The Synthesis and Structure of Trimetaphosphimato Complexes of Hafnium and Zirconium

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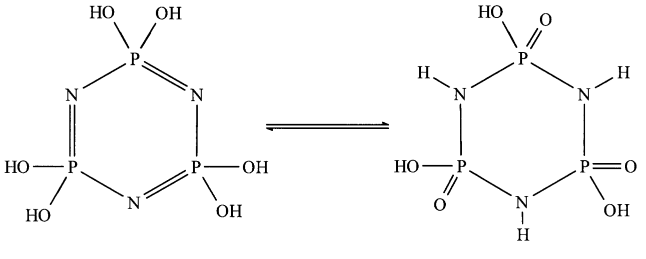
The (trimetaphosphimato)hafnates and -zirconates $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O$ [**1**, $Pa\bar{3}$, a = 22.687(3) Å, Z = 8], $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O$ [**2**, $R\bar{3}$, a = 14.350(2), c = 50.348(10) Å, Z = 6], $Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O$ [**3**, $Pa\bar{3}$, a = 22.693(3) Å, Z = 8], and $Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O$ [**4**, $R\bar{3}$, a = 14.303(2), c = 50.284(10) Å, Z = 6] were obtained by the stoichiometric reaction of $HfOCl_2\cdot 8\ H_2O$ and $ZrOCl_2\cdot 8\ H_2O$ with an aqueous solution of $Na_3(PO_2NH)_3\cdot 4\ H_2O$, followed by the diffusion-controlled addition of methanol. During these reactions compounds **1** and **2**, or **3** and **4**, crystallized simultaneously and the hafnium and zirconium complexes **1** and **3**, as well as **2** and **4**, were found to be isostructural and isomorphous. The characteristic structural feature which is central to **1**, **2**, **3**, and **4** is the complex tetranuclear anion $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ with M = Zr or Hf. The anion consists of five corner-sharing adamantanoid cages. The central cage, $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6\}^{8+}$, has a tetracoordinated oxygen atom in the middle, and the other cages are formed by the trimetaphosphimate ions acting as tridentate ligands which coordinate to Hf or Zr. The water content of the compounds **1**−**4** could not be determined unequivocally by chemical analyses since the compounds are always obtained as mixtures of the rhombohedral (**2**/**4**) and cubic (**1**/**3**) phases. Thermal decomposition of compounds **1**−**4** starts above 120 °C and leads to the formation of HfP_2O_7 and ZrP_2O_7/$NaZr_2(PO_4)_3$, with the evolution of H_2O and NH_3. DSC measurements gave no evidence that the compounds **1** and **2**, or **3** and **4**, might be transformed into each other by heating.

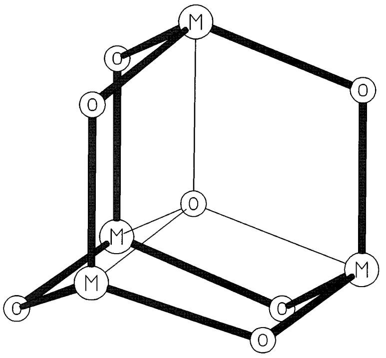
In contrast to the cyclotrimetaphosphates[1], whose structures have been well investigated, little is known concerning the X-ray-crystallographic results of the cyclotrimetaphosphimates (tri-μ-imidocyclotriphosphates), although the first synthesis of cyclotrimetaphosphimates was described in 1896.[2] Since there is the possibility of tautomeric forms, $[P(NH)O_2]_3{}^{3-}$ and $[PNO(OH)]_3{}^{3-}$, these compounds have been investigated intensively using IR spectroscopy,[3] but until now only a few crystal structures of the trimetaphosphimates have been known.[4] The two tautomeric forms of trimetaphosphimic acid are shown in Figure 1. IR spectroscopy, as well as single-crystal structure analyses, have confirmed the existence of the μ-imido form in both the solid state and solution. In principle coordination by both nitrogen and oxygen is possible, but up to the present exclusively coordination via oxygen has been found. Nevertheless, interactions between Ag and N are observed in $Ag_3(PO_2NH)_3$, leading to a strong distortion of the P_3N_3 ring.[4c] This interaction is also confirmed by the existence of $Ag_6(PO_2N)_3$, which was first described by Stokes;[2] however, the crystal structure has not yet been determined. The trimetaphosphimate ion can act as a monodentate ligand in combination with monovalent ions such as Na^+, K^+, Ag^+, $NH_4{}^+$, or $C(NH_2)_3{}^+$,[4] as bidentate and bridging ligand with the divalent ions Cu^{2+}, Co^{2+}, Zn^{2+} in $Na_4\{Cu[(PO_2NH)_3]_2\}\cdot 10\ H_2O$ and $Na\{M(PO_2NH)_3\}\cdot 7\ H_2O$ (M = Zn, Co),[5] as a tridentate ligand with Ga^{3+} in $Na_3\{Ga[(PO_2NH)_3]_2\}\cdot 12\ H_2O$,[6] and as tridentate and bridging ligand in $K_{1.3}(NH_4)_{1.7}\{Pr[(PO_2NH)_3]_2\}\cdot 8\ H_2O$.[7]

Figure 1. Tautomeric forms of trimetaphosphimic acid $H_3(PO_2NH)_3$



Because of the interesting properties of zirconium phosphates and zirconium phosphorus oxide nitrides, which means that they can be used as ion exchangers and catalysts,[8][9] we investigated the reaction of $Na_3(PO_2NH)_3\cdot 4H_2O$ with zirconium or hafnium salts, and the use of these trimetaphosphimates as nitrogen-containing precursors for the synthesis of oxonitridophosphates.

