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Relation among the 2:2-, 1:1- and 1:2-type complexes of hafnium(IV)/zirconium(IV) with mono-lacunary α_2-Dawson polyoxometalate ligands: Synthesis and structure of the 2:2-type complexes $[\{\alpha_2\text{-}P_2W_{17}O_{61}M(\mu\text{-}OH)(H_2O)\}_2]^{14-}$ (M = Hf, Zr)

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ABSTRACT

The synthesis and characterization of di-nuclear Hf^{IV} and Zr^{IV} complexes (the Dawson 2:2-type complexes) sandwiched between 2 mono-lacunary α_2-Dawson polyoxometalate (POM) ligands, *i.e.*, $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]\cdot 17H_2O$ (Me_2NH_2-**1**) and $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Zr(\mu\text{-}OH)(H_2O)\}_2]\cdot 16H_2O$ (Me_2NH_2-**2**) are described. [*Note:* the moieties of their polyoxoanions are abbreviated simply as **1** and **2**, respectively.] A pair of Hf^{IV}- and Zr^{IV}-containing POMs belonging to the same family were herein isolated as dimethylammonium salts and were unambiguously characterized by complete elemental analysis, in addition to potassium analysis, TG/DTA, FTIR, single-crystal X-ray structure analysis, and solid-state (^{31}P CPMAS) and solution (^{31}P and ^{183}W) NMR spectroscopy. Polyoxoanions **1** and **2** were isostructural with each other. The central $[M_2(\mu\text{-}OH)_2(H_2O)_2]^{6+}$ (M = Hf, Zr) cation unit was composed of 2 polyhedral M units, which were linked through 2 μ-OH groups and contained 1 water molecule coordinated to each metal center. Since the mono-lacunary Dawson POM acts as an oxygen-donor quadridentate ligand, the Hf and Zr centers are 7-coordinate. The Dawson 2:2-type complexes were converted to the Dawson 1:2-type complexes $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Hf, Zr), or *vice versa*, in solution under appropriate conditions. Also, the Dawson 2:2-type complex can be reversibly converted to the 1:1-type complex under the pH-dependent conditions. The Dawson 2:2-type POMs **1** and **2** can be compared with the recently reported, Keggin 2:2-type POMs, *i.e.*, $[M_2(\mu\text{-}OH)_2(H_2O)_2]^{6+}$ (M = Hf, Zr) complexes sandwiched between 2 mono-lacunary α-Keggin POM ligands.

1. Introduction

The coordination chemistry of polyoxometalates (POMs) with d^0 transition-metals has been particularly well documented in the past few decades. Indeed, the d^0 transition-metal derivatives of polyoxoanions have attracted considerable attention in the fields of catalysis, surface science, and materials science, since POMs are often considered as molecular analogues of oxides in terms of structural analogy [1–13].

The Zr and Hf atoms in group IV metals, compared with the Ti atom which generally displays a maximum coordination number of 6 in POMs, show higher coordination numbers (6, 7 and 8) and, therefore, if they are incorporated in the POMs, a wide variety of molecular structures are anticipated. Furthermore, Lewis acid catalysis in the unsaturated coordination complexes of Zr and Hf atoms is also anticipated [14,15].

Following the development of titanium(IV)-containing POMs, there has been a dramatic advance in recent years in studies on various types of zirconium(IV) complexes in combination with several POMs [16–31]. On the other hand, very recently several examples of structurally characterized hafnium(IV)-containing POMs have been published. The following have been reported as a set with the zirconium analogue: mono-nuclear, 8-coordinate metal complexes (the 1:2-type complexes) with 2 mono-lacunary α-Keggin- and α_2-Dawson-type POMs, $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ and $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Hf, Zr) [32,33], di- and tetra-nuclear metal complexes sandwiched between 2 γ-Keggin silicotungstates $[(\gamma\text{-}SiW_{10}O_{36})_2\{M(H_2O)\}_2(\mu\text{-}OH)_2]^{10-}$ and $[(\gamma\text{-}SiW_{10}O_{36})_2\{M(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]^{8-}$ (M = Hf, Zr) [15], and hexa-nuclear metal complexes formed with 3 γ-Keggin silicotungstates $[M_6(O_2)_6(\mu\text{-}OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Hf, Zr) [34]. Of particular interest is the finding of the spontaneous resolution of the chiral POM, $[Hf(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ [35]. As a molybodo-POM, the 8-coordinate Hf complex, *i.e.*, $\{Hf[PMo_{12}O_{40}][(NH_4)PMo_{11}O_{39}]\}^{5-}$, has also recently been reported [36]. Very recently, 3 6-coordinate prismatic Hf^{IV}

