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Complexes of Zr^{IV} and Hf^{IV} with monolacunary Keggin- and Dawson-type anions

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The reactions of the tetranuclear hydroxo complexes $[M_4(\mu_2\text{-}OH)_8(H_2O)_{16}]^{8+}$ (M = Zr or Hf) with the lacunary Keggin-type ($[\alpha\text{-}PW_{11}O_{39}]^{7-}$) and Dawson-type ($[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$) phosphotungstates in aqueous solutions produce the sandwich polyoxometalate complexes $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ (M = Zr (**1**) or Hf (**2**)) and $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Zr (**3**) and Hf (**4**)). The complexes were isolated and structurally characterized as salts with potassium and dimethylammonium cations. The zirconium and hafnium atoms have a square antiprismatic coordination environment (coordination number is 8). In all complexes, the mutual arrangement of the ligands corresponds to the *syn* isomer. Hafnium complexes **2** and **4** are the first structurally characterized polyoxometalate complexes of this metal. The structures of the resulting compounds were confirmed also by ^{31}P NMR spectroscopy in solution.

Key words: zirconium, hafnium, phosphotungstate, crystal structure, NMR spectroscopy.

Monolacunary polyoxometalate anions having defect Keggin- and Dawson-type structures can serve as tetradentate ligands with respect to quadruply and triply charged lanthanide and actinide ions of large radii (Th^{4+}, U^{4+}, Np^{4+}, Pu^{4+}, Am^{4+}, Cm^{4+}, Cf^{4+}, Ce^{4+}, Pr^{4+}, Ln^{3+}, Np^{3+}, Pu^{3+}, and Am^{3+}).[1–9] This gives rise to complexes with a metal : ligand ratio of 1 : 2, in which the metal atom has a typical square-antiprismatic coordination with the coordination number 8. Although this coordination environment is also typical of Zr^{IV} and Hf^{IV}, complexes of these metals with monolacunary Keggin- and Dawson-type anions were not documented. At the same time, it is known that in an aqueous medium, Zr^{IV} and Hf^{IV} are highly prone to hydrolysis and exist as the tetranuclear hydroxo complexes $[M_4(\mu_2\text{-}OH)_8(H_2O)_{16}]^{8+}$. Hence, it is not inconceivable that the tetranuclear $[M_4(\mu_2\text{-}OH)_8(H_2O)_{16}]^{8+}$ group can be involved in the structure as a whole. In recent years, several Zr^{IV} complexes with bi- and trilacunary ligands, which are derivatives of Keggin- and Dawson-type structures, have been synthesized. Among these structures are $[Zr_3(\mu_2\text{-}OH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{11-}$, $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$, $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$, $[Zr_2(\mu\text{-}OH)(H_2O)_2(AsOH)_2(AsW_7O_{28})(AsW_{10}O_{36})]^{9-}$, $[Zr_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$, $[Zr(PMo_{12}O_{40})(PMo_{11}O_{39})]^{6-}$, $[(\alpha\text{-}P_2W_{16}O_{59})Zr_2\text{-}(\mu_3\text{-}O)(Mal)]_2^{18-}$ (Mal is malate),[10–15] and the chiral tartrate complexes $[\{\alpha\text{-}P_2W_{15}O_{55}(H_2O)\}Zr_3\text{-}(\mu_3\text{-}O)(H_2O)(\text{L/D-tartH})(\alpha\text{-}P_2W_{16}O_{59})]^{15-}$.[16] In addition, the $[(PW_{11}NbO_{40})_2ZrCp]^{6-}$ (see Ref. 17) and $[\{ZrW_5O_{18}(\mu\text{-}OH)\}_2]^{6-}$ compounds were described. The latter complex was considered[18] as a molecular analog of heterogeneous ZrO_2-based catalysts on a WO_3 substrate. Tetrabutylammonium salts of the Zr-containing monolacunary Keggin-type anions $[CpZrXW_{11}O_{39}]^{n-}$ (X = Si, Ge, Ga, or B) exhibit catalytic activity in ethylene polymerization.[19] No data are available on Hf complexes with polyoxometalates. In the present study, we synthesized Zr^{IV} and Hf^{IV} complexes with the lacunary Keggin- ($[\alpha\text{-}PW_{11}O_{39}]^{7-}$) and Dawson-type ($[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$) phosphotungstates and established their crystal structures.

