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New synthetic route for organic polyoxometallic clusters: synthetic and structural investigations on the first dumb-bell shaped polyoxozirconium hydroxide with the $[Zr_9(\mu_5\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_4(\mu\text{-}OH)_8]$ core structure†

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A new route for organic polyoxometallic clusters describes the first dumb-bell-like organic polyoxozirconium hydroxide $[\{(Cp*Zr)_4(\mu_5\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}OH)_4\}_2Zr(\mu\text{-}O)_4]\cdot2C_7H_8$ (2; Cp* = C₅Me₅) involving the treatment of the Brønsted acidic organozirconium hydroxide $[(Cp*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8]\cdot2C_7H_8$ (1) with organozirconium compounds.
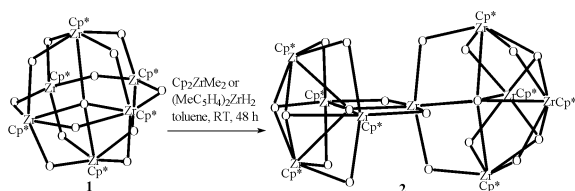
Organometallic oxides that are soluble analogues of discrete fragments of solid metal oxides are of considerable interest because of their catalytic properties, as catalyst supporting materials, and as modeling system for the reactions and properties of metal oxides in solution.[1] Zirconium oxides provide valuable catalysts for the hydrogenation, isomerization and selective oxidation reactions.[2] The most important method for the synthesis of organic polyoxometallic compounds is the hydrolysis of organometallic complexes.[3] However, the synthesis of a halogen-free aggregate of organozirconium oxide is very difficult to achieve.[4] We have reported the synthesis and characterization of the organozirconium oxide clusters $[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8$ and $[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_9H_{12}$, which can be viewed as soluble analogues of solid zirconium oxide.[5] More recently, an organic polyoxozirconium hydroxide $[(Cp*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8]\cdot2C_7H_8$ (1) was synthesized *via* the hydrolysis of an organozirconium chloride in a liquid ammonia/toluene two phase system.[6] The latter species is of interest in that its off-center interstitial oxygen core structure, its Brønsted acidic μ-OH groups and its model character as a support for transition metal catalysts are unique in this system.

In this communication, we report the synthesis and structural characterization of the first dumb-bell-like organic polyoxozirconium complex *via* the reaction of cluster **1** with organozirconium compounds. Treatment of **1** with $(MeC_5H_4)_2ZrH_2$ or alternatively with Cp_2ZrMe_2 in toluene at room temperature results in the formation of the organic polyoxozirconium cluster $[\{(Cp*Zr)_4(\mu_5\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}OH)_4\}_2Zr(\mu\text{-}O)_4]\cdot2C_7H_8$ (**2**; Scheme 1).‡ Although the formation of **2** is elusive, it is most likely that the central Zr is introduced by the complete cleavage of Cp'_2ZrR_2 (Cp′ = Cp, MeC_5H_4; R = H, Me). The OH protons on the surface of cluster **1** react with the R groups of Cp'_2ZrR_2 leading to the new Zr–O bonds. This is presumably the first step of the reaction. Subsequently, these intermediates react with the elimination of the Cp′H and the degradation of cluster **1** with concomitant