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and Zr^{IV} ions, *i.e.*, the $[M_3(\mu\text{-OH})_3]^{9+}$ cluster cations (M = Hf, Zr), as compounds sandwiched between 2 tri-lacunary α-Keggin POMs such as $[M_3(\mu\text{-OH})_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$, were reported [37]. The di-nuclear, 7-coordinate Hf and Zr cluster cations (the Keggin 2:2-type complexes) sandwiched between 2 mono-lacunary α-Keggin POMs, $[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-OH})(H_2O)\}_2]^{8-}$ (M = Hf, Zr) [38] and the tetra-nuclear cluster cation species $[M_4(\mu_3\text{-O})_2(\mu\text{-OH})_2(H_2O)_4]^{10+}$ (M = Zr [23], Hf [39]) sandwiched between 2 di-lacunary Dawson POMs, *i.e.*, $[M_4(\mu_3\text{-O})_2(\mu\text{-OH})_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$, have also recently been reported.

The most important features in Zr- and Hf-containing POMs are seen in the architecture of the sandwich structure. A combination of the sandwiched cluster cations of Zr and Hf centers with the 2 lacunary POMs constitutes various types of sandwich POMs [16–39]. These aspects are characteristic of Zr- and Hf-containing POMs, but scarcely seen in Ti-containing POMs. In the traditional sandwich-type POM $[M_4(H_2O)_2\{P_2W_{15}O_{56}\}_2]^{n-}$ (M = transition-metal ions), made up of 2 tri-lacunary Dawson POMs, the Ti-containing sandwich POM was recently reported as a di-lacunary species containing 2 central titanium(IV) octahedra, *i.e.*, $[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]^{14-}$ [40] and $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$ [41].

In this work, we prepared di-nuclear hafnium(IV) and zirconium(IV) cluster cations, $[M_2(\mu\text{-OH})_2(H_2O)_2]^{6+}$ (M = Hf, Zr), sandwiched between 2 mono-lacunary α_2-Dawson POMs, *i.e.*, the Dawson 2:2-type complexes $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-OH})(H_2O)\}_2]\cdot 17H_2O$ (Me_2NH_2-**1**) and $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Zr(\mu\text{-OH})(H_2O)\}_2]\cdot 16H_2O$ (Me_2NH_2-**2**). A pair of Hf- and Zr-containing POMs belonging to the same structure-family was built up herein.

In this work, we clarified that the Dawson 2:2-type compounds (**1** and **2**) undergo a conversion to the previously reported Dawson 1:2-type complexes $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Hf, Zr) [32,33], respectively, or *vice versa*, in solution under appropriate conditions. From the pH-dependent ^{31}P NMR, we have also shown the relation between the dimeric (2:2-type) and monomeric (1:1-type) complexes [42].

Herein, we report full details of the synthesis and structure of Me_2NH_2-**1** and Me_2NH_2-**2**, and discuss the relation among the 2:2-type, 1:1-type and 1:2-type complexes.

2. Experimental

2.1. General

The following reactants were used as received: 0.1, 1 and 6 M aqueous HCl solutions (quantitative analysis grade), MeOH, Et_2O, Me_2NH_2Cl, Na_2CO_3, zirconium(IV) dichloride oxide octahydrate, hafnium(IV) dichloride oxide octahydrate (all from Wako); D_2O (Isotec). The precursor or the mono-lacunary α_2-Dawson POM, $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$ [43,44], and the Dawson 1:2-type complexes, *i.e.*, $K_{16}[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 27H_2O$ and $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 24H_2O$ [32], were prepared according to the literature and identified by FTIR, TG/DTA and ^{31}P NMR.

CHN elemental analyses were carried out with a Perkin–Elmer 2400 CHNS Elemental Analyzer II (Kanagawa University). Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under 10^{-3}–10^{-4} Torr overnight before analysis. Infrared spectra were recorded on a Jasco 4100 FTIR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku Thermo Plus 2 series TG/DTA TG 8120 instrument.

