

# Bimetallic alkoxides of aluminium-hafnium and aluminium-zirconium. X-ray structure of $\text{Al}_2\text{Hf}(\text{OPr}^i)_{10}$

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**Abstract**—The solubility studies in the  $\text{Al}(\text{OR})_3\text{-M}(\text{OR})_4\cdot\text{ROH-ROH}$  ( $\text{R} = \text{Pr}^i$ ) systems at 20°C revealed the existence of the only complex,  $\text{Al}_2\text{M}(\text{OR})_{10}$ , [ $\text{M} = \text{Hf}(\text{I}), \text{Zr}(\text{II})$ ]. The literature data on the existence of the  $\text{AlM}(\text{OR})_7$  species were disproved. According to the results of the single crystal X-ray diffraction study of **I**, its molecule has a two-fold symmetry axis and involves two peripheral tetrahedrally coordinated Al atoms, each of their coordination tetrahedra sharing one common edge with the coordination octahedron of the central Hf atom,  $[(\text{RO})_2\text{Al}(\mu\text{-OR})_2]\text{Hf}(\text{OR})_2$ . The mean planes of almost planar  $[\text{AlO}_2\text{Hf}]$  cycles form the dihedral angle of 82° with each other. Mass-spectra of **I** and **II** show two fragmentation pathways, viz.: (1) the elimination of the ether molecule accompanied by the formation of oxo groups, and (2) the  $\text{Al}(\text{OR})_3$  molecule abstraction producing the  $\text{AlM}(\text{OR})_6^+$  ions. According to the X-ray powder diffraction data crystals of **I** and **II** are isostructural. The influence of the oligomeric Zr and Hf oxoalkoxides, formed as a result of partial thermolysis of  $\text{M}(\text{OR})_4\cdot\text{ROH}$ , on the processes of formation of complexes with  $\text{Al}(\text{OR})_3$  has been elucidated. The non-crystalline solid  $\text{Al}_2\text{Hf}(\text{OEt})_{10}$  was isolated from ethanol solution, its mass-spectral fragmentation being analogous to that of **I** and **II**. Copyright © 1996 Elsevier Science Ltd

**Keywords:** aluminium alkoxozirconates; -hafnates; single-crystal X-ray diffraction; mass-spectral study; physico-chemical analysis.

The alkoxy-derived  $\text{Al}_2\text{O}_3$  and  $\text{MO}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) based materials find extensive applications in the production of optical, refractory materials and solid electrolytes. The existence of aluminium alkoxozirconates and alkoxohafnates of two compositions,  $\text{Al}_2\text{M}(\text{OR})_{10}$  and  $[\text{AlM}(\text{OR})_7]_2^\ddagger$  has been reported in the earlier literature [1–4]. Later on the physico-chemical analysis of the  $\text{Al}(\text{OR})_3\text{-Zr}(\text{OR})_4\cdot\text{ROH-ROH}$  system led to the conclusion, that in this system only one complex, viz.,  $\text{AlZr}(\text{OR})_7$ , actually exists [5].

The present paper reports the results of the studies of composition of aluminium alkoxohafnates and alkoxozirconates by means of physico-chemical

analysis, single crystal X-ray diffraction, and mass spectrometry.

## EXPERIMENTAL

Drying of ROH ( $\text{R} = \text{Pr}^i, \text{Et}$ ) was carried out by the prolonged refluxing over crystalline  $\text{Al}(\text{OPr}^i)_3$  or  $\text{Ca}(\text{OEt})_2$  respectively and subsequent distillation.  $\text{Al}(\text{OR})_3$  ( $\text{R} = \text{Pr}^i, \text{Et}$ ) was prepared by reaction of the metal with absolute ROH, complexes  $\text{M}(\text{OR})_4\cdot\text{ROH}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ;  $\text{R} = \text{Pr}^i$ ) and  $\text{Hf}(\text{OEt})_4$  were synthesized by anodic oxidation of the metal in the alcohol in the presence of LiCl [6].

