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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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First published on: 13 July 2010

To cite this Article Zhang, Ru-Fen , Li, Cui-Ping , Wang, Qing-Feng and Ma, Chun-Lin(2010) 'Ligand-assisted assembly of polyoxozirconium clusters: syntheses and characterizations of tri- and tetranuclear half-zirconocene complexes', Journal of Coordination Chemistry, 63: 12, 2105 – 2112, First published on: 13 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.497838

URL: <http://dx.doi.org/10.1080/00958972.2010.497838>

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Ligand-assisted assembly of polyoxozirconium clusters: syntheses and characterizations of tri- and tetranuclear half-zirconocene complexes

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(Received 6 December 2009; in final form 30 March 2010)

Two different polyoxozirconium oxide clusters tri- and tetranuclear half-zirconocene complexes assisted by 2,3,4,5-tetrafluorobenzoic acid and 3,4,5,6-tetrafluorophthalic acid have been synthesized and characterized by elemental analysis, FT-IR, NMR (¹H, ¹⁹F, and ¹³C) spectroscopy, and X-ray crystallography. The structure analyses reveal that **1** is trinuclear with a μ₃-oxygen bridge, central to a Zr–O backbone; **2** is a tetranuclear complex with four Zr's tetrahedrally arranged around a μ₄-oxygen.

Keywords: Clusters; Zirconocene; Ligand-assisted; Crystal structures

1. Introduction

The chemistry of polyoxometal clusters has attracted much attention for their catalytic properties and their use as models for reactivities and properties of metal oxides in solution [1–4]. We are particularly interested in zirconocene complexes not only because of their catalytic activities in polymerization, hydrogenation, isomerization, and selective oxidation reactions [5–11], but also due to the considerable structural diversity and various coordination numbers that they possess. Efforts have been done to synthesize polyoxozirconium clusters by the hydrolysis of zirconocene complexes. Royo [12], for example, synthesized $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}\}_3(\mu\text{-Cl})_4(\mu_3\text{-O})]$ by the hydrolysis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrCl}_3]$ with a stoichiometric amount of water in toluene. Erker *et al.* [13] reported the preparation of a zirconocene oxide cluster $[\{(\text{Cp}_2\text{Zr})_3(\mu\text{-OH})_3(\mu_3\text{-O})\}^+(\text{BPh}_4)^-]$ by the hydrolysis of Jordan's cation and in particular, Roesky *et al.* [14, 15] have carried out some elegant work on such systems, preparing a series of organozirconium oxide clusters such as $[\{(\text{EtMe}_4\text{C}_5)\text{Zr}\}_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_7\text{H}_8$ and $[\{(\text{EtMe}_4\text{C}_5)\text{Zr}\}_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_9\text{H}_{12}$ by the hydrolysis of metal chlorides in a liquid ammonia/toluene two-phase system at low temperatures. Although considerable advances have been made in the development

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of the assembly of these clusters, relatively little work has been undertaken on the assembly of polyoxozirconium clusters assisted by organic ligands which play important roles in the coordination structure of the metal.

Out of the above consideration, we chose to investigate the assembly of organozirconium oxide clusters assisted by 2,3,4,5-tetrafluorobenzoic acid and 3,4,5,6-tetrafluorophthalic acid and succeeded in obtaining tri- and tetranuclear half-zirconocene complexes. Herein we reported the syntheses and characterizations of polyoxozirconium clusters derived from these two kinds of acids.

2. Experimental

2.1. Materials and measurements

2,3,4,5-Tetrafluorobenzoic acid, 3,4,5,6-tetrafluorophthalic acid, and Cp_2ZrCl_2 were commercially available and used without purification. The melting points were obtained with an X-4 digital micromelting-point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-5700 spectrophotometer using KBr disks and sodium chloride optics at room temperature (298 K). ^1H , ^{19}F , and ^{13}C -NMR spectra were obtained on a Varian Mercury Plus 400 MHz NMR spectrometer. The chemical shifts are stated relative to external tetramethylsilane (TMS). Element analyses were performed with a PE-2400 II apparatus.

2.2. X-ray structure analyses of 1 and 2

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-100 CCD area detector with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXS-97. Hydrogens were placed in calculated positions. Crystal data and experimental details of the structure determination of **1** and **2** are listed in table 1.