^{31}P NMR (161.70 MHz) spectra in a D_2O solution were recorded in 5-mm outer diameter tubes on a JEOL JNM-EX-400 FT-NMR spectrometer with a JEOL EX-400 NMR data-processing system. The ^{31}P NMR spectra were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. The ^{31}P NMR signals were shifted to +0.544 ppm by using 85% H_3PO_4 as a reference instead of 25% H_3PO_4.[1] ^{183}W NMR (16.50 MHz) spectra were recorded in 10-mm outer diameter tubes on a JEOL JNM-EX-400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system. The ^{183}W NMR spectra, referenced to an external standard of a saturated Na_2WO_4-D_2O solution, of the 2 compounds, Me_2NH_2-**1** and Me_2NH_2-**2**, were measured in a 0.1 M aqueous HCl solution, because the compounds were much more soluble in an acidic solution than in water so concentrations high enough to measure ^{183}W NMR were attained. The ^{183}W NMR signals were shifted to −0.787 ppm by using a 2 M Na_2WO_4 solution as a reference instead of the saturated Na_2WO_4 solution.

Solid-state ^{31}P CPMAS NMR (121.00 MHz) spectra were recorded in 6-mm outer diameter tubes on a JEOL JNM-ECP-300 FT-NMR spectrometer with a JEOL ECP-300 NMR data-processing system and were referenced to an external standard of $(NH_4)_2HPO_4$. Chemical shifts are reported as negative for resonances upfield of $(NH_4)_2HPO_4$ (δ 1.60).

2.2. Synthesis of $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-OH})(H_2O)\}_2]\cdot 17H_2O$ (Me_2NH_2-**1**)

$HfCl_2O\cdot 8H_2O$ (0.451 g, 1.10 mmol) was dissolved in 60 mL of water. To the solution was added 4.95 g, (1.00 mmol) of solid $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$, followed by stirring for 15 min. The dispersed solution was slowly adjusted to pH 2.0 with a 1 M aqueous HCl solution. This solution was stirred for 30 min in a water-bath at >90 °C. To the colorless solution cooled to room temperature, 12.0 g (147 mmol) of Me_2NH_2Cl was added, followed by stirring for 30 min. The white precipitate formed was collected on a membrane filter (JG 0.2 μm), washed with MeOH (30 mL × 3) and Et_2O (50 mL × 3), and dried *in vacuo* for 2 h. At this stage, dimethylammonium salt was obtained in a yield of 4.56 g.

Crystallization. The powder sample (0.5 g) was dissolved in 7 mL of an HCl acidic aqueous solution at pH 2.0 in a water-bath at 50 °C. After cooling to room temperature, the colorless solution was slowly evaporated at room temperature. After three days, colorless, clear granular crystals formed, which were collected on a membrane filter (JG 0.2 μm), washed with MeOH (30 mL × 3) and Et_2O (50 mL × 3), and dried *in vacuo* for 2 h. Yield 0.25 g (47.0% based on $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$).

The crystalline samples were soluble in water, but insoluble in diethyl ether and methanol. *Anal.* Calc. for $C_{28}H_{118}N_{14}O_{126}P_4W_{34}Hf_2$ or $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-OH})(H_2O)\}_2]$: H, 1.27; C, 3.58; N, 2.09; K, 0.00; O, 21.45; P, 1.32; W, 66.50; Hf, 3.80%. Found (CHN analysis of an independent preparation): H, 1.20 (1.19); C, 3.66 (3.46); N, 2.06 (2.02); K, <0.05; O, 20.9; P, 1.34; W, 67.3; Hf, 3.81%. Total 100.27%. A weight loss of 3.15% (weakly solvated or adsorbed water) was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis, suggesting the presence of 17 water molecules.

TG/DTA under atmospheric conditions: a weight loss of 3.47% due to dehydration was observed at below 150.3 °C; calc. 3.41% for a total of 19 water molecules, *i.e.*, 2 coordinated water molecules plus $x = 17$ hydrated water molecules in $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-OH})(H_2O)\}_2]\cdot xH_2O$. A weight loss of 7.79% was observed between 150.3 and 500.0 °C with an exothermic peak at 388.6 °C. IR (KBr) (polyoxometalate region): 1086 s, 1063 w, 1018 m, 947 vs, 924 m, 897 m, 783 vs, 679 m, 602 w, 565 w, 523 cm^{-1}. ^{31}P NMR (23.0 °C, D_2O): δ −9.84, −13.77. ^{31}P NMR (22.8 °C, 0.1 M aqueous HCl solution): δ −10.08, −13.72. ^{183}W

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[1] We have erroneously stated so far that the ^{31}P NMR signals were shifted to −0.101 ppm by using 85% H_3PO_4 as a reference instead of 25% H_3PO_4 [32,37,41,49].