formation of **2**. The elimination of the Cp′ groups during the preparation of **2** is similar to that observed in the preparation of $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$[7] and $[(CpTi)_6(\mu_3\text{-}O)_8]$,[8] where the starting materials are $(MeC_5H_4)_2ZrCl_2$ and $Cp_2Ti(CO)_2$, respectively. Evidently, the R groups are essential for the cleavage of Cp′–Zr bonds. It is possible that the two coordinatively unsaturated zirconium atoms in **1**, resulting from the off-center interstitial μ₄-O core structure, led to the degradation of the cluster when **1** was treated with an organometallic compound. The two units of cluster **2** should originate from at least two molecules of **1**, where the μ₄-O becomes a μ₅-O in **2**. Although the zirconium atoms increase from 6 (in **1**) to 9 (in **2**), the ratio of zirconium to oxygen in both compounds (1 : 2.17, 1 : 2) is nearly the same (the most stable compound $[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8$ in this series contains a Zr : O ratio of 1 : 1.5). Therefore, it is predictable that within the Zr : O ratios of 1 : 1.5 to 1 : 2.17 further polyoxozirconium hydroxides should exist.
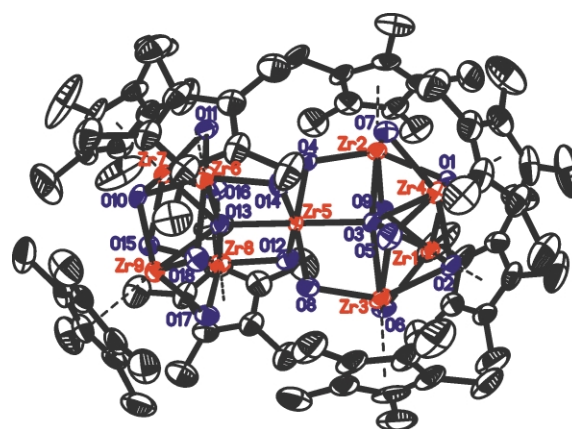
Compound **2** is a colorless crystalline solid that melts above 410 °C. The IR spectrum of **2** shows a weak absorption at 3666 cm⁻¹, due to the O–H bond.

The molecular structure of **2**, shown in Fig. 1, consists of two highly distorted square pyramids with eight Cp*Zr fragments and one Zr atom arranged around two interstitial μ₅-O oxygen atoms.§ The central Zr(5) occupies the vertex shared by the two square pyramids forming the dumb-bell shaped core structure. The Zr(5) and the two μ₅-O atoms are almost linearly arranged ((μ₅-O)–Zr(5)–(μ₅-O), 177.80(15)°). The nine Zr atoms are bridged or capped by oxygen atoms resulting in two four-membered $Zr_2(\mu_3\text{-}O)_2$, eight four-membered $Zr(\mu\text{-}O)Zr(\mu_3\text{-}O)$, eight four-membered $Zr(\mu\text{-}O)Zr(\mu_5\text{-}O)$, twelve four-membered

Fig. 1 A view of **2** with 50% thermal ellipsoids. H atoms bonded to C and O and the toluene molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)–O(1) 2.125(4), Zr(1)–O(2) 2.121(4), Zr(1)–O(6) 2.159(4), Zr(1)–O(9) 2.144(4), Zr(1)–O(3) 2.333(4), Zr(2)–O(4) 2.007(4), Zr(5)–O(4) 2.057(4), Zr(5)–O(3) 2.111(4), Zr(1)···Zr(2) 3.2092(11), Zr(2)···Zr(5) 3.3109(9); O(1)–Zr(1)–O(9) 79.12(15), O(3)–Zr(1)–O(6) 72.20(14), O(1)–Zr(1)–O(2) 79.82(15), O(1)–Zr(1)–O(3) 68.91(13), O(3)–Zr(2)–O(4) 75.36(13), O(3)–Zr(5)–O(4) 80.34(14), O(3)–Zr(5)–O(13) 177.80(15), Zr(1)–O(9)–Zr(2) 96.13(16), Zr(1)–O(1)–Zr(2) 95.88(15), Zr(1)–O(3)–Zr(2) 86.11(12), Zr(2)–O(4)–Zr(5) 109.11(16), Zr(2)–O(3)–Zr(5) 85.18(14).

Scheme 1 The H atoms bonded to O and the toluene molecules of **1** and **2** are omitted for clarity.