Figure 2. Adamantanoid metal-oxygen cage in the $[M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]^{8+}$ core (M = Zr, Hf)



Results

The reaction of $Na_3(PO_2NH)_3 \cdot 4\ H_2O$ with $HfOCl_2 \cdot 8\ H_2O$ or $ZrOCl_2 \cdot 8\ H_2O$, leads to the formation of the four new compounds $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 18\ H_2O$ (**1**), $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 21\ H_2O$ (**2**), $Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 18\ H_2O$ (**3**) and $Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 21\ H_2O$ (**4**) which are always obtained as mixtures (**1/2** and **3/4**) of the rhombohedral (**2/4**) and cubic (**1/3**) phases. The respective Zr and Hf compounds (**1/3** and **2/4**) are isotypic and isomorphous, with distinct crystals of cubic and rhombohedral habit. The characteristic structural feature of all four compounds are the tetranuclear complex anions $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ with M = Hf, Zr. Despite the topologically differing crystal structures of **1/3** (cubic phase) and **2/4** (rhombohedral phase) the anions $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ have almost exactly the same topology in both cases. The cores of the $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions consist of a slightly distorted tetrahedral arrangement of the transition metal, Hf or Zr (Table 1), with six edge-bridging OH groups (μ-OH) and one tetracoordinated O atom (μ_4-O) at the center of the M_4 tetrahedron, thus forming an adamantanoid cage $M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6{}^{8+}$ as shown in Figure 2. The H atoms of the bridging μ-OH groups have not been localized, but on the basis of the analytical results which show the molar ratio to be Na/P/N/M = 1:3:3:1 for all four compounds, the μ-OH groups have to be assumed to be connecting the Zr and Hf atoms. In addition to this centered cage, four more adamantanoid cages are formed by tridentate coordination of the trimetaphosphimate ions, $(PO_2NH)_3{}^{3-}$, to the metal ions. The trimetaphosphimate ions exhibit the chair conformation and are bound to the metal centers through the three oxo groups. The entire complex ion $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$, consisting of five corner-linked adamantanoid cages, is shown in Figure 3. Similar to monoclinic ZrO_2 (baddeleyite), and one polymorphic form of HfO_2, the metal atoms exhibit the coordination number seven. The anions have the crystallographic symmetry C_3 with the tetracoordinated oxygen atom and one of the metal atoms (M2, M = Hf, Zr) situated on the threefold axes. The M–O bond lengths of the adamantanoid central cages in **1**–**4** (Table 1) compare well with the average bond lengths in corresponding compounds which have a coordination number of seven $\{[Zr_4(\mu_4\text{-}O)(\mu\text{-}OnPr)_6]^{8+}/Zr{-}O$: 215–223 pm[10], monoclinic HfO_2: 203–225 pm[11], monoclinic ZrO_2: 205–227 pm[12]}. The $M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6{}^{8+}$ cage is only slightly distorted from the ideal tetrahedral symmetry. Unlike the situation for the trimetaphosphimato zirconates, where the distortion of the $Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6{}^{8+}$ cage in the cubic phase (**3**) is slightly smaller than in the rhombohedral phase (**4**), the opposite is found for the distortion of the $Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6{}^{8+}$ cages in the (trimetaphosphimato)hafnates **1** and **2** (Table 1). Therefore, within the accuracy of the measurements, the metal atoms of the central ada-

Figure 3. View of the $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions (M = Hf, Zr) in the cubic phase and rhombohedral phase [top: ball-stick model; bottom: polyhedron formed by metal (grey) and P atoms (white)]

