Syntheses and Crystallographic Characterizations of Trinuclear (μ_3-O) Zirconium Complexes

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The new trinuclear complex [{(η^5-C_5H_5)$_2$ZrO}$_3$(μ_3-O)] **5** shows unexpected interatomic distances and angles and a planar μ_3-O, while the related trinuclear zirconium cation cluster [{(C_5H_5)Zr}$_3$(μ_3-O)(μ-OH)$_3$(μ_2-HCO_2)$_3$]Cl·$HCONMe_2$·0.5H_2O **7** exhibits a pyramidal μ_3-O.

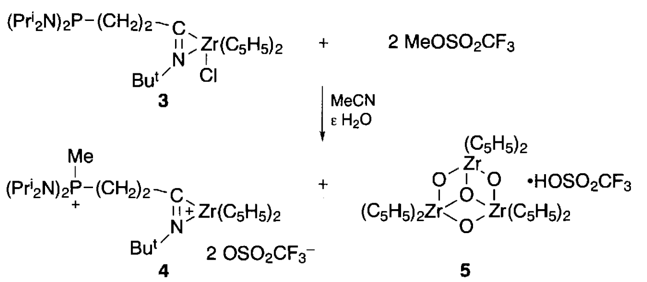
Few trinuclear complexes with a backbone of alternating zirconium and oxygen atoms have been reported. The formation of the first one {(C_5H_5)$_2$ZrO}$_3$ **1**, obtained by the addition of carbon dioxide to (C_5H_5)$_2$Zr(CO)$_2$, involves the trimerization of the transient species [(C_5H_5)$_2$Zr=O].[1] Reaction of bis(cyclopentadienyl)zirconium dichloride with sodium benzoate in aqueous solution yields the trinuclear complex [Zr_3(μ_3-O)(μ-OH)$_3$(μ-PhCO_2)$_3$(η^5-C_5H_5)$_3$]$^+$PhCO_2^-·OEt_2 **2**.[2] A similar titanium complex is also known.[3]

We report here the syntheses of two trinuclear complexes with μ_3-oxygen bridging ligands, central to a Zr–O backbone.

We have recently demonstrated that the addition of methyltrifluoromethane sulfonate (2 equiv.) to the phosphane **3** (1 equiv.) in MeCN leads to the formation of the dication **4**[4] (Scheme 1). During work-up, we isolated the phosphorus-free coproduct **5** in 10% yield.† The ^{1}H NMR spectrum exhibits a C_5H_5 singlet at δ 6.35. The mass spectrum of **5** shows a peak at 727 in agreement with a (C_5H_5)$_6Zr_3O_4$ formula while the elemental analysis is consistent with the empirical formula (C_5H_5)$_6Zr_3O_4$·CF_3SO_3H. Complex **5** was characterized by an X-ray analysis (Fig. 1).‡ The Zr(1)O(2)Zr(3)O(3)Zr(2)O(4) six-membered ring is planar, with typical Zr–O single bond lengths (2.192–2.232 Å) and Zr–O–Zr internal angles between 106.4 and 108.5°. These data can be compared to those obtained for the six-membered ring {(C_5H_5)$_2$ZrO}$_3$ **1**: in this derivative, the Zr–O bond distances are considerably shorter (1.94–1.95 Å) and the internal Zr–O–Zr angles are considerably larger (142.5°).

The most interesting feature of the structure is the planar central oxygen atom O(1) [118.7(6) < Zr–O(1)–Zr < 122.4(6)]. This is in marked contrast with the tetrahedral central oxygen atom of compound **2** (Zr–O–Zr angle values from 107.3 to 108.9°). Lastly, the internal O(1)–Zr(1), O(1)–Zr(2), O(1)–Zr(3) distances of **5** are shorter (2.04– 2.09 Å) than those of the six-membered ring.

One molecule of triflic acid crystallizes with the trinuclear complex **5**. Interatomic distances between oxygen atoms of triflic acid and O(3), C(28) and C(29) atoms of species **5** (Fig. 2) point to the presence of hydrogen bonds between these two compounds in the solid state.



Scheme 1

A related compound was formed when (C_5H_5)$ZrCl_3$(dmf)$_2$ **6**[5] was dissolved in water (Scheme 2). In this case we have obtained some additional information about the initial hydrolytic reaction course taken. Dissolving complex **6** in H_2O (or in a 9 : 1 H_2O–dmf mixture) produced a strongly acidic solution (c = 0.05 mol l^{-1}, pH = 1.39) with a conductivity of 11.2 mS cm^{-1} (c = 0.05 mol l^{-1} in H_2O). Apparently, complex **6** dissolves in water with the formation of a 1 : 1 electrolyte, potentially a [(C_5H_5)$ZrCl_2$(dmf)]$^+$Cl$^-$ salt. Consequently, the starting material (C_5H_5)$ZrCl_3$(dmf)$_2$ was recovered when the water solvent was removed from the solution *in vacuo* after a short period of time (< 1 h). With time the dmf ligand at the activated [(C_5H_5)$ZrCl_2$]$^+$ moiety is attacked by water and hydrolysed to the formate ligand. After 4 d at ambient