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Zr(μ_3-O)Zr(μ_5-O), and four four-membered Zr(5)(μ-O$_b$)Zr(μ_5-O) rings (O$_b$ = O(4), O(8), O(12), and O(14)). The coordination sphere of each Zr atom on the surface of the core is completed by the Cp* ligand. The bond lengths of Zr–(μ-O) (2.139(4) to 2.198(4) Å, av 2.169 Å), Zr–(μ_3-O) (2.108(4) to 2.197(4) Å, av 2.144 Å), and Zr(5)–(μ_5-O) (2.111(4) Å) are similar to the Zr–(μ-O) bond distances in **1** (2.072(2) to 2.171(2) Å, av 2.106 Å) and the Zr–(μ_3-O) bond lengths in [{(EtMe$_4$C$_5$)Zr}$_6$(μ_6-O)(μ_3-O)$_8$]·C$_7$H$_8$ (2.136(2) to 2.169(2) Å, av 2.156 Å).[5] The Zr–(μ-O$_b$) bond lengths (1.985(4) to 2.070(4) Å, av 2.026 Å) are shorter than those of Zr–(μ-O) in **2** and of Zr–(μ-OH) in [{(Cp*ZrCl)(μ-OH)}$_3$(μ_3-OH)(μ_3-O)]·2THF (2.160(2) Å),[9] and are comparable with those in [{Cp$_2$Zr(μ-O)}$_3$] (Zr–(μ-O) 1.959(3) Å).[10] Therefore, we assume that the eight hydrogen atoms of the OH groups are distributed over eight μ-O edges on the surface of the core. The Zr–(μ_5-O) bond lengths (2.275(4) to 2.432(2) Å, av 2.347 Å) of **2** are slightly longer than those found in [{(EtMe$_4$C$_5$)Zr}$_6$(μ_6-O)(μ_3-O)$_8$]·C$_7$H$_8$ (Zr–(μ_6-O) 2.231(2) to 2.247(2) Å, av 2.241 Å).[5] The distances of the (Zr(5)) center to the (Zr(2), Zr(3), Zr(6), Zr(8); (3.3007(11) to 3.3123(12) Å, av 3.3077 Å) are slightly longer than those of the adjacent Zr atoms on the core (3.1302(9) to 3.2409(9), av 3.2031 Å) which are similar to those exhibited by [{(EtMe$_4$C$_5$)Zr}$_6$(μ_6-O)(μ_3-O)$_8$]·C$_7$H$_8$ (3.1542(9) to 3.1709(11) Å, av 3.1635 Å).

The Zr–(μ_3-O)–Zr (95.07(14) to 98.00(15)°, av 96.20°), Zr–(μ-O)–Zr (95.06(16) to 96.82(16)°, av 95.90°), and Zr(5)–(μ_5-O)–Zr (93.36(14) to 95.73(14)°, av 94.56°) angles are larger than Zr–(μ_5-O)–Zr (85.19(12) to 88.01(13)°, av 86.39°), but also smaller than the Zr(5)–(μ-O$_b$)–Zr angles (108.30(17) to 110.60(18)°, av 109.47°) and the Zr–(μ-O)–Zr angles in **1** (118.70(14) to 122.78(12)°, av 120.56°). In addition, the (μ_3-O)–Zr–(μ_3-O) (79.66(14) to 80.32(15)°, av 79.99°), (μ-O)–Zr–(μ_3-O) (75.94(15) to 79.12(15)°, av 77.66°), and (μ-O$_b$)–Zr–(μ_5-O) (74.75(14) to 75.87(14)°, av 75.33°) angles are larger than those of (μ-O)–Zr–(μ_5-O) (69.43(14) to 72.86(14)°, av 71.35°) and (μ_3-O)–Zr–(μ_5-O) (66.39(13) to 70.03(13)°, av 68.64°), but smaller than (μ-O)–Zr–(μ-O) angle (82.76(6) to 88.94(10)°, av 86.11°) in **1**. Nonetheless, the (μ-O$_b$)–Zr(5)–(μ_5-O) angles (80.03(15) to 81.30(15)°, av 80.64°; 97.99(15) to 100.67(15)°, av 99.36°) in **2** are not similar.