Results and Discussion

Complexes **1—4** are easily formed from stoichiometric mixtures of the reagents and isolated from aqueous solutions in high yields as mixed potassium dimethylammonium salts or pure potassium salts with a large number of hydrate water molecules:

$K_3(Me_2NH_2)_7[Zr(PW_{11}O_{39})_2] \cdot 13H_2O$ (**1**),
$K_3(Me_2NH_2)_7[Hf(PW_{11}O_{39})_2] \cdot 13H_2O$ (**2**),
$K_{16}[Zr(P_2W_{17}O_{61})_2] \cdot 44H_2O$ (**3**),
$K_{16}[Hf(P_2W_{17}O_{61})_2] \cdot 46H_2O$ (**4**).

For complexes with Dawson-type anions, it was demonstrated that the same products with a metal to ligand molar ratio of 1 : 2 are formed also from reaction mixtures containing reagents in a ratio of 1 : 1 at pH 5—6. In the latter case, excess Zr^{IV} is removed as insoluble hydroxide. Hence, the behavior of Zr^{IV} and Hf^{IV} in the systems under study differs from that of Ln^{III} and Ce^{IV}, for which

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both 1 : 1 and 1 : 2 complexes were isolated as solid phases.[19—21] All these compounds can be recrystallized from aqueous or aqueous methanolic solutions without decomposition.

The IR spectra of complexes **1** and **2** retain splitting of the ν(P—O) line into two bands (at 1056 and 1122 cm^{-1} for **1** and at 1057 and 1124 cm^{-1} for **2**) characteristic of the lacunary anion $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, which is indicative of the absence of interactions between the oxygen atoms of the phosphate group and the Zr and Hf atoms. The intense band at 957 (958) cm^{-1} corresponds to $W{=}O_{term}$ vibrations. The W—O—W and W—O—Zr(Hf) vibrations appear as a set of bands at 739, 814, 885 cm^{-1} (**1**) and 748, 824, 888 cm^{-1} (**2**). The IR spectra of complexes **3** and **4** show bands belonging to ν(P—O) vibrations at 1016, 1035, 1061, and 1085 cm^{-1}, which can be compared with a set of bands at 1012, 1050, and 1084 cm^{-1} in the spectrum of the lacunary phosphotungstate $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}] \cdot 19H_2O$ and at 1012 and 1090 cm^{-1} in the spectrum of the symmetrical Dawson-type anion $K_6[P_2W_{18}O_{62}] \cdot 14H_2O$. The intense band at 945 cm^{-1} corresponds to $W{=}O_{term}$ vibrations. The W—O—W and W—O—Zr(Hf) vibrations appear as a set of bands at 741—923 cm^{-1}.

The structure of the anion in complex **1** is shown in Fig. 1, *a*. The crystal structure contains one symmetrically independent anion in a general position. The coordination polyhedra of the zirconium and hafnium atoms can be described as slightly distorted square antiprisms with broken square faces. Each $[PW_{11}O_{39}]^{7-}$ anion serves as a tetradentate ligand with a set of donor atoms $O^A{}_2O^B{}_2$.