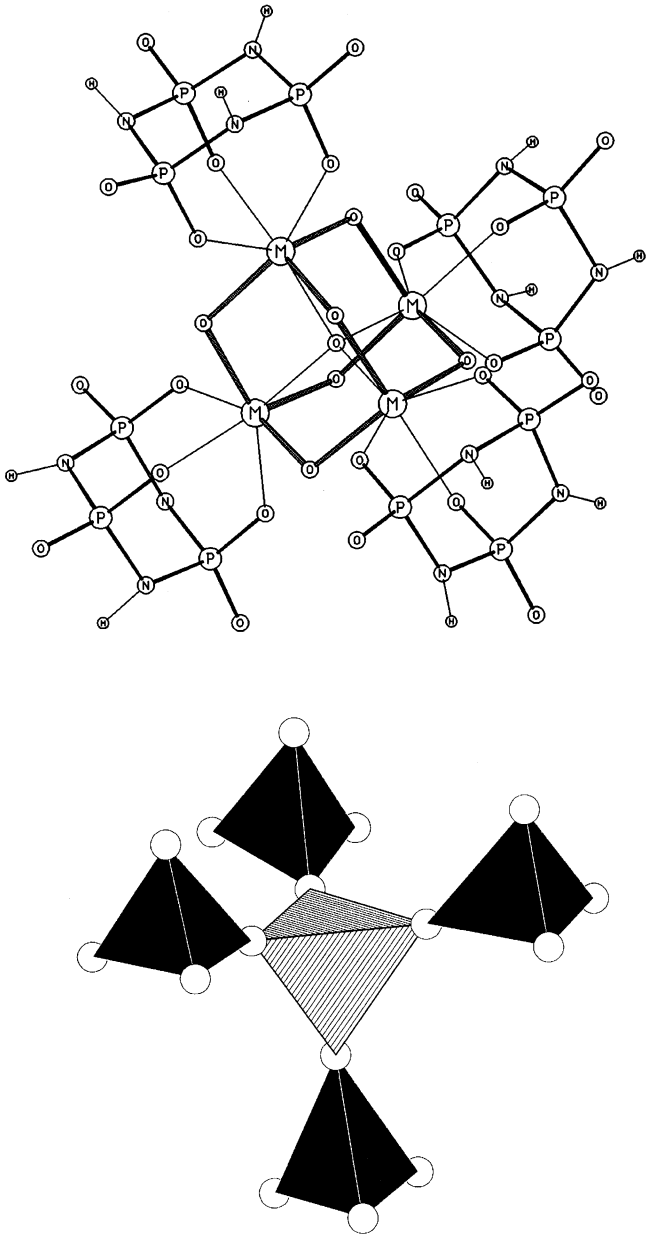


Table 1. Interatomic distances [pm] and angles [°] of **1** and **2**

$Na_4\{Hf_4(\mu_4\text{-}O)\text{-}(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O$ (cubic, **1**)		$Na_4\{Hf_4(\mu_4\text{-}O)\text{-}(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O$ (rhomb., **2**)	
Hf(1)−Hf(1)	348.7(1)	Hf(1)−Hf(1)	351.0(1)
−Hf(2)	349.4(1)	−Hf(2)	351.0(1)
$-\mu_4O$	214.3(2)	$-\mu_4O$	214.6(2)
−O(11)	211.7(4), 209.6(4)	−O(11)	211.9(3), 212.8(3)
−O(12)	211.4(4)	−O(12)	211.6(3)
−O(1A)	216.8(4)	−O(1A)	213.5(3)
−O(2A)	213.5(4)	−O(2A)	214.2(3)
−O(3A)	213.8(4)	−O(3A)	212.8(3)
Hf(2)$-\mu_4O$	212.0(6)	Hf(2)$-\mu_4O$	216.1(5)
−O(12)	210.7(4)	−O(12)	210.1(3)
−O(4A)	214.4(4)	−O(4A)	213.9(3)
P(1)−N(1)	167.4(5)	P(1)−N(1)	168.3(4)
P(1)−N(3)	167.8(5)	P(1)−N(3)	167.3(4)
P(1)−O(1A)	151.6(4)	P(1)−O(1A)	151.7(3)
P(1)−O(1B)	148.2(5)	P(1)−O(1B)	147.9(4)
P(2)−N(2)	167.3(5)	P(2)−N(2)	167.4(4)
P(2)−N(1)	168.9(5)	P(2)−N(1)	167.2(4)
P(2)−O(2A)	151.9(4)	P(2)−O(2A)	152.6(3)
P(2)−O(2B)	147.2(4)	P(2)−O(2B)	148.8(3)
P(3)−N(3)	167.2(5)	P(3)−N(3)	166.7(4)
P(3)−N(2)	166.6(5)	P(3)−N(2)	168.1(4)
P(3)−O(3A)	152.1(4)	P(3)−O(3A)	152.3(3)
P(3)−O(3B)	148.7(4)	P(3)−O(3B)	148.3(3)
P(4)−N(4)	168.6(5)	P(4)−N(4)	168.1(4)
P(4)−N(4)	167.8(5)	P(4)−N(4)	168.0(4)
P(4)−O(4A)	151.4(4)	P(4)−O(4A)	151.8(3)
P(4)−O(4B)	146.8(4)	P(4)−O(4B)	147.7(4)
Na(1)−O	234.6(8)−256.6(6)	Na(1)−O	239.4(4)−249.5(5)
Na(2)−O	236(2)−276(2)	Na(2)−O	217(7)−277(6)
Hf(2)−Hf(1)−Hf(1)	60.068(4)	Hf(2)−Hf(1)−Hf(1)	59.99(1)
Hf(1)−Hf(1)−Hf(1)	60	Hf(1)−Hf(1)−Hf(1)	60
Hf(1)−Hf(2)−Hf(1)	59.857(8)	Hf(1)−Hf(2)−Hf(1)	60.00(1)
N(3)−P(1)−N(1)	104.8(2)	N(3)−P(1)−N(1)	105.0(2)
N(1)−P(2)−N(2)	104.6(2)	N(1)−P(2)−N(2)	104.8(2)
N(2)−P(3)−N(3)	104.4(2)	N(2)−P(3)−N(3)	104.2(2)
N(4)−P(4)−N(4)	105.7(3)	N(4)−P(4)−N(4)	105.9(3)
P(1)−N(1)−P(2)	117.6(3)	P(1)−N(1)−P(2)	117.9(2)
P(2)−N(2)−P(3)	119.4(2)	P(2)−N(2)−P(3)	118.3(2)
P(3)−N(3)−P(1)	118.7(3)	P(3)−N(3)−P(1)	119.5(2)
P(4)−N(1)−P(4)	118.4(3)	P(4)−N(1)−P(4)	118.2(2)
O(1A)−P(1)−O(1B)	116.8(2)	O(1A)−P(1)−O(1B)	117.9(2)
O(2A)−P(2)−O(2B)	117.8(2)	O(2A)−P(2)−O(2B)	116.0(2)
O(3A)−P(3)−O(3B)	115.1(2)	O(3A)−P(3)−O(3B)	115.6(2)
O(4A)−P(4)−O(4B)	117.2(2)	O(4A)−P(4)−O(4B)	117.8(2)
O−P(1)−N	111.3(3), 105.1(2), 110.6(3), 107.5(2)	O−P(1)−N	110.7(2), 106.0(2), 110.7(2), 105.5(2)
O−P(2)−N	110.6(3), 105.7(2), 111.1(3), 106.0(2)	O−P(2)−N	111.7(2), 105.4(2), 110.4(2), 107.7(2)
O−P(3)−N	111.5(3), 105.2(2), 112.9(2), 107.0(2)	O−P(3)−N	111.3(2), 105.5(2), 112.9(2), 106.4(2)
O−P(4)−N	110.3(3), 106.1(2), 111.8(3), 104.9(2)	O−P(4)−N	111.1(2), 104.7(2), 110.4(2), 106.3(2)

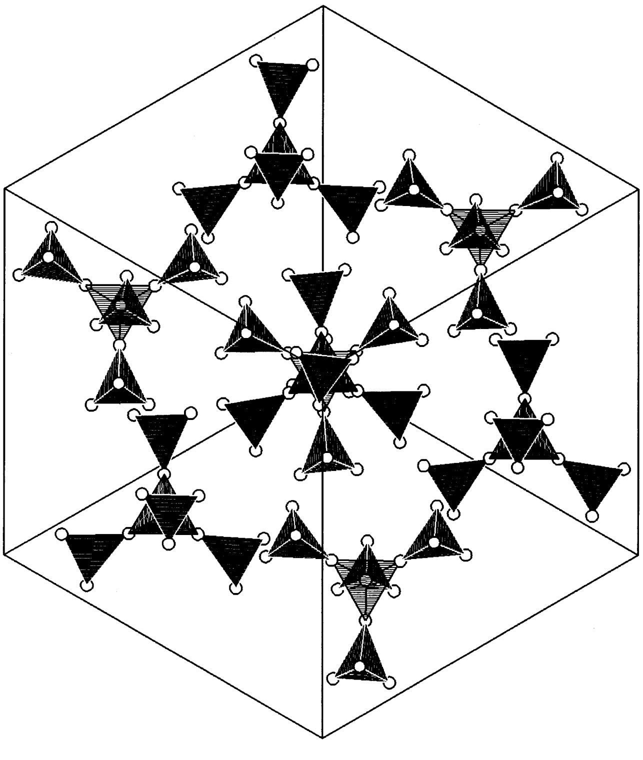
mantanoid cage $M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6^{8+}$ in **1** and **4** exhibit the ideal tetrahedral symmetry.

