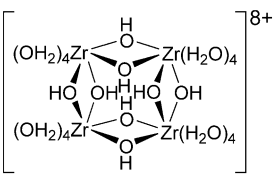
Cluster Compounds

A Water-Soluble Tetranuclear Zr^{IV} Compound Supported by the Kläui Tripodal Ligand: A Model of Zr^{IV} in Aqueous Media**

*Qian-Feng Zhang, Tony C. H. Lam, Eddie Y. Y. Chan, Samuel M. F. Lo, Ian D. Williams, and Wa-Hung Leung**

The aqueous chemistry of metal ions[1] is of significance owing to its relevance to metal-catalyzed organic reactions in water and the important roles of metal ions in biological systems.[2] We are particularly interested in the Zr^{IV}(aq) species that was found to be capable of hydrolyzing both activated and non-activated phosphodiesters in weakly acidic solutions with efficiency similar to that of Ce^{IV}.[3] The Zr^{IV}-based hydrolysis of phosphodiesters is potentially useful in molecular biology because unlike Ce^{IV}, Zr^{IV} is not redox active. In addition, the hydrolysis chemistry of Zr^{IV} is relevant to aqueous nuclear-fuel processing of tetravalent ions of the heavier metals.[4] In acidic solutions, depending upon pH and concentration, Zr^{IV} is known to exist in the forms of hydroxo-bridged trinuclear, tetranuclear, and octanuclear species.[1,4] The tetranuclear core $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ **1** (Scheme 1) has been characterized spectroscopically in solutions[5] and observed in the solid-state structure of $ZrOCl_2{\cdot}8H_2O$.[6] To better understand the chemistry of Zr^{IV} in water, we seek to synthesize models of Zr^{IV}(aq) based on the Kläui tripodal oxygen ligand $[CpCo\{P(O)(OR)_2\}_3]^-$ (denoted as L_{OR}^-, R = alkyl or aryl) (Scheme 2).[7] $[(L_{OR})ZrCl_3]$ and $[(L_{OR})_2Zr]^{2+}$ were synthesized by treating NaL_{OR} (R = Et, Ph) with $[CpZrCl_3]$ and $ZrCl_4$, in non-aqueous media.[8] Previously, we demonstrated that in aqueous solutions, the zirconyl species could be trapped by L_{OEt}^- and the resulting Zr^{IV}–L_{OEt} species reacted with HBF_4 to give $[L_{OEt}ZrF_3]$.[9] Herein, we report on the crystal structure of a water-soluble tetranuclear Zr^{IV}-L_{OEt} compound isolated from the reaction of zirconyl nitrate with NaL_{OEt} in water, and its reactions with phosphodiesters.



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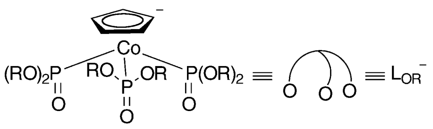
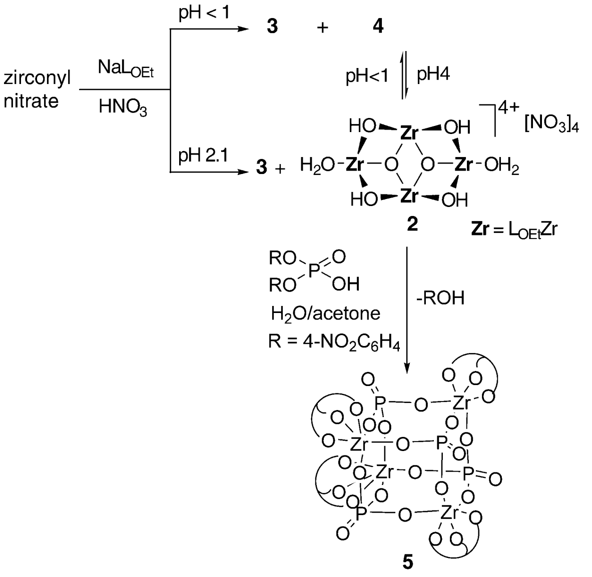
Scheme 1. Structure of **1**.