2.3. Syntheses of 1 and 2

2.3.1. Synthesis of $[(\text{C}_5\text{H}_5\text{Zr})_3(\mu_3\text{-O})(\mu_2\text{-OH})_3(\text{C}_6\text{HF}_4\text{CO}_2)_3] \cdot (\text{C}_6\text{HF}_4\text{CO}_2^-) \cdot \text{CH}_3\text{OH}$ (**1**).

The 2,3,4,5-tetrafluorobenzoic acid (0.338 g, 2 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to benzene solution in a Schlenk flask and stirred for 10 min. Then Cp_2ZrCl_2 (0.292 g, 1 mmol) was added and the reaction mixture was stirred for 12 h at 40°C , filtered, and the solvent gradually removed by evaporation under vacuum until solid is obtained. The solid was recrystallized from methanol and a transparent colorless crystal was formed. Yield: 80%. m.p. $167\text{--}169^\circ\text{C}$. Anal. Calcd for $\text{C}_{44}\text{H}_{26}\text{F}_{16}\text{O}_{13}\text{Zr}_3$: C, 39.43; H, 1.96%. Found: C, 39.75; H, 2.31%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1581; $\nu_{\text{s}}(\text{COO})$, 1385; $\nu(\text{Zr-O-Zr})$, 727; $\nu(\text{Zr-O})$, 472. $^1\text{H-NMR}$ [$(\text{CD}_3)_2\text{SO}$, ppm]: $\delta = 6.21\text{--}6.61$ (m, 15H, C_5H_5), 1.51 (s, 3H, OH), 7.56 (s, 4H, C_6HF_4), 2.17 (m, 1H, $\text{CH}_3\text{O-H}$), and 3.35 (s, 3H, CH_3). $^{13}\text{C-NMR}$ [$(\text{CD}_3)_2\text{SO}$, ppm]: $\delta = 170.39$

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Complex	1	2
Empirical formula	C ₄₄ H ₂₆ F ₁₆ O ₁₃ Zr ₃	C ₄₀ H ₄₀ F ₈ O ₁₈ Zr ₄
Formula weight	1340.31	1325.59
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Cubic
Space group	<i>P</i> $\bar{1}$	<i>Fd-3c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	10.3456(9)	50.692(4)
<i>b</i>	15.8125(14)	50.692(4)
<i>c</i>	16.460(2)	50.692(4)
α	98.2600(10)	90
β	106.573(2)	90
γ	97.2390(10)	90
Volume (Å ³), <i>Z</i>	2514.2(4), 2	130262(19), 96
Calculated density (mg m ⁻³)	1.770	1.622
Absorption coefficient (mm ⁻¹)	0.730	0.837
<i>F</i> (000)	1316	62975
Crystal size (mm ³)	0.30 × 0.18 × 0.13	0.21 × 0.18 × 0.15
Reflections collected	12856	115807
Independent reflection	8500 [<i>R</i> (int) = 0.0675]	4813 [<i>R</i> (int) = 0.1344]
Data/restraints/parameters	8500/1267/688	4813/1/363
Goodness-of-fit on <i>F</i> ²	0.946	1.109
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0926, <i>wR</i> ₂ = 0.2234	<i>R</i> ₁ = 0.0654, <i>wR</i> ₂ = 0.1766
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1652, <i>wR</i> ₂ = 0.2839	<i>R</i> ₁ = 0.1230, <i>wR</i> ₂ = 0.233

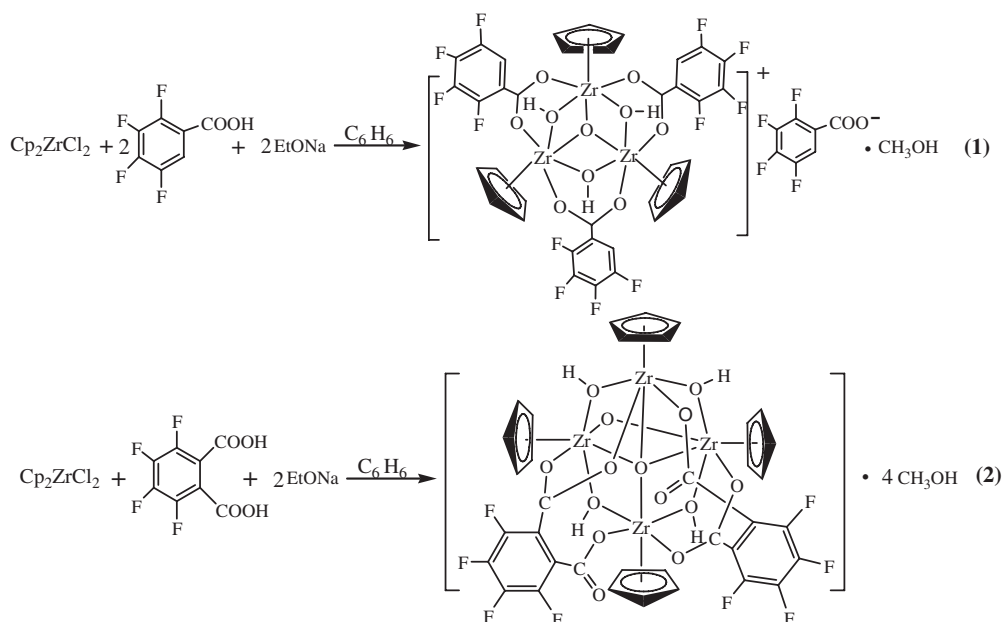
(COO), 117.9 (C₅H₅), and 134.3–146.7 (C₆HF₄). ¹⁹F-NMR [(CD₃)₂SO, ppm] δ = -132.9, -137.5, -145.1, and -153.0.