Zr and Hf in the presence of Al were determined by complexometric titration in acidic medium ( $\text{pH} = 1\text{--}2$ ) using xylenol orange for indication (the solution colour changed from pink to yellow). The

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‡ In this case and further on in the text  $\text{R} = \text{Pr}^i$ .

Al content was calculated from the difference after determination of the sum of all oxides, obtained after calcination of the solutions or solid phases at 800°C.

#### *Synthesis of aluminium alkoxohafnate and -zirconate*

Reactions were carried out by 1–2 h refluxing of the mixture of the solutions of crystalline  $\text{Al(OR)}_3$  and  $\text{Hf(OR)}_4 \cdot \text{ROH}$  in ROH taken in the ratio of 2 : 1. The concentration of the initial solutions after complete dissolution of the components amounted to 8–10% with respect to the sum of both alkoxides. It is noteworthy that simple cooling of the hot initial solutions containing both alkoxides without the refluxing resulted in the crystallization of the starting material  $\text{Hf(OR)}_4 \cdot \text{ROH}$  solvate. The precipitation of a fine crystalline sample of  $\text{Al}_2\text{Hf(OR)}_{10}$  (**I**) from reaction solutions obtained after partial removal of the solvent (up to the concentration of 40–50%) begins after about 3 days. After complete evaporation of the solvent the yellowish liquids are formed which become solid after standing for about a month. The recrystallization of the fine powder of **I** from the alcohol produced the single crystals suitable for X-ray diffraction study (yield ~ 50%). Found: Al 6.5; Hf 21.1; C 43.3; H 8.5. Calc. for  $\text{Al}_2\text{Hf(OR)}_{10}$ : Al 6.6; Hf 21.7; C 43.8; H 8.5%.

It should be also mentioned that large crystals of **I** were isolated along with the fine crystalline powder of  $\text{Hf(OR)}_4 \cdot \text{ROH}$  (according to the X-ray powder diffraction data) from the reaction mixture in those cases, where the starting solutions were taken in Al : Hf = 1 : 1 ratio. Crystals of **I** melt at 57–62°C.

When carrying out the synthesis of alkoxozirconate of the 2 : 1 composition under the conditions described above for the synthesis of **I**, the crystallization of the fine crystalline powder from the 40–50% solutions was observed only after 7–10 days (yield ~ 30%). Found: Al 7.5; Zr 12.5; C 48.4; H 9.5. Calc. for  $\text{Al}_2\text{Zr(OR)}_{10}$ : Al 7.3; Zr 12.4; C 48.9; H 9.5%.

Attempts to use the solutions with higher concentrations has led to the solidification of the entire reaction mixture and no crystalline phase could be isolated. Further efforts to obtain the bimetallic complex by recrystallization of the solidified mass yielded only the well-formed crystalline product, which, according to the X-ray powder diffraction data, represented  $\text{Al(OR)}_3$ .

In order to determine the composition of zirconium and hafnium isopropoxides after their refluxing in isopropanol, the special experiments were carried out. Thus, after refluxing of the 6% solution of  $\text{Zr(OR)}_4 \cdot \text{ROH}$  in ROH for 1 h the crystallization of monosolvate was observed, and the concentration of the mother liquor proved to be significantly higher than the equilibrium values for 20°C (3.3%  $\text{Zr(OR)}_4$  rather than 1.7% [6]). The refluxing of 3–4% solution is accompanied by even more profound destruction, so that the concentration of the mother liquor over the

1 : 1 sample turns out to be as high as 10% (after evaporation of the solvent *in vacuo*). The melting of these samples occurs in a rather wide temperature range of 100–128°C (according to [6] m.p. of  $\text{Zr(OR)}_4 \cdot \text{ROH}$  is equal to 138–141°C). The results are analogous to those observed for the desolvation of Zr and Hf isopropoxides, which occurs at higher temperatures and results in the formation of  $\text{M}_3\text{O(OR)}_{10}$  and  $\text{Zr}_4\text{O(OR)}_{14}$  oxoisopropoxides [6].