Scheme 2. Structure of $[CpCo\{P(O)(OR)_2\}_3]^-$ (L_{OR}^-).

Treatment of a solution of zirconyl nitrate (ca. 1.0 mM) in dilute HNO_3 (pH 2.1) with 1 equivalent of NaL_{OEt} gave a yellow solution, from which amixture (ca. 1:1) of $[(L_{OEt})_4Zr_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2][NO_3]_4$ **2** and $[(L_{OEt})_2Zr(NO_3)][NO_3]$ **3** were isolated (Scheme 3). At lower pH (< 1), the same reaction yielded a mixture (ca. 2:3) of **3** and $[L_{OEt}Zr(NO_3)_3]$ **4**. A pure sample of **3** was obtained in good yield by treating zirconyl nitrate with excess NaL_{OEt} in dilute HNO_3. The tetranuclear core of **2** is stable in both aqueous (at pH between 1 and 6, see below) and non-aqueous solutions, as evidenced by NMR spectroscopy and ESI mass spectrometry. The ^1H NMR spectrum of **2** exhibits two resonance signals for the Cp protons, consistent with its solid-state structure (see below). Compounds **2**–**4** could be identified by ^{31}P NMR spectroscopy (in $[D_6]$acetone: δ = 121.3, 120.9, and 123.8 ppm; in D_2O, δ = 121.9, 127.0, and 124.0 ppm]. In aqueous solutions at pH > 2, **4** hydrolyzed cleanly to give **2** according to ^{31}P NMR spectroscopy. As the pH of the resulting solution was gradually lowered to about 1, the ^{31}P resonance attributable to **4** started to appear, thus demonstrating the interconversion between mononuclear and



Scheme 3. Syntheses of **2**–**5**.

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tetranuclear Zr–L_{OEt} species in acidic solutions. However, a further decrease in pH resulted in precipitation of **4**, which has a low solubility in the HNO_3 solution.