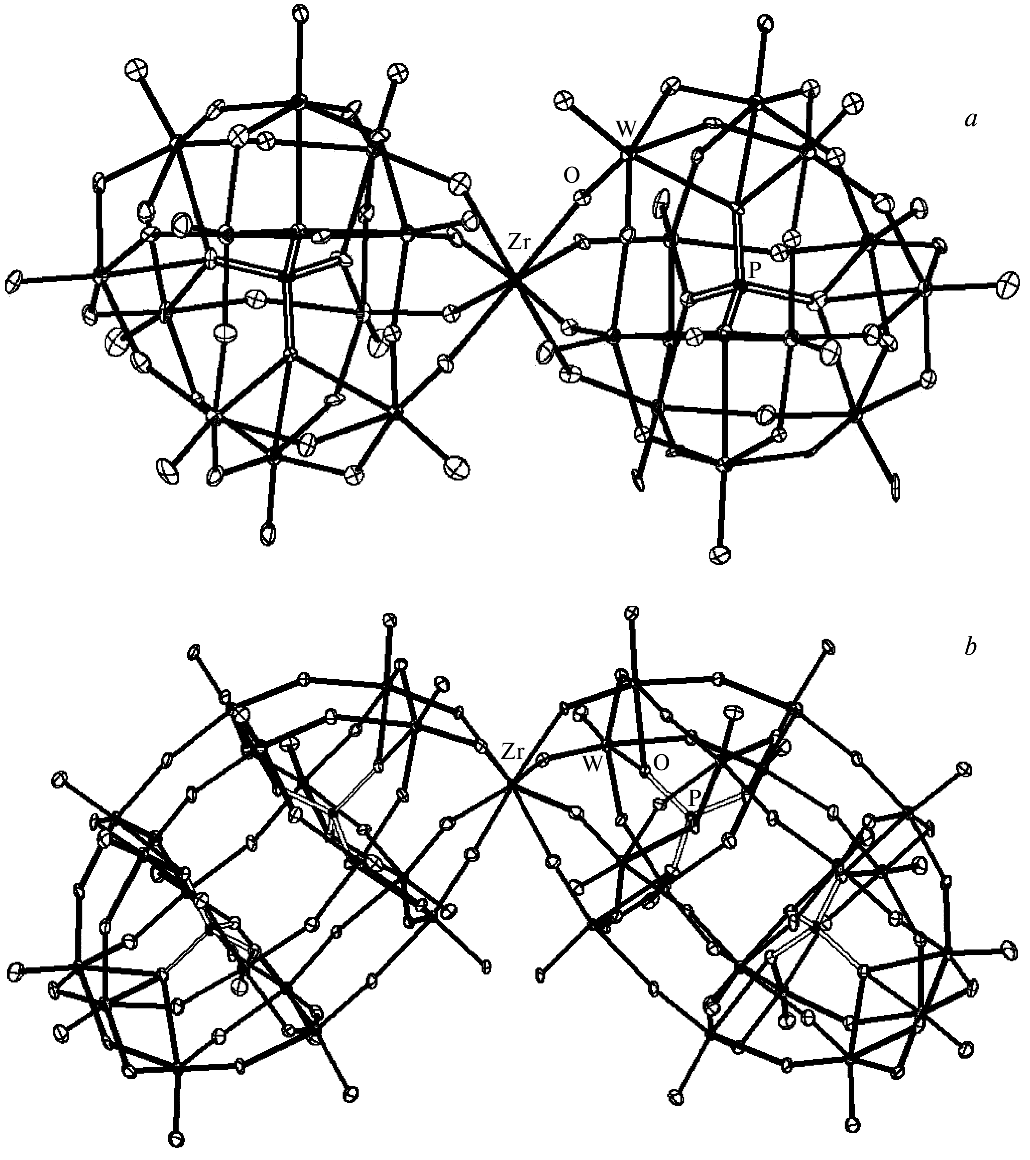

Fig. 1. Structures of the anions in the crystal structures of **1** (*a*) and **3** (*b*) represented by anisotropic displacement ellipsoids drawn at the 50% probability level.

The A-type oxygen atoms are coordinated to the tungsten atoms, which share the μ_3-oxygen atom with the phosphate group (after removal of one tungstyl group from the normal Keggin-type structure $[\alpha\text{-PW}_{12}O_{40}]^{3-}$). The B-type oxygen atoms are coordinated to the tungsten atoms, which are involved in one of the three remaining W_3O_{13} moieties containing the μ_4-oxygen atom. The *syn* configuration exists as a result of such arrangement that only the A-type oxygen atoms are at one side of the plane perpendicular to the square faces of the square antiprism, whereas only the B-type oxygen atoms are at the opposite side. The P—Zr—P angle is 159.7°. In the crystal structure, the *syn* isomer is apparently stabilized by K^+—O interactions (Fig. 2, *a*). The average Zr—O distance is 2.21(3) Å. The other distances have typical values. The overall sizes of the anion are ~10×11×19 Å taking into account the distances to the most remote oxygen atoms in three directions. In the crystal packing, the highly charged anions are completely isolated from each other by a coat of potassium and dimethylammonium cations. In the mixed-ligand complex $[Zr(PMo_{12}O_{40})(PMo_{11}O_{39})]^{6-}$, the $[PMo_{11}O_{39}]^{7-}$ anion coordinates the Zr^{IV} atom in a similar fashion as a tetradentate ligand (Zr—O, 2.15 and 2.21 Å).**[14]**