The reaction of " $\text{Hf(OEt)}_4$ " with  $\text{Al(OEt)}_3$  was carried out under the same conditions as the synthesis of complexes **I** and **II**. A few crystals of hafnium ethoxoaluminate (**III**) were in some cases precipitated from the viscous solution obtained by evaporation of the solvent from reaction mixture *in vacuo*. Found: Al 7.3; Hf 25.9; C 35.7; H 7.6. Calc. for  $\text{Al}_2\text{Hf(OEt)}_{10}$ : Al 7.9; Hf 26.1; C 35.2; H 7.3%.

#### *Study of the solubility diagrams*

The solubility in the  $\text{Al(OR)}_3\text{-M(OR)}_4 \cdot \text{ROH-ROH}$  systems were studied by the analytical method at 20°C. Solubilities of **I** and **II** were determined by saturation of alcohol with the corresponding crystalline complexes. The eutronics were obtained after agitation of alcohol with two solid phases:  $\text{Al(OPr)}_3$  and **I** (or **II**) and  $\text{M(OPr)}_4 \cdot \text{PrOH}$  with **I** (or **II**), respectively.

In each of the binary systems,  $\text{M(OR)}_4 \cdot \text{ROH-ROH}$  (M = Hf, Zr), there exists the only solid phase, *viz.* monosolvate, which shows rather low solubility (1.9% and 1.5% for M = Hf and Zr, respectively) [6]. The solubility of  $\text{Al(OR)}_3$  (with m.p. of 140°C) in the alcohol is equal to 4.3% at 20°C [7]. Figure 1 shows that **I** and **II** are congruently soluble and may be crystallized from a sufficiently broad region on both sides of the 2 : 1 section. It has already been mentioned that **I** also precipitates from the solutions with 1 : 1 component ratio. It should be particularly emphasized that in many cases in these systems supersaturated solutions are formed, which have concentrations significantly higher than those corresponding to the equilibrium values and yet do not yield the crystalline phase even after standing for several days.

The crystallization region of **II** is sufficiently large. The solubility values are substantially higher than those reported in [5] (Tables 1 and 2).

#### *X-ray diffraction study*

$\text{C}_{30}\text{H}_{70}\text{Al}_2\text{HfO}_{10}$ ,  $M = 823.31$ , monoclinic, space group  $C2/c$ , at 293°  $a = 23.311(5)$ ,  $b = 11.176(2)$ ,  $c = 17.372(4)$  Å,  $\beta = 104.94(3)^\circ$ ,  $V = 4373(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.251$  g cm<sup>-3</sup>,  $D_{\text{exp}} = 1.249$  g cm<sup>-3</sup>. X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer ( $T = 293$  K, graphite-monochromated Mo- $K\alpha$  radiation,  $\lambda = 0.71073$  Å  $\theta/2\theta$  scan technique, no absorption correction was applied,  $\mu(\text{Mo-K}\alpha) = 24.67$  cm<sup>-1</sup>,  $\theta = 2\text{--}29^\circ$ ). The structure