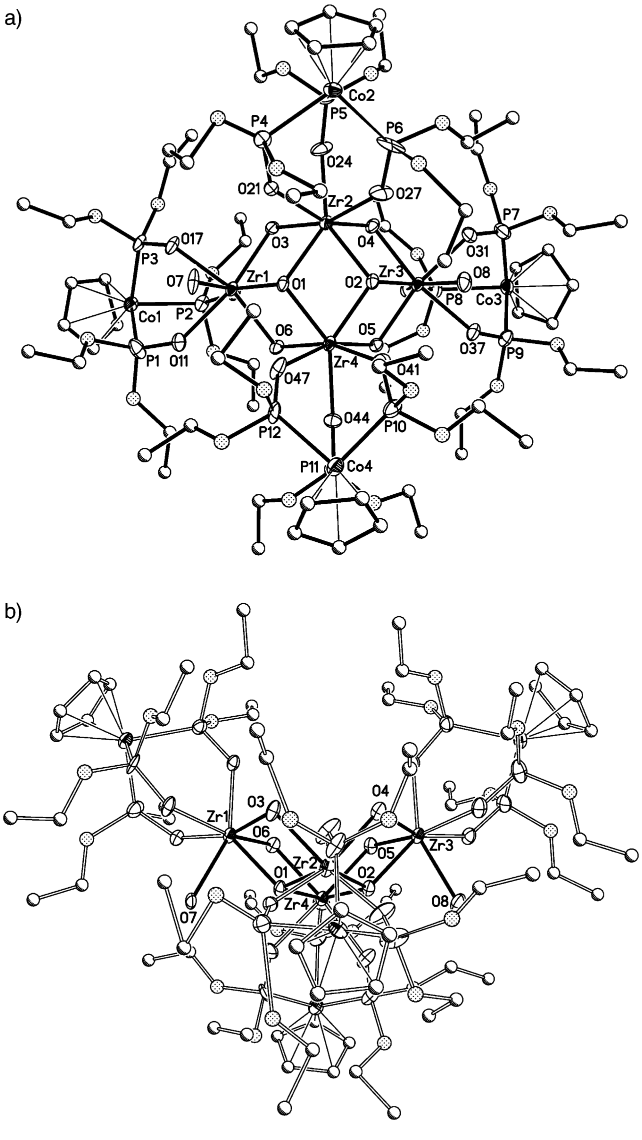


Figure 1. Molecular structure of $[(L_{OEt})_4Zr_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{4+}$ in **2**: a) top view; b) side view. Selected bond lengths [Å]: Zr-O(L_{OEt}) 2.122(8)–2.175(7), Zr-OH_2 2.211(7)–2.203(7), Zr-μ-OH 2.097(6)–2.157(7), Zr-μ_3-O 2.077(7)–2.096(7).

The solid-state structures of **2**–**4** have been established by X-ray crystallography.[10,11] The Zr_4 core in **2** (Figure 1) is similar to that in **1** except that it contains both 7- and 8-coordinated Zr centers and two μ_3-oxo ligands. The core structure of **2** can be described as bowl-shaped (Figure 1b) consisting of a $\{Zr_2(\mu_3\text{-}O)_2\}$ diamond base that contains 7-coordinated Zr centers linked to two 8-coordinated Zr centers through μ_3-oxo and μ-hydroxo bridges. The average Zr–μ-OH and Zr–OH_2 bond lengths of 2.140(7) and 2.207(7) Å, respectively, are comparable to those in **1**[6] but longer than the Zr–μ_3-O bond length (2.088(7) Å). It seems reasonable to assume that the μ_3-oxo bridges in **2** were formed by condensation of hydroxo bridges in **1** present in the zirconyl nitrate solution. The cation in mononuclear **3** consists of an 8-coordinated Zr center, two *fac*-κ_3-L_{OEt}^- and one κ^2-NO_3^- ligand with an average Zr–O(NO_3) bond length of 2.363(4) Å. Similar mononuclear Zr^{IV} bis-tripodal complexes have been previously reported.[8] The Zr atom in **4** is 9-coordinated containing one *fac*-κ_3-L_{OEt}^- and three unsymmetrically bonded κ_2-NO_3^- ligands with average longer and shorter Zr–O(NO_3) distances of 2.361(2) and 2.277(2) Å, respectively.[11]

The similarity of the core structure in **2** and **1** led us to investigate the reaction of **2** with the phosphodiester $(4\text{-}NO_2C_6H_4O)_2P(O)OH$ (BNPP), which is commonly used to probe the activity of metal ions towards phosphodiester hydrolysis.[4] The reaction between **2** and BNPP was monitored by NMR spectroscopy. The addition of BNPP to **2** in D_2O–[D_6]acetone (1:3) led to formation of an intermediate (^{31}P NMR $\delta = -19$ ppm), presumably a BNPP adduct of **2**. Gradually, the intensity of the signal at $\delta = -19$ ppm (^{31}P NMR) dropped and signals due to a new Zr phosphate compound, **5**, (^{31}P NMR $\delta = -23.7$, 122.8 ppm) appeared as well as those of 4-nitrophenol in the ^1H NMR spectrum. The hydrolysis of BNPP was completed in about 2.5 h, and **5** was isolated as the major zirconium product. Compound **4** reacted with $Ph_2P(O)OH$ to yield **5** and phenol, but no evidence of a reaction between **4** and $(MeO)_2P(O)OH$ was found. Compound **5** was identified as the cubane cluster $[(L_{OEt})_4Zr_4(\mu_3\text{-}PO_3)_4]$ by X-ray diffraction (Figure 2).[10] Although Zr^{IV} phosphates synthesized hydrothermally are well documented,[12] to our knowledge, **5** is the first structurally characterized Zr^{IV} phosphate cubane cluster compound.[13] The core of **5** is made up of four Zr and four P atoms at the corners of a cube, with the O atoms roughly located at the middle of the edges. The volume of the cavity of the cage is