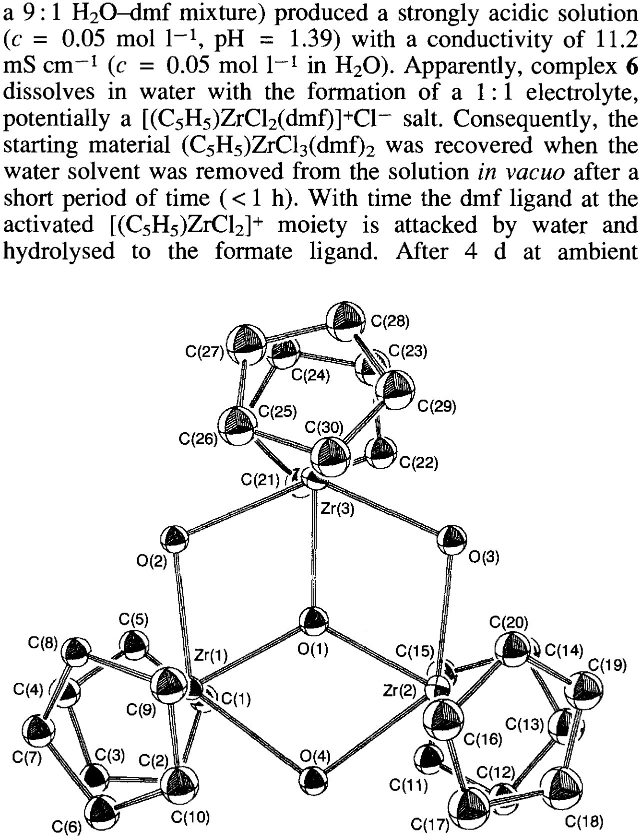


Fig. 1 Structure of the trinuclear complex **5**. Hydrogen atoms and external triflic acid are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O(1) 2.04(1), Zr(2)–O(1) 2.04(1), Zr(3)–O(1) 2.09(1), Zr(3)–O(2) 2.21(1), Zr(1)–O(2) 2.20(1), Zr(1)–O(4) 2.24(1), Zr(2)–O(4) 2.23(1), Zr(2)–O(3) 2.19(1), Zr(3)–O(3) 2.19(1), Zr(1)–O(1)–Zr(2) 122.4(6), Zr(1)–O(1)–Zr(3) 118.7(6), Zr(2)–O(1)–Zr(3) 119.0(7), Zr(1)–O(2)–Zr(3) 107.4(5), Zr(1)–O(4)–Zr(2) 106.4(5), Zr(2)–O(3)–Zr(3) 108.5(5).

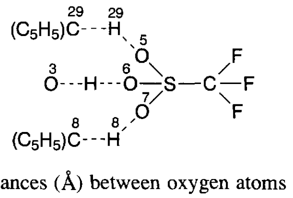
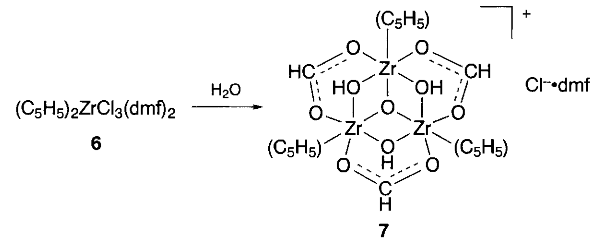


Fig. 2 Interatomic distances (Å) between oxygen atoms of triflic acid and [{(η^5-C_5H_5)$_2$ZrO}$_3$(μ_3-O)]: O(7)–C(8) 2.586, O(6)–O(3) 2.790, O(5)–C(29) 2.533

temperature the hydrolysis reaction was complete and the final product **7** crystallized from the solution.§

The hydrolysis product **7** was characterized by an X-ray crystal structure analysis (Fig. 3). It contains a trinuclear ligand-bridged $(C_5H_5)Zr$-cation cluster and a chloride anion. In addition, there is an independent dmf molecule and 0.5 equiv. H_2O in the crystal. The C_5H_5 ring at Zr(2) is disordered. The structure of the trinuclear zirconium cation cluster is close to C_{3v}-symmetry with the formate ligands orientated to one face and the μ-OH groups to the other. The average Zr–(μ-OH)–Zr angle is 104.4(1)°. Each formate ligand is symmetrically bridging between two zirconium centres [av. Zr–O(formate) 2.203(2), av. C–O(formate) 1.252(4) Å, av. Zr–O–C(formate) 129.9(2)°]. The centrally located oxygen atom O(1) is equally coordinated to all three zirconium atoms [Zr–O(1) 2.077(2) Å]. The central 'oxonium' oxygen centre is markedly pyramidal with an average Zr–O–Zr angle of 107.5(1)°. The zirconium coordination is distorted octahedral with the C_5H_5 group [av. Zr–(C_5H_5)(centroid) 2.544(6) Å] and the μ_3-O ligand *trans* orientated. The four *cis* oxygen–zirconium bonds are markedly bent toward the small μ_3-O centre with the zirconium placed *ca.* 0.5 Å above the best plane of the four 'equatorial' oxygen atoms.