The trimetaphosphimate rings in $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ M = Zr, Hf exhibit the chair conformation. The average P−O bond lengths of the oxygen atoms (O1A to O4A) coordinating to the metal (Zr: 152.1, 151.7 pm and Hf: 151.8, 152.1 pm for the cubic and the rhombohedral phase, respectively) are significantly longer than the average P−O bond lengths of oxygen atoms (O1B to O4B) coordinating to Na^+ or water molecules (Zr: 148.0, 147.7 pm and Hf: 147.7, 148.2 for the cubic and the rhombohedral phase, respectively). These values, as well as the corresponding P−N bond lengths and angles, differ only slightly among the compounds **1**, **2**, **3**, and **4**. Thus, the average P−N bond length is 167.6 pm and the average P−N−P angle is 118.4°. These findings are in accordance with the results obtained from trimetaphosphimates of monovalent cations, where there is a larger range of values but they are nevertheless similar to the results obtained in this work. The μ-imido H atoms have been unambiguously located in all four compounds by difference Fourier analyses. In comparison to other trimetaphosphimates these μ-imido groups are structurally directing, by forming hydrogen bonds between the trimetaphosphimate rings as can be seen by comparing the structures of analogous trimetaphosphates with the corresponding trimetaphosphimates.[4] In the latter compounds the N−H groups of the $(PO_2NH)_3^{3-}$ are usually involved in extensive hydrogen-bonding interactions, forming a three-dimensional network in $(NH_4)_3(PO_2NH)_3\cdot H_2O$[4a], bilayers in $Ag_3(PO_2NH)_3$,[4c] and pairs in $Na_3(PO_2NH)_3\cdot H_2O$,[4b] and $K_3(PO_2NH)_3$.[4c]

Arrangement of the Complex Ions $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ in the Cubic Phase

The two cubic compounds $Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O$ (**1**/**3**) with M = Zr, Hf were found to be isostructural and isomorphous. The arrangement of the $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions is shown in Figure 4. The anions are interconnected by coordination to the sodium ions and by hydrogen bonding, forming a three-dimensional network. Thus all H atoms of the μ-NH groups are bound to O atoms of the trimetaphosphimato ligands [N1−H1···O1B, N2−H2···O3B, N2−H2···O4B, N3−H3···O1B, N4−H4···O3B, N···O: 289−315 pm, N−H···O: 121−142° for **1** and N···O: 288−313 pm, N−H···O: 121−142° for **3**]. Na1 is octahedrally surrounded by three oxygen atoms of the water molecules [Na1−Ow1, −Ow2, −Ow3: 248.7(8), 234.6(8), 254.6(11) pm for **1** and 247.1(6), 234.1(6), 253.8(8) pm for **3**] and three oxygen atoms of the trimetaphosphimate rings [Na1−O2B, −O3B, −O4B: 237.9(5), 256.6(6), 236.0(5) pm for **1** and 236.7(4), 257.8(4), 235.2(4) pm for **3**]. The other sodium ion Na2 is located in a general position with an occupancy factor 1/3. Na2 is surrounded by five oxygen atoms of the water molecules [Na2−Ow1, −Ow2, −Ow3, −Ow4, −Ow6: 252(2), 276(2), 236(2), 262(2), 243(2) pm for **1** and 252(2), 281(2), 245(2), 252(2), 244(2) pm for **3**], as well as by two oxygen atoms of the trimetaphosphimate rings [Na2−O1B, −O2B: 276(2) and 242(2) for **1** and 274(2), 240(2) pm for **3**]. The residual electron density found for **1** (2.75 $e^-/Å^3$) and **3** (3.10 $e^-/Å^3$) is located on a special position $^1/_2{}^1/_2 0$. No other atoms are located within a radius of 3 Å around this site.

Figure 4. Crystal-packing diagram of the $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions (M = Hf, Zr) in the cubic phase, view along [111]



Arrangement of the Complex Ions $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ in the Rhombohedral Phase

The two rhombohedral compounds $Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O$ (**2**/**4**) with M = Zr, Hf, were found to be isostructural and isomorphous. The arrangement of the $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ ions is shown in Figure 5. The structure consists of bilayers with a stacking sequence $A_\downarrow B_\uparrow C_\downarrow A_\uparrow B_\downarrow C_\uparrow$ of the anionic layers along [001]. The arrows describe the direction of the tip of the anion, i.e. the position of M2 (M = Hf, Zr), relative to the center of gravity of the cages with respect to [001]. Within the bilayers the anions are connected by hydrogen bonds N−H···O between the trimetaphosphimate rings [N3−H3···O3, N3−H3···O4, N4−H4···O3, N···O: 290−321 pm, N−H···O: 122−136° for **2** and N···O: 286−320 pm, N−H···O: 121−137° for **4**] and by coordination to Na1. The sodium ion Na1 is coordinated by six O atoms, three oxygen atoms of the water molecules Ow1, Ow2, Ow3 [Hf: $d_{av.}$ Ow−Na: 244.1 pm, Zr: $d_{av.}$ Ow−Na: 244.1 pm] and three O atoms of the trimetaphosphimate rings O1B, O3B, O4B [Hf: $d_{av.}$ O−Na: 241.8 pm, Zr: $d_{av.}$ O−Na: 241.8 pm], forming a distorted octahedron. The other sodium ion Na2 is located on a general position with an occupancy factor of 1/3. These Na2 ions are surrounded by six oxygen atoms, two oxygen atoms of the trimetaphosphimate rings [O1B, O2B: 278(6), 266(6) pm for **2**, 258(3), 278(3) pm for **4**] and four oxygen atoms of the water molecules [Ow2, Ow5, Ow7, Ow7′: 277(6), 217(7), 241(7) 246(7) pm for **2**, 260(3), 228(3), 241(6), 265(4) pm for **4**] thus connecting the bilayers. This connection is reinforced by extensive hydrogen bonding with O2B acting as a bridging atom [N1−H1···O2B···H2−N2; N1···O2···N2: 296, 299 for **2** and 295, 293 for **4**]. Thus a void centered at $00^1/_2$ is formed by connecting six $\{M_4[(PO_2NH)_3]_4(\mu_4\text{-}O)(\mu\text{-}OH)_6\}^{4-}$ units by hydrogen bonding between the $(PO_2NH)_3^{3-}$ rings. The hole has a radius of approximately 3 Å. The residual electron density which is found for **2** (2.27 $e^-/Å^3$) is located on the special position $^1/_3{}^2/_3{}^1/_6$ and no other atoms are located within a radius of 3 Å. In **4** no notable residual electron density was observed.