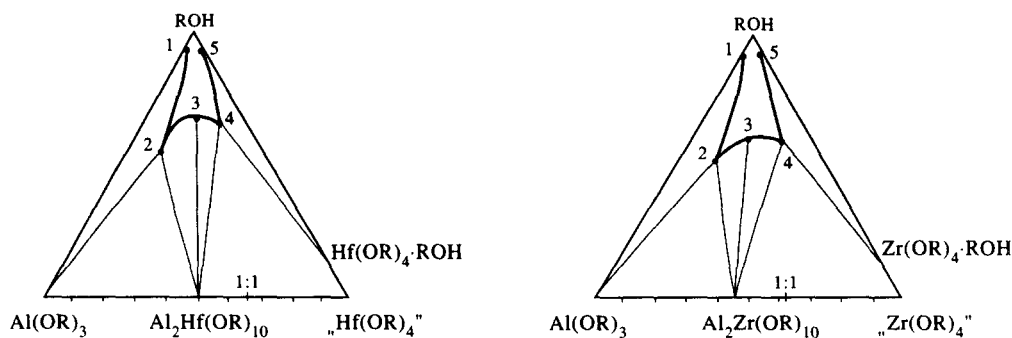


Fig. 1. Solubility in the  $\text{Al}(\text{OR})_3\text{-M}(\text{OR})_4 \cdot \text{ROH-ROH}$  systems at 20 °C (mass. %).

was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation. All H atoms were placed in geometrically calculated positions and included in the refinement using the riding model approximation with the  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the methyne and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups, where the  $U_{\text{eq}}(\text{C})$  is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding H atom. Final discrepancy factors are:  $R1 = 0.0500$  (on  $F$  for 4057 reflections with  $I > 2\sigma(I)$ ),  $wR2 = 0.1458$  (on  $F^2$  for all 5810 reflections used in the refinement of 195 parameters). All calculations were carried out on IBM PC with the help of SHELXTL PLUS 5 (gamma version) program. Atomic coordinates are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

Mass-spectra were measured using an AEI MS-30 mass-spectrometer, the temperature of the injected sample was 150 °C, ionization potential was 70 eV, the

masses of the ions involving the  $^{180}\text{Hf}$ ,  $^{90}\text{Zr}$  and  $^{12}\text{C}$  isotopes are listed.

## RESULTS AND DISCUSSION

It is noteworthy that the mere simultaneous presence of two alkoxides in the solution does not provide sufficient condition for their chemical interaction. Complex formation actually occurs only in the course of the prolonged refluxing of the solutions. It was established that this process, as well as the desolvation of  $[\text{M}(\text{OR})_4(\text{ROH})]_2$  in the absence of the solvent [6], is accompanied by the partial thermolysis of the components.

One may suggest that it is actually the presence of the oxo group in Zr and Hf alkoxides, which makes possible the formation of bimetallic isopropoxide complexes. We have already come across the similar phenomena earlier, when studying the chemistry of

Table 1. Solubility in the  $\text{Al}(\text{OR})_3\text{-Hf}(\text{OR})_4 \cdot \text{ROH-ROH}$  system at 20 °C

Number of the point	The composition of solution (mass %)		Solid phase
	$\text{Al}(\text{OR})_3$	$\text{Hf}(\text{OR})_4$	
1	4.3	—	$\text{Al}(\text{OR})_3$
2	36.2	11.5	$\text{Al}(\text{OR})_3 + \text{Al}_2\text{Hf}(\text{OR})_{10}$
3	15.5	15.8	$\text{Al}_2\text{Hf}(\text{OR})_{10}$
4	8.9	24.8	$\text{Al}_2\text{Hf}(\text{OR})_{10} + \text{Hf}(\text{OR})_4 \cdot \text{ROH}$
5	—	1.9	$\text{Hf}(\text{OR})_4 \cdot \text{ROH}$

Table 2. Solubility in the system  $\text{Al}(\text{OR})_3\text{-Zr}(\text{OR})_4 \cdot \text{ROH-ROH}$  at 20 °C

Number of the point	The composition of solution (mass %)		Solid phase
	$\text{Al}(\text{OR})_3$	$\text{Zr}(\text{OR})_4$	
1	4.3	—	$\text{Al}(\text{OR})_3$
2	34.6	12.5	$\text{Al}(\text{OR})_3 + \text{Al}_2\text{Zr}(\text{OR})_{10}$
3	21.1	16.9	$\text{Al}_2\text{Zr}(\text{OR})_{10}$
4	8.6	31.1	$\text{Al}_2\text{Zr}(\text{OR})_{10} + \text{Zr}(\text{OR})_4 \cdot \text{ROH}$
5	—	1.5	$\text{Zr}(\text{OR})_4 \cdot \text{ROH}$