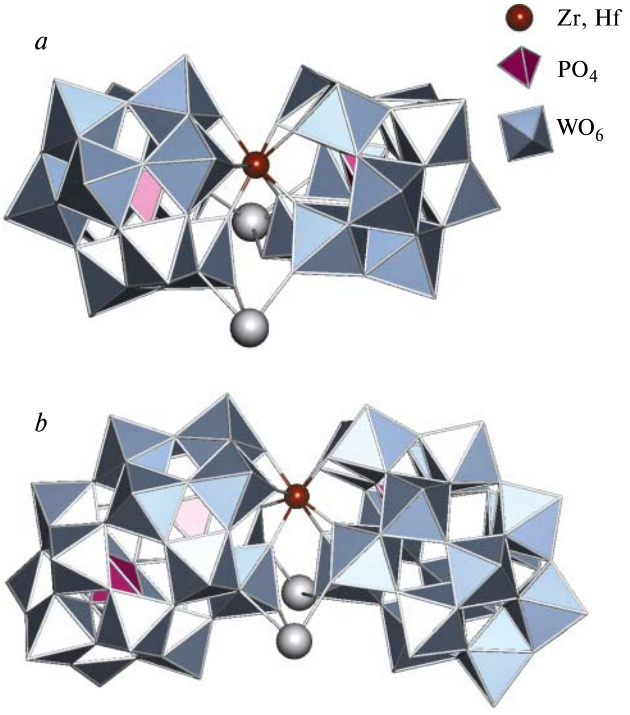

Fig. 2. Polyhedral representation of the structures of anions **1**, **2** (*a*) and **3**, **4** (*b*). Two potassium cations, which link two phosphotungstate fragments to each other, are indicated by spheres.

Note. Figure 2 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

The structures of the anions in **3** and **4** are shown in Fig. 1, *b*. The anions occupy special positions on a twofold axis. The heterometal atom occupies a vacant position of the lacunary anion (see Fig. 1, *b*). The coordination polyhedra of the zirconium and hafnium atoms are slightly distorted square antiprisms with broken square faces. The $[M(P_2W_{17}O_{61})_2]^{16-}$ anions adopt a *syn* conformation, which is stabilized *via* coordination of two K^+ ions in a half-closed cavity between two coordinated anions (tightening effect, see Fig. 2, *b*). The same *syn* conformation is typical of structurally characterized Lu^{3+}, Ce^{3+}, Ce^{4+}, U^{4+}, and Th^{4+} complexes with the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ anion.**[9]** The average Zr—O distance in complex **3** is 2.20(3) Å; Hf—O in **4**, 2.19(2) Å. The W—O and P—O distances have typical values. The sizes of the anion are ~10×12×23 Å. In the crystal packings, the anions are completely isolated from each other by potassium cations and water molecules.

The ^{31}P NMR spectra of aqueous solutions of the complexes are consistent with the structural data. The spectrum of complex **1** shows one signal at δ −14.6 shifted upfield compared to that of the uncoordinated $[\alpha\text{-PW}_{11}O_{39}]^{7-}$ anion (δ −10.6). The spectra of complexes **3** and **4** have two signals with equal intensity corresponding to two different types of phosphorus atoms, which is in complete agreement with the proposed structure.

To summarize, we synthesized the first complexes of monolacunary Keggin- and Dawson-type anions with Zr^{IV} and Hf^{IV}. In both cases, the coordination number of the heterometal atom is 8 and its coordination sphere is completely saturated due to the presence of the oxygen atoms of polyoxotungstate. The existence of 1 : 1 complexes with monolacunary anions, which are characteristic of lanthanide ions (along with 1 : 2 complexes)**[20]** but are unknown for Zr^{IV} and Hf^{IV}, remains an open question.

Experimental

The starting lacunary phosphotungstates $K_7[\alpha\text{-PW}_{11}O_{39}]\cdot14H_2O$ and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot19H_2O$ were synthesized according to known procedures.**[22,23]** Oxochlorides $MOCl_2\cdot8H_2O$ ($[M_4(\mu_2\text{-OH})_8(H_2O)_{16}]Cl_8$) were synthesized by dissolution of tetrachlorides MCl_4 in a 3 *M* HCl solution followed by crystallization from the resulting solution. Other commercial reagents were used without additional purification. The IR spectra in the 4000—400 cm^{-1} region were recorded on a Scimitar FTS 2000 instrument in KBr pellets. The weight loss curves were measured at a heating rate of 10 deg min^{-1} under helium on a TGD-7000RH thermal analyzer. The ^{31}P NMR spectra were recorded on a Bruker MSR-400 instrument using 85% H_3PO_4 as the external standard.