Discussion

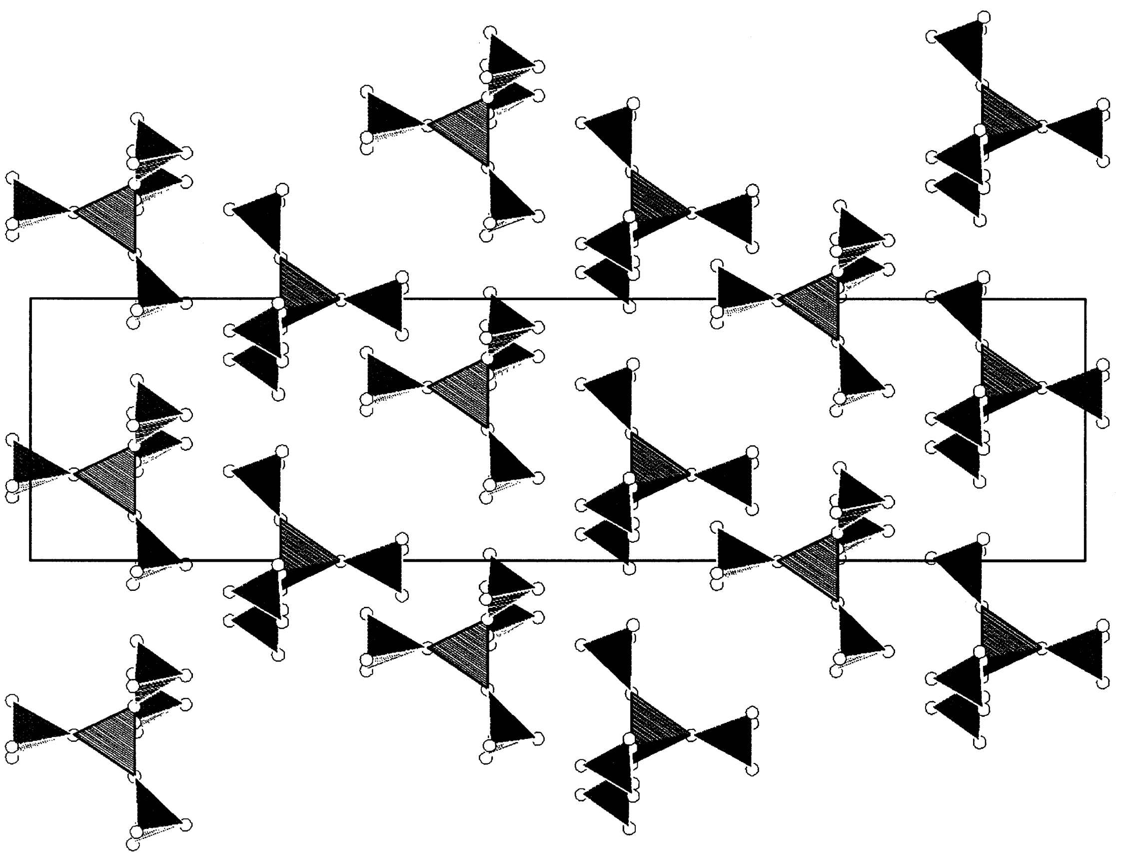
In the (trimetaphosphimato)hafnates and -zirconates having the general composition $Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O$ (**1**, **3**) and $Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O$ (**2**, **4**) with M = Zr, Hf, for the first time a metal oxide fragment incorporating four metal atoms was stabilized by trimetaphosphimate ions acting as tridentate ligands, thus stabilizing the tetranuclear anion. The synthesis of the compounds **1**−**4** succeeded when zirconyl chloride and hafnyl chloride were used, whereas the use of $ZrCl_4$ or $ZrSO_4 \cdot 4\ H_2O$ led to the formation of X-ray-amorphous products. The assumption that the preformed eight-membered rings $\{M(OH)_2\}_4^{8+}$ in the solutions of $HfOCl_2 \cdot 8\ H_2O$ and $ZrOCl_2 \cdot 8\ H_2O$ is preserved during the syntheses could not unambiguously be confirmed since the use of a mixture of $HfOCl_2 \cdot 8\ H_2O$ and $ZrOCl_2 \cdot 8\ H_2O$ in one reaction led to the formation of mixed crystals, containing Hf as well as Zr, in a 1:1 ratio. This was confirmed by EDX analysis.

Neither the cubic nor the rhombohedral phase of the (trimetaphosphimato)zirconates or -hafnates have been obtained as a single-phase product. Although the addition of NaCl during the synthesis of (trimetaphosphimato)zirconates resulted in the formation of some large single crystals of the cubic phase (**4**) analogous experiments using $HfOCl_2 \cdot 8\ H_2O$ did not lead to a pure single-phase cubic product **1**. In the same way neither varying the reaction temperature, nor varying the pH value by the addition of NaOH or HCl, resulted in single-phase products. Since the formulas of the cubic and rhombohedral phases obtained from the single-crystal structure determination differ only in their water content, and because the characteristic structural feature in the compounds **1**−**4** are the discrete tetranuclear complex anions $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6[(PO_2NH)_3]_4\}^{4-}$, a direct structural correlation between the respective cubic and rhombohedral phases was anticipated. However, a direct structural correlation (e.g. stacking variants, group-subgroup relations) can be ruled out since strongly differing arrangements of the anions occur.