polymeric  $M(OR)_2$  ( $M = Co, Ni, Cr, Fe$ ). These alkoxides react with Al, Nb and other alkoxide species only in the presence of traces of water, i.e. only after oxo groups are introduced into the coordination sphere of metal atom [8,9]. Another process, which is known to be a source of oxo groups in alkoxide molecules, thus promoting the formation of complexes, is the oxidation by traces of oxygen, occurring, for instance, for alkaline and alkaline-earth alkoxides. Such oxidation process is especially well documented in case of the reaction between Ba and Ti alkoxides [10].

The present work provides additional evidence for the role of the presence of the traces of oxo groups in the process of complex formation. It does not exclude, however, the possibility of crystallization of bimetallic alkoxides, without oxo groups from such solutions. Along with the complexes I and II we have observed the crystallization of such complexes in the course of the synthesis of  $LaNb_2(OR)_{13} \cdot 2ROH$  [8] and  $Ba_2Zr(OR)_8 \cdot 5ROH$  [11]. The yields in all cases were far from being quantitative, as the mother liquors in both cases were known to contain oxo groups, either within the  $La_5O(OR)_{13}$  component (in case of the lanthanum–niobium system) or as a result of  $Ba(OR)_2$  oxidation (in case of barium–zirconium complex). The composition of the bimetallic complexes, which are formed eventually, *viz.*, the presence or absence of the oxo groups in such complexes, is determined in each particular case by the energy of crystal lattice.

Therefore, on carrying out the synthesis of bimetallic alkoxides, one should pay special attention to the possibly full separation of the crystalline phase from the mother liquors, as the oxo complexes are frequently accumulated in one of the phases. Otherwise, it may well happen that it would be impossible to have definite data on the individual character and composition of bimetallic complexes. Thus, the difficulties with crystallization of complexes II and its incomplete separation from the liquid phase resulted in incorrect determination of its composition as 1:1 [5].

The single-crystal X-ray diffraction study has shown that the crystal of I is built of trinuclear molecules (Fig. 2, Table 3) which have the structure, first suggested by Mehrotra [3]. The molecule occupies a special position on the two-fold axis, which passes through the Hf atom and involves the central coordination octahedron  $[Hf(OR)_6]$  sharing common edges with each of the two peripheral coordination tetrahedra  $[Al(OR)_4]$ . The metal–oxygen core of the complex I is analogous to that of the trinuclear aluminium isopropoxochloride derivative,  $Al_3Cl_5(OPr^i)_4$  [12] (the latter is believed to be structurally related to trimeric aluminium isopropoxide,  $[Al(OPr^i)_3]_3$ ), the only difference being the higher coordination number of the central atom in case of six-coordinated Hf rather than five-coordinated aluminium. Molecule I also shows some structural similarity with tetranuclear alkoxides  $[Al(OPr^i)_3]_4$  [13, 14] and