Tripotassium heptakis(dimethylammonium) bis(undecatungstophosphate)zirconate tridecahydrate, $K_3(Me_2NH_2)_7[Zr(PW_{11}O_{39})_2]\cdot13H_2O$ (1). A freshly prepared solution of $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ (0.16 g, 0.50 mmol) in water (5 mL) and a solution of $[Me_2NH_2]Cl$ (0.40 g, 4.94 mmol) in water (5 mL) were added with vigorous stirring to a freshly prepared hot solution of $K_7[PW_{11}O_{39}] \cdot 14H_2O$ (3.20 g, 1.0 mmol) in water (15 mL). The hot turbid solution was filtered and allowed to evaporate in an open beaker at ~20 °C. After 2 days, colorless long needle-like crystals of the complex were obtained. Single crystals suitable for X-ray diffraction were grown by vapor diffusion of methanol into an aqueous solution of the complex. The yield was 2.50 g (83%). Found (%): C, 2.75; H, 1.13; N, 1.61. $C_{14}H_{82}K_3N_7O_{91}P_2W_{22}Zr$. Calculated (%): C, 2.75; H, 1.35; N, 1.60. IR, ν/cm^{-1}: 439 v.w, 486 sh, 516 m, 598 v.w, 739 s, 814 s, 885 s, 958 s, 1017 w, 1056 s, 1122 m, 1413 w, 1439 v.w, 1465 m, 1616 m (br.), 2802 m, 2969 w, 3028 w, 3147 (br.), 3504 s (br.). ^{31}P NMR, δ: −14.6 (1 P).

Tripotassium heptakis(dimethylammonium) bis(undecatungstophosphate)hafnate tridecahydrate, $K_3(Me_2NH_2)_7[Hf(PW_{11}O_{39})_2] \cdot 13H_2O$ (2). Complex **2** was synthesized analogously from $K_7[PW_{11}O_{39}] \cdot 14H_2O$ (3.20 g, 1.0 mmol), $[Hf_4(OH)_8(H_2O)_{16}]Cl_8$ (0.21 g, 0.5 mmol), and $[Me_2NH_2]Cl$ (0.40 g, 4.94 mmol) as colorless needle-like crystals in a yield of 2.60 g. Found (%): C, 2.34; H, 1.39; N, 1.30. $C_{14}H_{82}HfK_3N_7O_{91}P_2W_{22}$. Calculated (%): C, 2.71; H, 1.33; N, 1.58. IR, ν/cm^{-1}: 439 v.w, 486 sh, 517 m, 599 v.w, 748 s, 824 s, 888 s, 959 s, 1016 w, 1057 s, 1124 m, 1413 w, 1439 v.w, 1465 m, 1616 m (br.), 2798 w, 2965 w, 3034 w, 3151 (br.), 3465 s (br.).

Hexadecapotassium bis(heptadecatungstodiphosphate)zirconate tetratetracontahydrate, $K_{16}[Zr(P_2W_{17}O_{61})_2] \cdot 44H_2O$ (3). A freshly prepared solution of $[Zr_4(OH)_8(H_2O)_{16}]Cl_8$ (33 mg, 0.10 mmol) in water (5 mL) was added with vigorous stirring to a freshly prepared solution of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}] \cdot 19H_2O$ (1.00 g, 0.20 mmol) in water (50 mL). The solution, which initially turned turbid, became transparent after 15 min. Potassium chloride (8.25 g) was added to the resulting solution, and a white crystalline precipitate of complex **3** immediately formed. The precipitate was filtered off and dissolved in hot water (100 mL). The solution was filtered. After 1 day, colorless crystals of the complex precipitated from the filtrate cooled to ~20 °C. The yield was 1.15 g (71%). IR, ν/cm^{-1}: 479 w, 528 m, 567 v.w, 604 w, 741 s, 806 s, 923 m, 945 s, 1016 w, 1035 w, 1061 w, 1085 s, 1620 m, 1729 sh, 3486 sh, 3562 s. TGA data: the weight loss is 7.87% (−44 H_2O, theoretically, 8.49%). ^{31}P NMR, δ: −9.4, −14.1 (1 P each).

Hexadecapotassium bis(heptadecatungstodiphosphate)hafnate hexatetracontahydrate, $K_{16}[Hf(P_2W_{17}O_{61})_2] \cdot 46H_2O$ (4). Complex **4** was prepared analogously to complex **3** from $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}] \cdot 19H_2O$ (1.00 g, 0.20 mmol) and $[Hf_4(OH)_8(H_2O)_{16}]Cl_8$ (42 mg, 0.10 mmol). The yield was 1.53 g (75%). The IR spectrum is identical within experimental error (±1 cm^{-1}) to the spectrum of the Zr complex. TGA data: the weight loss is 7.64% (−46 H_2O, theoretically, 8.23%). ^{31}P NMR, δ: −9.5, −14.1 (1 P each).