Conclusion

Unlike the known trimetaphosphimato complexes where only monometallic complexes are formed in the title compounds, the trimetaphosphimato groups stabilize the metal oxide fragments $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6\}^{8+}$ (M = Zr, Hf) by acting as tridentate ligands. Thus the tetranuclear complex anion $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6[(PO_2NH)_3]_4\}^{4-}$ is obtained. The existence of a tetranuclear ring in $\{M_4[(OH)_2]_4(H_2O)_{16}\}^{8+}$ as the starting material seems to be important for the formation of the adamantanoid cage $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6\}^{8+}$, which is then stabilized by trimetaphosphimate ions. Despite the similarity of the characteristic anion $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6[(PO_2NH)_3]_4\}^{4-}$ in the four title compounds, cubic (**1**/**3**) and rhombohedral (**2**/**4**) products have been obtained exhibiting strongly differing topologies. As with many other Hf and Zr compounds isotypic products (**1**/**3** and **2**/**4**) are formed.

Figure 5. Crystal-packing diagram of the $\{M_4(\mu_4\text{-O})(\mu\text{-OH})_6[(PO_2NH)_3]_4\}^{4-}$ ions (M = Hf, Zr) in the rhombohedral phase, view along [010]



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Experimental Section

$Na_3(PO_2NH)_3 \cdot 4\ H_2O$ was obtained by a procedure described previously {Eq. (a)[13]}. $(PNCl_2)_3$ (Fluka, purum, 5 g, 14.38 mmol) was dissolved in 20 ml of dioxane (Merck, p.a.) in a round-bottom flask. A solution of $NaOOCCH_3 \cdot 3\ H_2O$ (Merck, p.a., 25 g, 0.184 mol) in 40 ml of H_2O was added while stirring (60°C, 24 h). The product precipitated as a white microcrystalline powder which was filtered and washed with ethanol and acetone. The product was recrystallized from water by the addition of ethanol (yield: 4.5 g, 83%).

$$(PNCl_2)_3 + 9\ Na(OOCCH_3) \cdot 3\ H_2O \rightarrow Na_3(PO_2NH)_3 \cdot 4\ H_2O + 6\ NaCl + 9\ HOOCCH_3 + 17\ H_2O \quad (a)$$

$HfOCl_2 \cdot 8\ H_2O$ (Alfa) was used as obtained, and $ZrOCl_2 \cdot 8\ H_2O$ (Fluka, puriss.) was recrystallized, from hydrochloric acid according to the literature.[14] For the synthesis of the (trimetaphosphimato)hafnates and -zirconates equimolar (3.35×10^{-5} M) aqueous solutions of $Na_3(PO_2NH)_3 \cdot 4\ H_2O$ (25 mg, 6.67×10^{-2} mmol in 2 ml of H_2O) and $HfOCl_2 \cdot 8\ H_2O$ (27.3 mg, 6.67×10^{-2} mmol in 2 ml of H_2O) or $ZrOCl_2 \cdot 8\ H_2O$ (21.5 mg, 6.67×10^{-2} mmol in 2 ml of H_2O) were mixed together at room temperature in a small glass vessel (V = 8 ml). The mixtures became turbid at once but cleared after 5 min without further stirring. They were cautiously covered with methanol and placed in a larger vessel (V = 40 ml) filled with 25 ml of methanol allowing very slow diffusion. The mixture was kept undisturbed at room temperature. After 3 d, crystals were observed growing on the inner glass wall of the smaller vessels. The crystallization was complete after approximately 8 d and led to the formation of two distinct types of crystals, exhibiting rhombohedral and quadratic habit. The reaction of $HfOCl_2 \cdot 8\ H_2O$ resulted in large crystals with rhombohedral as well as quadratic contours. In the case of $ZrOCl_2 \cdot 8\ H_2O$ the same procedure led to the formation of large crystals of only rhombohedral contour (however, small quadratic crystals of 10 μm edge length were observed under the scanning electron microscope). Large crystals of the (trimetaphosphimato)zirconate with a quadratic shape were obtained by adding sodium chloride (12 mg, 0.2 mmol) to the solution of $Na_3(PO_2NH)_3 \cdot 4\ H_2O$.

After the precipitation was complete, the mother liquor was removed and the crystals were washed with acetone (yield: 70%). Energy-dispersive X-ray microanalyses (Fa. Leo, Oberkochen) showed the atomic ratio Na/P/M (M = Hf, Zr) to be 1:3:1 for all four compounds. Chemical analysis of **4** was performed for Na, Zr, O, N, P, H and for **1** and **2** for Na and Hf, to confirm the occupancy factor of $^1/_3$ for Na2 in the general position. Phase separation was accomplished manually according to the shape of the crystals and due to their optical properties under the polarization microscope. $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 18\ H_2O$ (**1**, 2184.11 g/mol): calcd. Hf 32.69, Na 4.21; found Hf 31.6, Na 4.06. $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 21\ H_2O$ (**2**, 2238.16 g/mol): calcd. Hf 31.90, Na 4.11; found Hf 31.5, Na 4.06. $Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 21\ H_2O$ (**4**, 1889.08 g/mol): calcd. H 3.20, N 8.89, Na 4.87, O 44.04, P 19.68, Zr 19.32; found H 3.3, N 8.63, Na 4.96, O 42.0, P 19.3, Zr 18.6.

As the products **1/2** and **3/4** are always obtained as mixtures, the water content was not determined by chemical analysis but taken from the structural determination. Powder-diffraction investigations (Siemens D5000) revealed the existence of only two phases, **1/2** and **3/4**. All reflections have been indexed and their observed intensities correspond to a calculated diffraction pattern based on the single-crystal-structural data.

All four compounds are obtained as colorless solids and transparent crystals with well developed faces. They are stable in air and are water-soluble, however recrystallization from these solutions was not possible. Furthermore the existence of a ^{31}P-NMR signal [δ^{31}P (D_2O) = −0.544] in the solution NMR spectra (Bruker ARX 250) of **1/2** indicated decomposition of the complex anion $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{8-}$ (M = Hf, Zr) in water. This NMR shift is in accordance with the ^{31}P-NMR signal of the free $(PO_2NH)_3^{3-}$ ion as found in aqueous solutions of $K_3(PO_2NH)_3$ [δ^{31}P (D_2O) = −0.553].[4c]

Thermal decomposition of the products starts above 120°C with evolution of H_2O and NH_3. Reaction of mixtures of (**1/2**) or (**3/4**), respectively, for 2 d at 200−700°C were carried out in sealed quartz ampoules. The only X-ray crystalline products detectable were HfP_2O_7 and ZrP_2O_7 as well as $NaZr_2(PO_4)_3$. Therefore, nitrogen was not incorporated into the products, but NH_3 was formed as a condensation product.