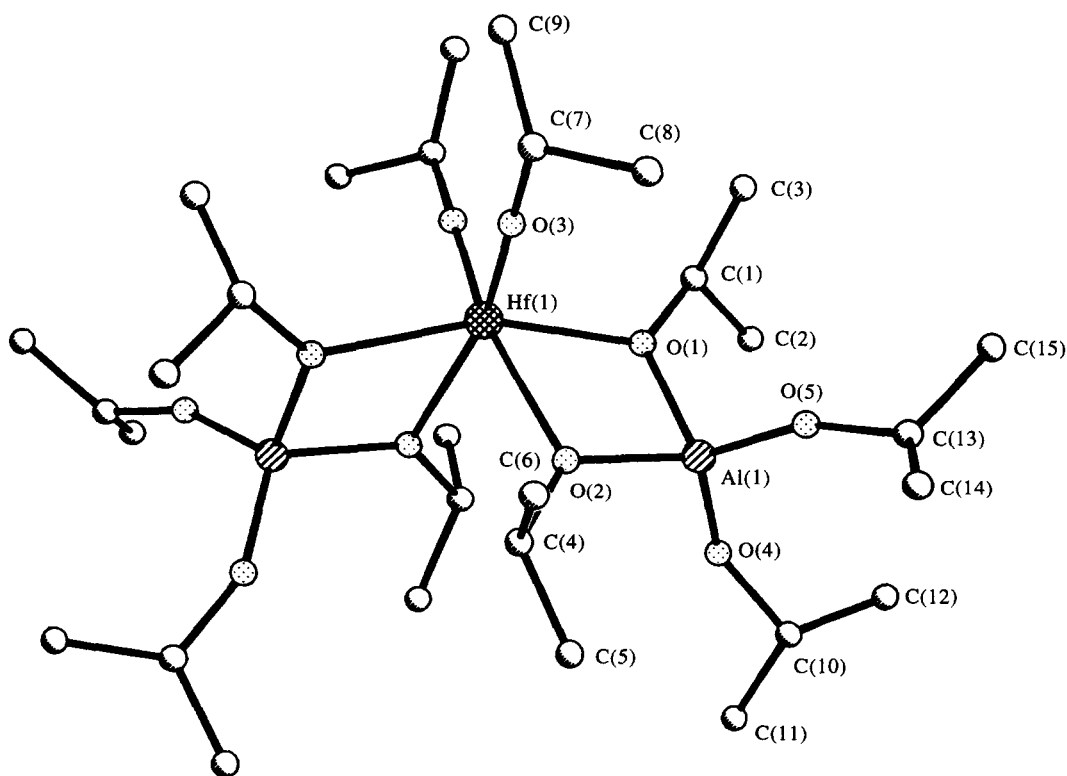


Fig. 2. Molecular structure of  $Al_2Hf(OPr)_{10}$  (I).

Table 3. Bond lengths (Å) and angles (°) in **I**

Hf(1)—O(3)	1.913(4)	O(5)—C(13)	1.288(12)
Hf(1)—O(1)	2.140(4)	C(1)—C(2)	1.40(2)
Hf(1)—O(2)	2.213(3)	C(1)—C(3)	1.425(14)
Hf(1)—Al(1)	3.125(2)	C(4)—C(5)	1.434(12)
Al(1)—O(5)	1.667(6)	C(4)—C(6)	1.491(12)
Al(1)—O(4)	1.689(5)	C(7)—C(9)	1.37(2)
Al(1)—O(2)	1.787(4)	C(7)—C(8)	1.43(2)
Al(1)—O(1)	1.803(5)	C(10)—C(11)	1.47(2)
O(1)—C(1)	1.454(8)	C(10)—C(12)	1.481(14)
O(2)—C(4)	1.450(6)	C(13)—C(15)	1.40(2)
O(3)—C(7)	1.377(9)	C(13)—C(14)	1.45(2)
O(4)—C(10)	1.379(9)		
O(3)—Hf(1)—O(3A)	100.8(3)	Al(1)—O(2)—Hf(1)	102.2(2)
O(3)—Hf(1)—O(1)	100.7(2)	C(7)—O(3)—Hf(1)	177.4(7)
O(3A)—Hf(1)—O(1)	92.4(2)	C(10)—O(4)—Al(1)	138.5(6)
O(1)—Hf(1)—O(1A)	159.4(2)	C(13)—O(5)—Al(1)	160.9(12)
O(3)—Hf(1)—O(2)	92.1(2)	C(2)—C(1)—C(3)	120.0(12)
O(3A)—Hf(1)—O(2)	158.3(2)	C(2)—C(1)—O(1)	112.2(8)
O(1)—Hf(1)—O(2)	67.9(2)	C(3)—C(1)—O(1)	111.0(8)
O(1A)—Hf(1)—O(2)	96.1(2)	C(5)—C(4)—O(2)	111.3(6)
O(2)—Hf(1)—O(2A)	81.5(2)	C(5)—C(4)—C(6)	113.8(9)
O(5)—Al(1)—O(4)	118.7(4)	O(2)—C(4)—C(6)	108.5(6)
O(5)—Al(1)—O(2)	112.2(3)	C(9)—C(7)—O(3)	115.0(12)
O(4)—Al(1)—O(2)	114.3(2)	C(9)—C(7)—C(8)	117.0(12)
O(5)—Al(1)—O(1)	112.4(4)	O(3)—C(7)—C(8)	113.5(10)
O(4)—Al(1)—O(1)	109.1(2)	O(4)—C(10)—C(11)	112.7(9)
O(2)—Al(1)—O(1)	85.3(2)	O(4)—C(10)—C(12)	113.3(9)
C(1)—O(1)—Al(1)	128.7(5)	C(11)—C(10)—C(12)	114.2(11)
C(1)—O(1)—Hf(1)	126.3(5)	O(5)—C(13)—C(15)	120(2)
Al(1)—O(1)—Hf(1)	104.5(2)	O(5)—C(13)—C(14)	119.5(12)
C(4)—O(2)—Al(1)	129.8(4)	C(15)—C(13)—C(14)	115.9(12)
C(4)—O(2)—Hf(1)	127.9(4)		