This study further supports the great importance of cationic complexes in the hydrolysis chemistry of (η^5-cyclopentadienyl)group 4 metal complexes.[6] Efforts are being directed toward an elucidation of the mechanisms and intermediates involved in the hydrolysis reactions as well as to the study of the reactivity of the fascinating μ-O_3 zirconium complexes that have now become quite easily available in great substituent and ligand variability.



Scheme 2

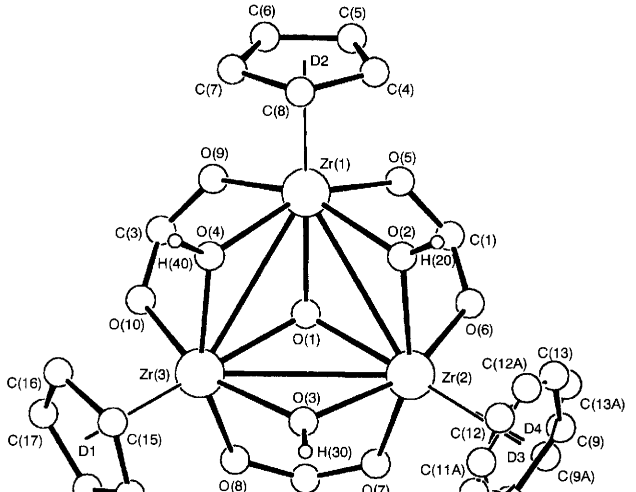


Fig. 3 A view of the molecular structure of **7** in the crystal

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Footnotes

† Mild hydrolysis of **4** also led to **5** in poor yield (8%); phosphorus derivatives arising from hydrolysis of **5** have not yet been identified.

‡ *Crystal data* for **5**: $C_{30}H_{30}O_4Zr_3 \cdot CF_3SO_3H$, M = 878, orthorhombic, space group $P2_12_12_1$, a = 10.027(3), b = 17.403(3), c = 17.893(6) Å, V = 3122(1) Å^3, Z = 4, F(000) = 1744, D_c = 1.866 g cm^{-3} λ(Mo-Kα) = 0.71073 Å, μ = 10.94 cm^{-1}. 5379 reflections were collected at 20 °C on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ mode (θ_{max} 31°) and an empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis using 2395 unique reflections with $I > 2\sigma(I)$ to R = 0.0623, R_w = 0.0681. Zirconium, oxygen and sulfur atoms were refined anisotropically, the other non-hydrogen atoms were refined isotropically. Hydrogen atoms were introduced in the calculation, but not refined. All calculations were performed on an ALLIANT VFX 80 mini super calculator using SHELX, CRYSTALS and ORTEP programs.

§ Synthesis and characterization of complex **7**: $(C_5H_5)ZrCl_3(dmf)_2$ **6** (2.04 g, 5.0 mmol) was dissolved in 100 ml of H_2O–dmf (9 : 1) under an argon atmosphere. After 4 d at ambient temperature, 0.91 g (23%) of product **7** of the composition $[\{(C_5H_5)Zr\}_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}HCO_2)_3]Cl \cdot HCONMe_2 \cdot 0.5H_2O$ were obtained. A satisfactory elemental analysis was obtained. ^1H NMR ($CDCl_3$): δ 1.57 (s, 3H, OH), 2.71 (s, 3H, HC), 2.87 and 2.95 (2s, 6H, NMe_2), 6.58 (s, 15H, C_5H_5), 6.69 (br s, 1H, H_2O), 8.05 (br s, 1H, dmf, HC=O). IR (KBr): ν/cm^{-1} 3270–2820 (br OH with overlapping sharp CH bonds), 1653, 1574, 1440, 1374, 1019, 820, 756, 606, 594. X-Ray crystal structure analysis: crystal size 0.24 × 0.34 × 0.47 mm, monoclinic, space group $C2/c$ (no. 15), a = 27.065(6), b = 10.729(2), c = 20.954(3) Å, β = 113.59(1)°, V = 5576.3 Å^3, Z = 8, D_c = 1.88 g cm^{-3}, F(000) = 3128, reflections used for cell parameters: $12.71 \leqslant \theta \leqslant 22.48°$, λ = 0.71069 Å. CAD-4 diffractometer, graphite monochromator, $[(\sin\theta)/\lambda]_{max}$ = 0.65 Å^{-1}, absorption coefficient μ = 12.35 cm^{-1}, absorption correction min. 1.304, max. 1.532, total reflections collected: 12467, ±*h*; ±*k*, +*l*, 6359 independent and 5730 observed reflections, 333 refined parameters, R = 0.030, R_w = 0.045, programs used: SHELX 86, SHELX 93, SCHAKAL.

Atomic coordinates, bond lengths and angles, and thermal parameters for **5** and **7** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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