IR spectra (Bruker IFS 66v; KBr pellets) of the cubic and rhombohedral (trimetaphosphimato)hafnates have been obtained after the separation of the crystals according to their shape and optical properties under the polarization microscope. The IR spectra of **1**−**4** are very similar, exhibiting the following IR absorptions $\tilde{\nu}$ cm^{-1}] = 3600, 3270, 2704, 1642, 1316, 1256, 1110, 1052, 919, 825, 642, 553, 415.

Crystal Structure Analyses: X-ray diffraction data were collected on an image-plate diffractometer (STOE IPDS). Reflections shaded by the goniometer head were removed. The data sets were employed in the crystal shape optimization and the subsequent numerical absorption correction using HABITUS.[15] Afterwards identical reflections, which were measured multiply due to the measurement method, were averaged, and their mean values were used for the structure determination. Relevant crystallographic data and details of the data collection of the compounds **1**−**4** are listed in Table 2. According to the observed extinctions for the cubic phases the space group $Pa\bar{3}$ (no. 205) was unequivocally determined and the structures were solved by direct methods using SHELXTL-Plus.[16] For the rhombohedral phases the space groups $R3$ (no. 146) and $R\bar{3}$ (no. 148) have been considered. The crystal structures of these compounds were solved by direct methods using SHELXTL-Plus[16] in the centrosymmetric space group $R\bar{3}$. After the anisotropic refinement of the displacement parameters of all non-hydrogen atoms except Na2 for the cubic and the hexagonal phases, the μ-imido hydrogen atoms were located and refined using a riding model with a fixed N−H distance of 86 pm. The sodium ions Na2 in **1**−**4** were located on the basis of bonding lengths and coordination. They were located on general positions occupied to $^1/_3$. Therefore these partially occupied Na positions were only refined using isotropic displacement parameters. Since the compounds were always obtained as mixtures of the cubic and rhombohedral phase, the water content was determined exclusively from the diffraction data. Tables 3 and 4 show the positional parameters and the equivalent isotropic displacement parameters U_{equiv} for **1** and **2**. Corresponding parameters of the isotypic zirconium compounds (**3** and **4**) are omitted. Table 1 gives interatomic distances and angles in **1** and **2**.[17]

Table 2. Crystallographic data of the compounds **1−4**

Formula	$Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4 \cdot 18\ H_2O$		$Na_4\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4 \cdot 21\ H_2O$	
M	Hf (**1**)	Zr (**3**)	Hf (**2**)	Zr (**4**)
form. mass [g mol^{-1}]	2184.11	1835.03	2238.16	1889.08
crystal system	cubic		trigonal	
space group	$Pa\bar{3}$ (no. 205)		$R\bar{3}$ (no. 148)	
diffractometer	STOE-IPDS			
radiation (monochromator)	Mo-K_α (graphite)			
unit cell	a = 22.678(3)	a = 22.693(3)	a = 14.350(2), c = 50.348(10)	a = 14.303(2), c = 50.284(10)
V [10^6 pm^3]	11663.9(23)	11685.7(23)	8979.2(25)	8908.4(25)
Z	8	8	6	6
X-ray density [g cm^{-3}]	2.488	2.086	2.481	2.113
abs. coefficient [cm^{-1}]	75.75	11.72	73.87	11.6
temperature [K]	293(2)	293(2)	293(2)	293(2)
crystal size [mm]	0.326 × 0.282 × 0.174	0.320 × 0.164 × 0.144	0.153 × 0.113 × 0.104	0.208 × 0.176 × 0.126
F(000)	8336	7312	6420	5664
θ range [°]	4.02−24.08	2.54−28.12	5.42−28.01	4.62−26.03
h, k, l	−25/25, −25/25, −25/25	−30/27, −29/30, −27/27	−18/18, −18/17, −66/66	−17/17, −17/17, −60/61
total no. of reflections	57257	86460	22606	18379
independent reflections	3053	4750	4769	3828
observed reflections	2786 [$I_o > 2\sigma(I_o)$]	3848 [$I_o > 2\sigma(I_o)$]	3942 [$I_o > 2\sigma(I_o)$]	3375 ([$I_o > 2\sigma(I_o)$]
refined parameters	246	255	255	255
corrections	Lorentz, polarization, extinction			
absorption corrections	numerical using HABITUS[15]			
min./max. transm. ratio	0.1110/0.3026	0.8201/0.9050	0.3408/0.5139	0.7916/0.8926
min./max. resid. e$^-$ dens.	−0.551/2.746	−0.662/3.098	−0.916/2.270	−0.661/1.041
extinction coefficient	0.00005(2)	−	0.00008(2)	0.00002(2)
GOF	1.140	1.156	1.138	1.084
R indices: $R1/wR2$	0.0267/0.0795	0.041/0.1439	0.0292/0.0799	0.0422/0.1154

Table 3. Atomic coordinates and anisotropic displacement parameters [pm^2] for $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 18\ H_2O$ (cubic phase)