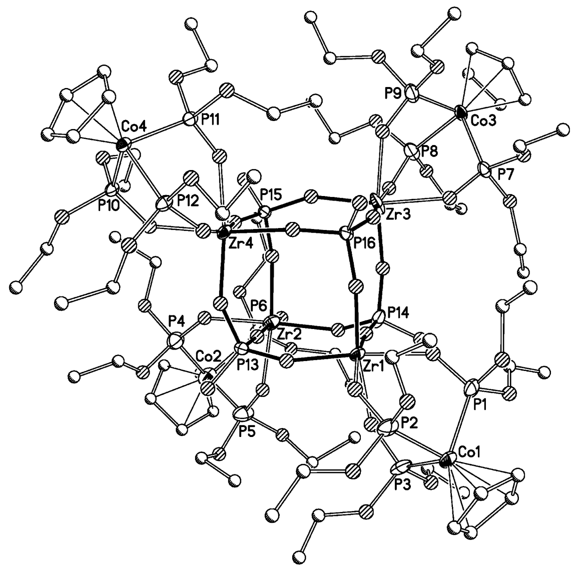
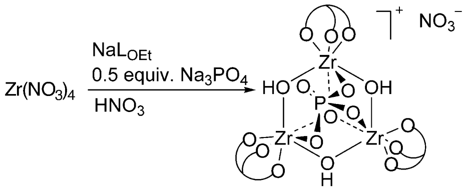


Figure 2. Molecular structure of $[(L_{OEt})_4Zr_4(\mu_3\text{-}PO_3)_4]$ **5**. Selected bond lengths [Å]: Zr-O(L_{OEt}) 2.109(9)–2.165(9), Zr-O(PO_4) 1.957(9)–2.040(9).

about 41 Å^3. The average Zr–O(phosphate) distance in **5** of 2.071(6) Å is comparable to those determined by powder diffraction (2.084(3) Å).[14] To gain further insight into the mechanism of formation of **5**, the reaction between zirconyl nitrate and Na_3PO_4 was studied. Treatment of a about 1 mM solution of zirconyl nitrate in dilute HNO_3 with 0.5 equivalent of Na_3PO_4 led to the isolation of the trinuclear cluster compound $[(L_{OEt})_3Zr_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu_3\text{-}PO_4)][NO_3]$, **6** (Scheme 4), which was characterized by single-crystal X-ray diffraction studies.[10] The cationic fragment in **6** consists of a $[(L_{OEt}Zr)_3(\mu\text{-}OH)_3]^{6+}$ core that is capped by one $\mu_3\text{-}O^{2-}$ and one $\mu_3\text{-}PO_4^{3-}$ ligand (Figure 3). Therefore, it seems likely that the BNPP first coordinates to Zr^{IV} and is then hydrolyzed to give PO_4^{3-}, which replaces the oxo and hydroxo ligands in **2** successively until the cubane cluster **5** is formed at the reaction ended. A preliminary result showed that $[(L_{OEt})_2Ce(NO_3)_2]$ prepared from $[NH_4]_2[Ce(NO_3)_6]$ and NaL_{OEt} is not capable of hydrolyzing BNPP. Treatment of $[(L_{OEt})_2Ce(NO_3)_2]$ with BNPP gave a structurally characterized bis-BNPP adduct $[(L_{OEt})_2Ce\{OP(O)(OC_6H_4NO_{2}\text{-}4)_2\}_2]$.[11]



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Scheme 4. Synthesis of **6**.