In summary, the treatment of the Brønsted acidic organozirconium hydroxide **1** with organometallic compounds provides a new route to larger polyoxometallic clusters that is otherwise difficult to achieve. Using this procedure, the largest organic polyoxozirconium cluster was prepared. According to the structure of **2**, it seems that two spheres of the dumb-bell are arranged in such a way that they can be regarded as two pentazirconium clusters that share the same zirconium vertex. The eight hydrogen atoms of the OH groups are distributed over eight μ-O positions on the surface of the spheres. Due to the Lewis acidic zirconium centers, the O–H groups of **2** are Brønsted acidic as evident in the IR spectrum of **2**.[11] The organic ligands and the reactive hydroxide groups on the cluster surface of **2** facilitate the solubility and further reactivity in solution. A wide variety of organometallic complexes should, therefore, react with the Brønsted acidic OH groups of **1** and **2** to produce soluble metal clusters. Unlike cluster **1**, cluster **2** has no coordinatively unsaturated zirconium atoms and therefore its core is more stable kinetically.

Notes and references

‡ Method A: A mixture of **1** (0.11 g, 0.06 mmol) and (MeC$_5$H$_4$)$_2$ZrH$_2$ (0.12 g, 0.48 mmol) in toluene (80 mL) was stirred at room temperature for 48 h. After filtration, the colorless filtrate was concentrated and stored at −20 °C for three weeks. Colorless crystals of **2** (0.04 g, 36%) were obtained. Method B: In a procedure similar to method A **1** (0.176 g, 0.10 mmol) and Cp$_2$ZrMe$_2$ (0.20 g, 0.80 mmol) in toluene (80 mL) were stirred at room temperature for 48 h. Colorless crystals of **2** (0.06 g, 32%) were obtained. Mp > 410 °C. IR (Nujol): 3666 w, 1260 s, 1092 vs, 1019 vs, 798 vs, 732 s cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 2.12, 1.54 (C$_5$Me$_5$). EI-MS: m/z (%): 1988 (1) [M − 3 C$_7$H$_8$ − Cp* − 4 H$_2$O − 3 H]$^+$, 1256 (2) [M − 3 C$_7$H$_8$ − 6 Cp* − 7 H$_2$O − 6 H]$^+$, 119 (100) [Cp* − CH$_4$]$^+$. Anal. calcd. for C$_{101}$H$_{152}$O$_{18}$Zr$_9$ (2475.2): C, 49.0; H, 6.2. found: C, 48.1; H, 5.4% (some toluene molecules in the crystal lattice presumably escaped during the evaporation of the solvent from the solution of **2** *in vacuo*).

§ Crystal data for **2**: C$_{80}$H$_{128}$O$_{18}$Zr$_9$·3C$_7$H$_8$ (the eight hydrogen atoms of the hydroxide groups could not be determined by X-ray diffraction), M = 2198.79 + 3 × 92.14, crystal size: 0.3 × 0.2 × 0.05 mm^3, monoclinic, space group $P2_1/c$, unit cell dimensions: a = 20.269(4), b = 16.745(3), c = 31.219(6) Å, β = 102.18(3)°, V = 10357(3) Å^3, Z = 4, ρ_{calcd} = 1.587 Mg m^{-3}, $F(000)$ = 5048, λ = 0.71073 Å, T = 133(2) K, μ(Mo$_{K\alpha}$) = 0.930 mm^{-1}; total number of reflections measured 80494, unique 16554 (R_{int} = 0.0598). Data/restraints/parameters: 16554/270/1196, data collection range: 12.36 ≤ 2θ ≤ 49.86°, completeness to θ = 24.93°: 91.5%. $R1$ = 0.0497 for $I > 2\sigma(I)$, $wR2$ = 0.1256 for all data. The final difference Fourier synthesis gave a min./max. residual electron density: +1.005/−0.870 e Å^{-3}. Diffraction data were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area detector with graphite-monochromated Mo-Kα radiation, performing φ and ω scans. The structure was solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXS-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. CCDC reference number 191340. See http://www.rsc.org/suppdata/cc/b2/b212281b/ for crystallographic data in CIF or other electronic format.

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