X-ray diffraction study. The structures of complexes **1**, **3**, and **4** were established by X-ray diffraction. Compound **2** was demonstrated to be isostructural to **1**. However, low quality of the crystals did not allow us to collect X-ray diffraction data and refine the unit cell parameters. Colorless needle-like crystals are very unstable in air. The X-ray diffraction data sets were collected on a four-circle automated Bruker X8APEX diffractometer equipped with a CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The

Table 1. Crystallographic data and the X-ray diffraction data statistics for complexes **1**, **3**, and **4**

Parameter	1	3	4
Molecular formula	$C_{14}H_{82}K_3N_7O_{91}P_2W_{22}Zr$	$H_{88}K_{16}O_{166}P_4W_{34}Zr$	$H_{92}HfK_{16}O_{168}P_4W_{34}$
Molecular weight	6052.43	9836.30	9950.60
T/K	100.0(2)	100.0(2)	100.0(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a/Å	12.2075(2)	47.368(3)	47.3869(19)
b/Å	20.3023(5)	14.5023(9)	14.5185(6) A
c/Å	22.8352(6)	22.7184(12)	22.7317(9)
α/deg	66.6010(10)	90	90
β/deg	79.3400(10)	91.272(2)	91.244(2)
γ/deg	77.6400(10)	90	90
V/Å^3	5042.0(2)	15602.6(15)	15635.4(11)
Z	2	4	4
d_{calc}/g cm^{-3}	3.987	4.187	4.227
μ/cm^{-3}	25.34	25.605	26.149
$2\theta_{max}$/deg	55.0	60.0	67.0
Number of measured/independent /observed ($I > 2\sigma(I)$) reflections	38306/22567/15146	83995/22157/18214	143832/28121/21564
R_{int}	0.042	0.0436	0.0559
Crystal dimensions/mm	0.23×0.11×0.11	0.178×0.065×0.041	0.315×0.156×0.064
Number of parameters in refinement	1044	1020	1014
R_1 ($I > 2\sigma(I)$)	0.044	0.0333	0.0509
wR_2 (based on all reflections)	0.105	0.0810	0.1480
GOOF	1.012	1.022	1.061
Residual electron density (min/max)/e Å^{-3}	−3.02/7.40	−2.676/6.917	−4.001/6.646

Table 2. Selected bond lengths (d) in the crystal structures of **1**, **3**, and **4**

Bond	d/Å		
	1	**3**	**4**
Zr(Hf)—O	2.166(10)—2.232(10) (2.21(3))	2.169(6)—2.230(6) (2.20(3))	2.163(7)—2.222(8) (2.19(2))
$W—O_{term}$	1.694(10)—1.736(11) (1.71(1))	1.708(6)—1.728(6) (1.718(6))	1.701(8)—1.731(8) (1.72(1))
$W—O_{brid}$	1.831(11)—2.046(11) (1.93(5))	1.826(6)—2.047(6) (1.94(9))	1.813(8)—2.061(7) (1.94(8))
P—O	1.500(11)—1.562(11) (1.54(2))	1.524(6)—1.574(6) (1.54(2))	1.525(8)—1.579(8) (1.54(2))

Note. The lower limit of the range corresponds to the minimum value; the upper limit, to the maximum value; the average value is given in parentheses.

crystallographic data and the X-ray data collection and refinement statistics are given in Table 1. Semiempirical corrections for absorption were applied based on the intensities of equivalent reflections with the use of the SADABS program.[24] The structures of **1** and **3** were solved by direct methods using the SIR2004 program package[25] and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the SHELXTL program package.[26] The structure of **4** is isostructural to **3** and was refined based on the model for **3**. The potassium cations in the structures of **3** and **4** and the solvate water molecules in all structures are disordered. The occupancies of the oxygen atom positions for each structure were refined independently and then fixed. The occupancies of the disordered potassium cations were refined with constraints imposed on the total occupancy corresponding to the requirements of electroneutrality of the crystals. In the crystal structure of **1**, one of the dimethylammonium cations is also disordered, and the atomic coordinates of this cation were refined with geometric constraints. Some of disordered atoms were refined isotropically. Selected bond lengths are given in Table 2.

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