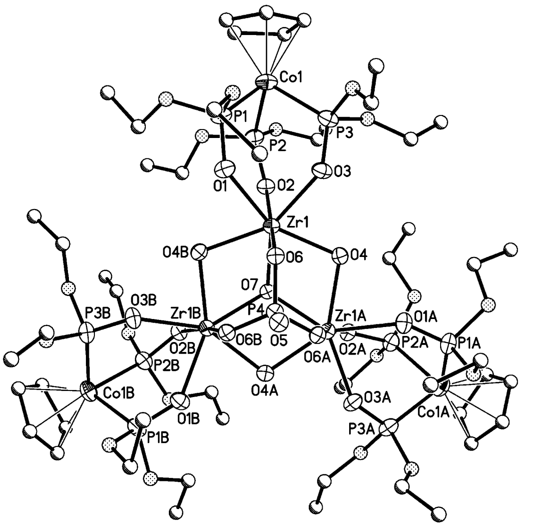

Figure 3. Molecular structure of the cation $[(L_{OEt})_3Zr_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu_3\text{-}PO_4)]^+$ in **6**. Selected bond lengths [Å]: Zr-O(L_{OEt}) 2.133(6)–2.199(7), Zr-μ-OH 2.164(6)–2.186(6), Zr-μ_3-O 2.078(3), Zr-O(PO_4) 2.071(6).

In conclusion, we have developed a new model for Zr^{4+} in water based on a water-soluble tetranuclear Zr^{IV}–L_{OEt} compound that can hydrolyze BNPP to give 4-nitrophenol and a Zr^{IV} phosphate cubane cluster. pH-dependent interconversion between monomeric and tetrameric $L_{OEt}Zr^{IV}$ species in aqueous media has been demonstrated. This modeling study offers an opportunity to better understand some reactions of Zr^{IV} in water that are otherwise difficult to follow by spectroscopic means. The investigation of structures and reactivities of polynuclear hydroxo/oxo-bridged $L_{OEt}Zr$ complexes in aqueous and non-aqueous media provides new insight into the complex aqueous chemistry of Group 4 metal ions.

Experimental Section

2: A mixture of zirconyl nitrate (0.674 mL of a 3.5 wt% solution in HNO_3, Aldrich, 0.102 mmol) and NaL_{OEt} (51 mg, 0.092 mmol) in water (12 mL) was stirred at room temperature for 30 min and filtered. The filtrate was extracted with CH_2Cl_2 (2 × 10 mL) and dried with anhydrous Na_2SO_4. The solvent was removed in vacuo to give a yellow solid (yield: 65%). ^{1}H NMR spectroscopy indicated that the crude product contained a mixture (ca. 1:1) of **2** and **3** that could be separated by fractional recrystallization. Single crystals of **2** were grown from acetone/hexane. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 1.46$ (t, ^3J(H,H) = 7 Hz, 72 H; CH_3), 4.28–4.38 (m, 48 H; OCH_2), 5.41 (s, 10 H; Cp), 5.46 ppm (s, 10 H; Cp). $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): $\delta = 121.3$ ppm (m). Elemental analysis (%) calcd for $C_{68}H_{148}N_4Co_4O_{56}P_{12}Zr_4$: C 28.3, H 5.16, N 1.94; found: C 28.6, H 5.41, N 1.69. MS (ESI): m/z 866.9721 ($[M-2H_2O-4NO_3-3H]^{3+}$).

5: BNPP (15 mg, 0.11 mmol) was added to a solution of **2** (35 mg, 0.043 mmol) in a mixture of acetone/water (3:1, 12 mL) and the solution was stirred at room temperature overnight. The volatile fractions were removed under vacuum, and the residue extracted into CH_2Cl_2. The solvent was removed under vacuum and the residue washed with water (3 × 2 mL) to give a yellow solid (yield: 80%). Recrystallization from acetone/hexane afforded X-ray quality yellow blocks. ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 1.40$ (t, ^3J(H,H) = 6.9 Hz, 72 H; CH_3), 4.35 (m, 48 H; OCH_2), 5.35 ppm (s, 20 H; Cp) and resonance signals due to co-crystallized 4-nitrophenol and BNPP. $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): $\delta = -23.7$ (m, PO_4), 122.8 ppm (m).

