solution of 3, 5-dichlorosalicylic acid (0.207 g, 1 mmol) in dichloromethane-ether (18 mL, V CH₂Cl₂/V ether = 5/1). The mixture was stirred at room temperature for 30 min.

Then the pale yellowish organic layer was separated and then dried with anhydrous MgSO₄ and filtered. The filtrate was evaporated under vacuum to give a pale yellowish solid. Recrystallization from CH₂Cl₂–Et₂O/hexane afforded X-ray quality pale yellowish blocks **1** (yield 61%). m.p. 215.8–217.4 °C (dec.), Anal. calcd for C₉₃H₅₆Cl₁₈O₃₁Zr₆: C 39.13, H 1.98; found: C 38.98, H 1.89%. ¹H NMR (300 MHz, CD₃SOCD₃, TMS): δ 6.16–6.57 (m, 30H; 6 × C₅H₅), 7.12–7.74 (m, 18H; ArH), 3.33 ppm (s, 10H; H₂O); IR (KBr) ν: 3429, 3082, 1597, 1561, 1528, 1502, 1453, 1381, 1247, 1020, 808, 781, 467 cm⁻¹.

3.2. X-ray crystal data for compound **1**

C₉₃H₅₆Cl₁₈O₃₁Zr₆, *M* = 2854.92, monoclinic, space group C2/c, *T* = 298(2) K; λ = 0.71073 Å; unit cell: *a* = 42.50(8) Å, *b* = 18.00(3) Å, *c* = 35.48(7) Å, β = 108.11(3)°, *V* = 25 792(83) Å³, *Z* = 8, μ = 0.905 mm⁻¹, *D*_c = 1.480 g cm⁻³, crystal size, 0.48 × 0.43 × 0.15 mm³, *F*(000) = 11 344, θ range for data collection, 1.62°–25.03°, limiting indices, –50 ≤ *h* ≤ 50, –21 ≤ *k* ≤ 19, –42 ≤ *l* ≤ 40, reflections: 64 735 collected, 22 733 independent (*R*_{int} = 0.0679), completeness to θ_{max}, 99.7%; refinement method, full-matrix least-squares on *F*² (22 733 data, 15 restraints, 1368 parameters); final indices for *I* > 2σ(*I*), *R*₁ = 0.0566, *wR*₂ = 0.1441; final indices for all data, *R*₁ = 0.1326, *wR*₂ = 0.1797; GOF on *F*²,

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**.

Bond distances (Å)					
Zr1–Cp1	2.232(10)	Zr2–Cp2	2.249(10)	Zr3–Cp3	2.267(10)
Zr5–Cp5	2.223(9)	Zr4–Cp4	2.232(11)	Zr6–Cp6	2.239(110)
Zr1–O1	2.138(6)	Zr1–O4	2.183(6)	Zr1–O6	2.074(6)
Zr1–O9	2.019(6)	Zr1–O7	2.255(6)	Zr2–O2	2.195(6)
Zr2–O3	2.024(6)	Zr2–O10	2.149(6)	Zr2–O13	2.234(5)
Zr3–O5	2.113(6)	Zr2–O15	2.052(5)	Zr3–O11	2.163(6)
Zr3–O12	2.044(6)	Zr3–O16	2.235(6)	Zr3–O18	2.045(6)
Zr4–O19	2.234(6)	Zr4–O8	2.122(5)	Zr4–O21	2.018(5)
Zr4–O25	2.095(6)	Zr4–O28	2.259(6)	Zr5–O14	2.076(6)
Zr5–O22	2.219(6)	Zr5–O20	2.149(6)	Zr5–O24	2.044(6)
Zr5–O29	2.244(7)	Zr6–O17	2.087(6)	Zr6–O23	2.149(6)
Zr6–O27	2.023(6)	Zr6–O26	2.244(6)	Zr6–O30	2.226(6)
Bond angles (°)					
O4–Zr1–O6	78.05(18)	O7–Zr1–O9	77.24(18)	O13–Zr2–O15	77.0(2)
O11–Zr3–O12	78.3(2)	O16–Zr3–O18	77.5(2)	O19–Zr4–O21	76.9(2)
O22–Zr5–O24	77.88(19)	O26–Zr6–O27	77.4(2)		

Cp, the centroid of the C₅ ring: Cp1 (C64–C68), Cp2 (C69–C73), Cp3 (C74–C78), Cp4 (C79–C83), Cp5 (C44–C88) and Cp6 (C89–C93).

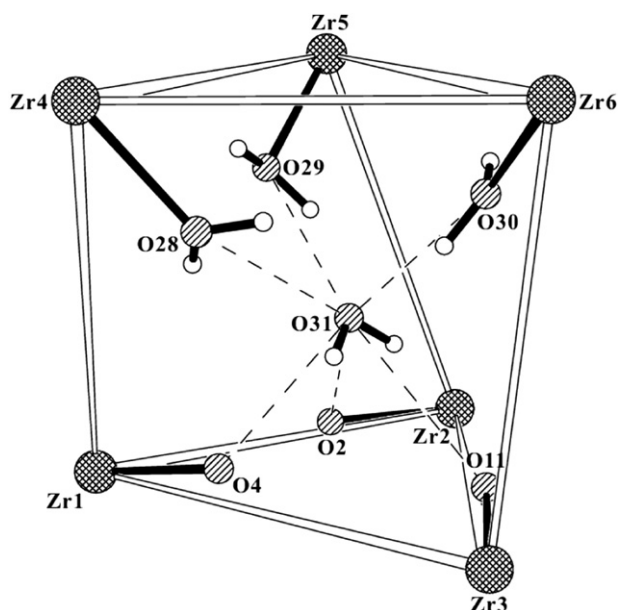


Fig. 3. Hydrogen bonds between the encapsulated water in the cavity of molecular **1** and its surrounding molecules. Only metal centers and oxygen atoms for O–H...O hydrogen-bonding interactions are maintained for clarity. The water molecule outside of the cage is omitted.

0.936; largest diff. peak and hole, 0.830 and $-0.512 \text{ e} \text{ \AA}^{-3}$. Data collection was performed on a Bruker Smart-1000 CCD detector, using graphite-monochromated Mo $K\alpha$ radiation ($\omega-2\theta$ scans, $\lambda = 0.71073 \text{ \AA}$) at room temperature. The structures were solved by direct method and refined on F^2 by full-matrix least-squares with Bruker's SHELXL-97 program system [13]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding mode. The crystals used for the diffraction study showed no decomposition during data collection.

Acknowledgments

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Appendix A. Supplementary material

CCDC no. 236400 for compound **1**. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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