2.3.2. Synthesis of [(C₅H₅Zr)₄(μ₄-O)(μ₂-OH)₄(μ-O){C₆F₄(COO)₂]₂·4CH₃OH (2). Complex **2** was prepared in the same way as **1** by adding Cp₂ZrCl₂ (0.292 g, 1 mmol) to a mixture of 3,4,5,6-tetrafluorophthalic acid (0.238 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from methanol and transparent colorless crystals were formed. Yield: 80%; m.p. > 260°C. Anal. Calcd for C₄₀H₄₀F₈O₁₈Zr₄: C, 36.24; H, 3.04%. Found: C, 36.61; H, 3.37%. IR (KBr, cm⁻¹): ν_{as}(COO), 1631, 1598; ν_s(COO), 1410, and 1384; ν(Zr–O–Zr), 733; ν(Zr–O), 471. ¹H-NMR [(CD₃)₂SO, ppm]: δ = 6.68 (s, 20H, C₅H₅), 1.52 (s, 4H, OH), 3.40 (t, 12H, CH₃), and 2.35 (m, 4H, CH₃OH). ¹³C-NMR [(CD₃)₂SO, ppm]: δ = 169.8 (COO), 116.8 (C₅H₅), and 131.7–143.2 (C₆F₄). ¹⁹F-NMR [(CD₃)₂SO, ppm] δ = -134.7, -147.1.

3. Results and discussion

3.1. Syntheses

Two different polyoxozirconium oxide clusters were obtained when we use the same experimental conditions, but change the organic ligands. In order to completely replace chloride, we use Cp₂ZrCl₂ reacting with the monocarboxylic acid in 2:1 ratio and the

Scheme 1. Synthesis of complexes **1** and **2**.

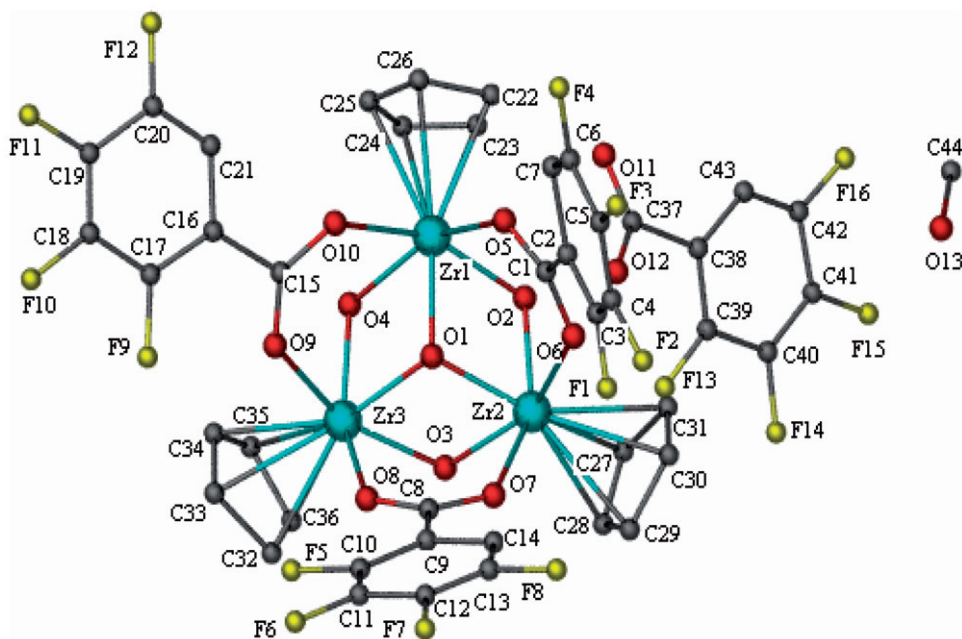
dicarboxylic acid in 1:1 ratio. The synthetic procedures of the clusters are shown in scheme 1.