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[10] a) Crystal data for **2**·0.5 H_2O: $C_{68}H_{149}N_4O_{50.5}P_{12}Co_4Zr_4$ (including half water molecule), $M_r = 2803.15$, monoclinic, space group $P2_1/n$, $a = 16.875(2)$, $b = 24.887(3)$, $c = 29.219(4)$ Å, $\beta = 94.06(3)°$, $V = 12241(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.521$ Mg m^{-3}, $F(000) = 5748$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $\mu(Mo_{K\alpha}) = 1.093$ mm^{-1}. The P, O, and C atoms in one of the OEt groups were clearly disordered. Their site occupancies each set to 0.5 were isotropically refined and the corresponding carbon atoms were described without hydrogen atoms. The nitrogen and oxygen atoms of the nitrate anions were rigidly refined with fixed N–O bond distances. The final $R1 = 0.0912$ and $wR2 = 0.1809$ for 13319 reflections with $I > 2.0\sigma(I)$ and 907 variable parameters. The largest peak in the final difference map is 1.726 e Å^{-3}. b) Crystal data for 2[**5**]·7(4-$NO_2C_6H_4OH$)·(BNPP)·H_2O: $C_{190}H_{325}N_9O_{135}P_{33}Co_8Zr_8$ (including one water molecule), $M_r = 7118.80$, triclinic, space group $P\bar{1}$, $a = 16.5064(7)$, $b = 29.7615(12)$, $c = 31.8243(13)$ Å, $\alpha = 71.040(1)$, $\beta = 85.907(1)$, $\gamma = 80.236(1)°$, $V = 14569.3(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.623$ Mg m^{-3}, $F(000) = 7278$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $\mu(Mo_{K\alpha}) = 0.993$ mm^{-1}. There are two perpendicular arrangements of the molecules **5** in the crystal. No significant differences in bonding parameters between two molecules **5** were found. Satisfactory convergence of the *R* factors was obtained by least-squares block-matrix refinement. The carbon atoms of two 4-$NO_2C_6H_4OH$ and BNPP molecules were rigidly refined with fixed C–C bond lengths. Several carbon atoms in part of ethyl moieties were disordered. Their site occupancies were 70:30 (C45/C45A), 50:50 (C58/C58A), and 50:50 (C62/C62A). All carbon atoms in the ethyl groups were refined without hydrogen atoms. The final $R1 = 0.0811$ and $wR2 = 0.1447$ for 25793 reflections with $I > 2.0\sigma(I)$ and 3183 variable parameters. The largest difference residue peak of 2.490 e Å^{-3} in the final difference map is near to a cobalt atom (Co2). e) Crystal data for **6**·3 H_2O: $C_{51}H_{114}NO_{41}P_{10}Co_3Zr_3$ (including three water molecules), $M_r = 2157.58$, rhombohedral, space group $R\bar{3}$, $a = 18.1251(6)$, $c = 50.282(3)$ Å, $V = 14305.6(12)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.503$ Mg m^{-3}, $F(000) = 6636$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $\mu(Mo_{K\alpha}) = 1.072$ mm^{-1}. Two separated nitrate anion moieties were refined with half-occupancy, which should add up to unity to balance the overall charge of cation in **6**, and were isotropically refined with fixed N–O bond lengths. The final $R1 = 0.0812$ and $wR2 = 0.1877$ for 3270 reflections with $I > 2.0\sigma(I)$ and 332 variable parameters. CCDC-222659 (**2**·0.5 H_2O), CCDC-222662 (2[**5**]·7(4-$NO_2C_6H_4$-OH)·(BNPP)·H_2O) and CCDC-222663 (**6**·3 H_2O) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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