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{equiv}[a]
Hf1	24d	0.7649(1)	0.3716(1)	0.1245(1)	155(1)
Hf2	8c	0.7647(1)	0.2647(1)	0.2353(1)	155(1)
OT	8c	0.8186(2)	0.3186(2)	0.1814(2)	145(2)
O11	24d	0.8240(2)	0.3195(2)	0.0745(2)	243(2)
O12	24d	0.7127(2)	0.3203(2)	0.1822(2)	289(2)
P1	24d	0.6517(1)	0.4665(1)	0.1032(1)	199(3)
P2	24d	0.7430(1)	0.4698(1)	0.0152(1)	194(3)
P3	24d	0.6613(1)	0.3724(1)	0.0184(1)	185(3)
P4	24d	0.6549(1)	0.1657(1)	0.2501(1)	202(3)
O1A	24d	0.6949(2)	0.4341(2)	0.1426(2)	207(9)
O1B	24d	0.6070(2)	0.5038(2)	0.1329(2)	318(10)
O2A	24d	0.7820(2)	0.4359(2)	0.0578(2)	191(8)
O2B	24d	0.7718(2)	0.5097(2)	−0.0270(2)	318(10)
O3A	24d	0.7036(2)	0.3409(2)	0.0598(2)	200(8)
O3B	24d	0.6264(2)	0.3332(2)	−0.0210(2)	285(10)
O4A	24d	0.6951(2)	0.2044(2)	0.2135(2)	213(8)
O4B	24d	0.6103(2)	0.1310(2)	0.2184(2)	286(10)
N1	24d	0.6936(2)	0.5063(2)	0.0573(2)	220(11)
H1	24d	0.6901(2)	0.5440(2)	0.0552(2)	260
N2	24d	0.7032(2)	0.4188(2)	−0.0202(2)	220(10)
H2	24d	0.7043(2)	0.4165(2)	−0.0581(2)	260
N3	24d	0.6190(2)	0.4161(2)	0.0600(2)	226(11)
H3	24d	0.5812(2)	0.4129(2)	0.0593(2)	270
N4	24d	0.7007(2)	0.1224(2)	0.2895(2)	238(11)
H4	24d	0.6990(2)	0.0847(2)	0.2867(2)	290
Na1	24d	0.7789(2)	0.4937(2)	−0.1305(2)	504(80)
OW1	24d	0.7760(3)	0.4999(4)	−0.2399(3)	820(20)
OW2	24d	0.7930(6)	0.5961(4)	−0.1332(4)	1410(50)
OW3	24d	0.8898(4)	0.4807(6)	−0.1429(6)	1440(40)
OW4	24d	0.8776(5)	0.5952(6)	−0.2363(5)	1390(40)
OW5	24d	0.6596(4)	0.0401(3)	0.1525(4)	910(30)
OW6	24d	0.5921(3)	0.3031(4)	0.1701(5)	1170(40)
Na2	24d[b][c]	0.5195(9)	0.2467(9)	0.1148(9)	1280(60)

[a] U_{equiv} is defined as one third of the trace of the U_{ij} tensors. − [b] Only isotropically refined. − [c] SOF = 1/3.

Table 4. Atomic coordinates and anisotropic displacement parameters [pm^2] for $Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\} \cdot 21\ H_2O$ (rhombohedral phase)

Atom	Wyckoff symbol	x/a	y/b	z/c	U_{equiv}[a]
Hf1	18f	0.5559(1)	0.3816(1)	0.0981(1)	162(1)
Hf2	3c	0.6667	0.3333	0.0412(1)	164(1)
O11	18f	0.5122(3)	0.2261(3)	0.1125(1)	239(7)
O12	18f	0.5541(3)	0.3728(3)	0.0562(1)	230(7)
OT	3c	0.6667	0.3333	0.0841(1)	134(9)
P1	18f	0.3069(1)	0.3469(9)	0.1002(1)	205(2)
P2	18f	0.4382(1)	0.4509(1)	0.1459(1)	207(2)
P3	18f	0.4790(1)	0.5673(1)	0.0967(1)	195(2)
P4	18f	0.7531(1)	0.2879(1)	−0.0169(1)	225(2)
O1A	18f	0.3863(2)	0.3108(3)	0.0927(1)	211(6)
O1B	18f	0.1932(3)	0.2775(3)	0.0923(1)	307(8)
O2A	18f	0.5132(3)	0.4105(3)	0.1368(1)	217(6)
O2B	18f	0.4331(3)	0.4648(3)	0.1750(1)	308(8)
O3A	18f	0.5544(3)	0.5256(2)	0.0891(1)	199(6)
O3B	18f	0.5052(3)	0.6725(3)	0.0851(1)	307(8)
O4A	18f	0.7517(3)	0.2914(3)	0.0132(1)	223(6)
O4B	18f	0.8215(3)	0.2506(3)	−0.0296(1)	319(8)
N1	18f	0.3175(3)	0.3638(3)	0.1334(1)	233(8)
H1	18f	0.2626(3)	0.3288(3)	0.1435(1)	280
N2	18f	0.4746(3)	0.5667(3)	0.1301(1)	254(8)
H2	18f	0.4907(3)	0.6244(3)	0.1388(1)	310
N3	18f	0.3565(3)	0.4709(3)	0.0877(1)	226(8)
H3	18f	0.3190(3)	0.4847(3)	0.0768(1)	270
N4	18f	0.6243(3)	0.2107(3)	−0.0265(1)	265(8)
H4	18f	0.6048(3)	0.1541(3)	−0.0360(1)	320
Na1	18f	0.1058(2)	0.3247(2)	0.0596(1)	485(6)
OW1	18f	−0.0164(5)	0.3567(6)	0.0329(1)	750(2)
OW2	18f	−0.0601(7)	0.1882(10)	0.0816(2)	1450(40)
OW3	18f	0.0874(12)	0.1759(12)	0.0326(3)	1970(60)
OW4	18f	0.4077(6)	0.3734(7)	0.0236(1)	820(20)
OW5	18f	0.3202(7)	0.0929(8)	0.1381(2)	1250(40)
OW6	18f	−0.1496(10)	0.1189(11)	0.0240(4)	2060(70)
OW7	18f	−0.0185(17)	−0.1248(18)	0.1515(6)	2820(110)
Na2	18f[b][c]	0.1548(53)	−0.0301(50)	0.1300(12)	3470(250)

[a] U_{equiv} is defined as one third of the trace of the orthogonalized U_{ij} tensors. − [b] Only isotropically refined. − [c] Na2: SOF = 1/3.

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[17] Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) by quoting the depository numbers CSD-407897 ($\mathrm{Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O}$), -407895 ($\mathrm{Na_4\{Hf_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O}$), -407898 ($\mathrm{Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 18\ H_2O}$) and -407896 ($\mathrm{Na_4\{Zr_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}\cdot 21\ H_2O}$).

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