3.2. IR spectra

Stretching frequencies of interest are those associated with COO, Zr–O, Zr–O–Zr, and μ_2 -OH. The absorption at 3430 cm^{-1} has been assigned to $\nu(\mu_2\text{-OH})$. The absorption at 470 cm^{-1} may be assigned to various Zr–O bonds and the absorption at 730 cm^{-1} is assigned to vibrations associated with the Zr–O–Zr stretch [16]. Asymmetric and symmetric stretching frequencies of the carboxylate of **1** are at 1581 cm^{-1} for asymmetric stretching and 1385 cm^{-1} for symmetric stretching. The magnitude of $\Delta\nu(\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO}))$ of 196 cm^{-1} reveals that the carboxylates function as bidentate ligands [17]. For **2**, the bands of carboxylate occur at 1631 and 1598 cm^{-1} for asymmetric stretching and at 1410 and 1384 cm^{-1} for symmetric stretching. The splitting of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ indicates that carboxylates function in two different coordination fashions. The magnitude of $\Delta\nu(\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO}))$ of 247 and 188 cm^{-1} , respectively, indicates that carboxylates are bidentate and monodentate [18, 19]. These are also confirmed by X-ray diffraction.

3.3. NMR spectra

In the $^1\text{H-NMR}$ spectra of the complexes, the $-\text{COOH}$ of the ligand is absent and a new signal at 1.50 ppm is attributed to the $\mu_2\text{-OH}$ of the oxygen bridge. In the ^{19}F spectrum,

Figure 1. Molecular structure of **1**.

four multiple resonance signals at $\delta = -132.9$, -137.5 , -145.1 , and -153.0 ppm are attributed to the fluorines of **1**. In **2**, there are two kinds of fluorines in the benzene ring and the ^{19}F signals appear at $\delta = -134.7$ and -147.1 ppm. The structural changes occurring in the ligand upon deprotonation and coordination to Zr should be reflected by the changes in ^{13}C -NMR spectra of our complexes. The ^{13}C -NMR spectra of all complexes show a significant downfield shift of all carbon resonances, compared with the free ligand, as a consequence of electron transfer from the ligand to the metal. Single resonances at about 170 ppm are attributed to the COO groups in the complexes.

3.4. X-ray crystallographic studies

3.4.1. Crystal structure of 1. The molecular structure of **1** is illustrated in figure 1. Selected bond lengths (\AA) and angles ($^\circ$) are listed in table 2.

X-ray structure analyses reveal that **1** is a monomer containing a trinuclear ligand-bridged $(\text{C}_5\text{H}_5)\text{Zr}$ -cation cluster and a $\text{C}_6\text{HF}_4\text{COO}$ anion. The structure of the trinuclear zirconium core is close to C_{3v} with the carboxylates orientated to one face and the $\mu\text{-OH}$ groups to the other. $\text{Zr}-(\mu\text{-OH})$ bond lengths (2.106(7)–2.133(7) \AA) and $\text{Zr}-(\mu\text{-OH})\text{-Zr}$ internal angles between $104.1(3)^\circ$ and $104.9(3)^\circ$ are all comparable with those reported in $[(\text{C}_5\text{H}_5\text{Zr})_3(\mu_3\text{-O})(\mu_2\text{-OCOPh})_3(\mu\text{-OH})_3][\text{PhCO}_2]$ [2.130(5)–2.144(3) \AA , $103.1(2)$ – $104.0(1)^\circ$] [19]. Each carboxylate is symmetrically bridging between two zirconium centers with Zr-O (carboxylate) distances between 2.191(7) and 2.219(8) \AA and Zr-O-C (carboxylate) angles from $128.4(8)^\circ$ to $131.7(8)^\circ$. All data are similar to those reported in the literature [20]. A centrally located μ_3 -oxygen is equally

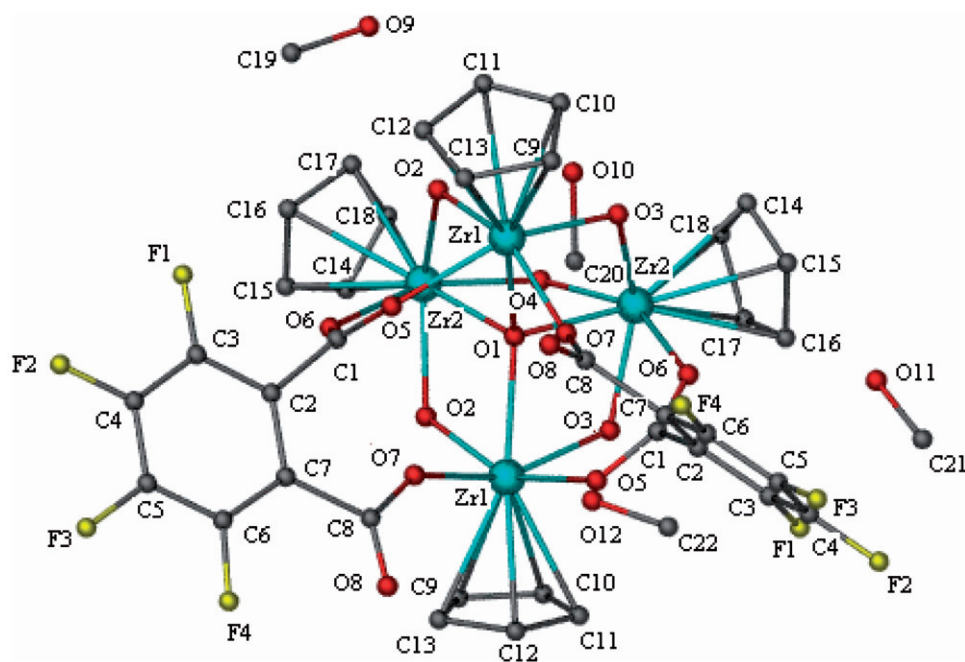
Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zr(1)–O(1)	2.072(7)	Zr(1)–O(2)	2.111(6)
Zr(1)–O(4)	2.122(7)	Zr(1)–O(5)	2.196(7)
Zr(1)–O(10)	2.215(7)	Zr(2)–O(1)	2.064(6)
Zr(2)–O(3)	2.106(7)	Zr(2)–O(2)	2.107(8)
Zr(2)–O(6)	2.191(7)	Zr(2)–O(7)	2.195(9)
Zr(3)–O(1)	2.072(6)	Zr(3)–O(4)	2.107(8)
Zr(3)–O(3)	2.133(7)	Zr(3)–O(8)	2.193(8)
Zr(3)–O(9)	2.219(8)	Zr(1)–Zr(2)	3.3259(15)
Zr(1)–Zr(3)	3.3526(16)	Zr(2)–Zr(3)	3.3402(14)
Zr(2)–O(1)–Zr(3)	107.7(3)	Zr(2)–O(1)–Zr(1)	107.0(3)
Zr(3)–O(1)–Zr(1)	108.0(3)	Zr(2)–O(2)–Zr(1)	104.1(3)
Zr(2)–O(3)–Zr(3)	104.0(3)	Zr(3)–O(4)–Zr(1)	104.9(3)
C(1)–O(5)–Zr(1)	130.3(8)	C(1)–O(6)–Zr(2)	130.4(8)
C(8)–O(7)–Zr(2)	131.7(8)	C(8)–O(8)–Zr(3)	128.4(8)
C(15)–O(9)–Zr(3)	130.8(9)	C(15)–O(10)–Zr(1)	130.6(8)
O(5)–C(1)–O(6)	125.0(12)	O(8)–C(8)–O(7)	126.2(13)
O(9)–C(15)–O(10)	127.2(12)		

coordinated to all three zirconiums, capping the Zr equilateral triangle [Zr(1)–Zr(2) 3.3259(15), Zr(1)–Zr(3) 3.3526(16), Zr(2)–Zr(3) 3.3402(14) Å]. The internal Zr–(μ_3 -O) distances (2.064(6)–2.072(6) Å) are similar to those of [Zr₃(μ_3 -O)(μ -OAc)₃(OAc)₂(μ -OPrⁱ)₂(OPrⁱ)₃] [21] and the Zr–(μ_3 -O)–Zr angles [107.0(3)–108.0(3)°] are near to those found in [{LOEtZr(H₂O)}₃(μ -OH)₃(μ_3 -O)][OTf]₄ [108.7(2)–109.5(2)°] [22]. Each metal center is in a distorted octahedral environment with the centroid of the C₅H₅ rings occupying one coordination site and the μ_3 -O trans. Lastly, there is one independent methanol co-crystallized in the crystal.

3.4.2. Crystal structure of 2. The molecular structure of **2** is illustrated in figure 2. Selected bond lengths (Å) and angles (°) are listed in table 3.

X-ray structure analyses revealed that **2** was isolated as the tetranuclear species, wherein four Zr's are tetrahedrally arranged around a μ_4 -O with internal Zr–(μ_4 -O) distances [2.305(3)–2.217(5) Å] and Zr–(μ_4 -O)–Zr angles [100.35(9)–144.0(4)°]. Each metal is surrounded by five oxygens derived from one μ_4 -O, two oxo/hydroxo bridges, and two carboxylates. Taking the centroid of the C₅H₅ rings as occupying one coordination site and the μ_4 -O trans, the zirconiums are all in distorted octahedral environments. The typical Zr–(μ_2 -OH) single bond lengths (2.120(7)–2.154(7) Å) are similar to those reported in literature [19] and Zr–(μ_2 -OH)–Zr internal angles from 110.0(3) to 111.2(3)° a little longer than those reported [23]. The oxide linking the Zr₂ and Zr₂(#1) (#1: $y - 1/4$, $x + 1/4$, $-z + 1$) is present as μ_2 -O with Zr–(μ_2 -O) distances [2.12(3)–2.15(2) Å] and Zr–(μ -O)–Zr(#1) internal angle of 107.2(5)°. The coordination modes of the ligands have each dicarboxylate linking three adjacent Zr's. One of the carboxylates is bidentate bridging a pair of Zr's [Zr–O distances 2.184(6)–2.238(7) Å and Zr–C–O angles 131.1(6)–131.3(7)°]; the remaining is non-bridging monodentate with the third Zr [Zr–O distance 2.138(7) Å and Zr–C–O angle 146.4(7)°]. Lastly, there are four independent methanols co-crystallized in the crystal.

Figure 2. Molecular structure of **2**.Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Zr(1)–O(3)	2.108(7)	Zr(1)–O(2)	2.120(7)
Zr(1)–O(7)	2.138(7)	Zr(1)–O(5)	2.184(6)
Zr(1)–O(1)	2.305(3)	Zr(2)–O(2)	2.121(7)
Zr(2)–O(4)	2.12(3)	Zr(2)–O(4)#1	2.15(2)
Zr(2)–O(3)#1	2.154(7)	Zr(2)–O(1)	2.217(5)
O(1)–Zr(2)#1	2.217(5)	O(1)–Zr(1)#1	2.305(3)
O(3)–Zr(2)#1	2.154(7)	O(4)–Zr(2)#1	2.15(2)
Zr(2)–O(6)	2.238(7)	Zr(1)–Zr(2)	3.4734(14)
Zr(1)–Zr(2)#1	3.5175(14)	Zr(2)–Zr(2)#1	3.442(2)
Zr(2)#1–O(1)–Zr(2)	101.8(3)	Zr(2)#1–O(1)–Zr(1)	102.12(9)
Zr(2)–O(1)–Zr(1)	100.35(9)	Zr(2)#1–O(1)–Zr(1)#1	100.35(9)
Zr(2)–O(1)–Zr(1)#1	102.12(9)	Zr(1)–O(1)–Zr(1)#1	144.0(4)
Zr(1)–O(2)–Zr(2)	110.0(3)	Zr(1)–O(3)–Zr(2)#1	111.2(3)
Zr(2)–O(4)–Zr(2)#1	107.2(5)	C(1)–O(5)–Zr(1)	131.3(7)
C(1)–O(6)–Zr(2)	131.1(6)	C(8)–O(7)–Zr(1)	146.4(7)

Symmetry code: #1: $y - 1/4, x + 1/4, -z + 1$.

4. Conclusion

This work studied the assembly of organozirconium oxide clusters assisted by 2,3,4,5-tetrafluorobenzoic acid and 3,4,5,6-tetrafluorophthalic acid and succeeded in obtaining two clusters, tri- and tetranuclear half-zirconocene complexes. Efforts to synthesize and characterize such complexes assisted by various ligands [24, 25] indicate that our approach could lead to numerous interesting organozirconium oxide clusters

with considerable coordination diversity of zirconium and chemical structures of various organic ligands.

Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of the compounds reported in this article (**1** and **2**) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC: 757056 for **1**, 757057 for **2**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgment

We thank the National Natural Science Foundation of China (20971096) for providing the financial support.

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