Atoms labelled by letter A are generated from the reference atoms by the  $-x, y, -z + 1/2$  symmetry transformation.

$\text{Er}[\text{Al}(\text{OR})_4]_3$  [15], which, in contrast to **I**, involve three, rather than two, peripheral  $[\text{Al}(\text{OR})_4]$  groups. Although compound **I** has two *cis*-terminal OR groups at the central Hf atom instead of the third four-membered cycle, two  $[\text{HfO}_2\text{Al}]$  cycles, which are present in the structure are geometrically close to those observed in the tetranuclear complexes. In particular the mean planes of two almost planar  $[\text{HfO}_2\text{Al}]$  cycles in **I** form the dihedral angle of  $82^\circ$  with each other, which is quite close to values of the corresponding dihedral angles in the structure of  $[\text{Al}(\text{OR})_3]_4$ .

The angular distortions of the Hf coordination octahedron and the Al tetrahedra are naturally due to the formation of the four-membered rings and are manifested in the significant decrease of the endocyclic bond angles  $[\text{O}(1)\text{—Hf}(1)\text{—O}(2), 67.9(2)^\circ$  and  $\text{O}(1)\text{—Al}(1)\text{—O}(2), 85.3(2)^\circ]$  and the simultaneous increase of most of those bond angles which are not involved in any cycles  $[\text{O}(1)\text{—Hf}(1)\text{—O}(3), 100.7(2)^\circ$ ;  $\text{O}(1)\text{—Hf}(1)\text{—O}(3A), 92.4(2)^\circ$ ;  $\text{O}(3)\text{—Hf}(1)\text{—O}(3A), 100.8(3)^\circ$  and  $\text{O}(1)\text{—Al}(1)\text{—O}(4), 109.1(2)^\circ$ ;  $\text{O}(1)\text{—Al}(1)\text{—O}(5), 112.4(4)^\circ$ ;

$\text{O}(2)\text{—Al}(1)\text{—O}(4), 114.3(2)^\circ$ ;  $\text{O}(2)\text{—Al}(1)\text{—O}(5), 112.2(3)^\circ$ ,  $\text{O}(4)\text{—Al}(1)\text{—O}(5), 118.7(4)^\circ]$ . The bridging as well as the terminal Hf—O bond lengths in **I** [ $\text{Hf}(1)\text{—O}(1) 2.140(4)$ ,  $\text{Hf}(1)\text{—O}(2) 2.213(3)$  Å and  $\text{Hf}(1)\text{—O}(3) 1.913(4)$  Å] do not differ from the distances observed for the corresponding Zr(Hf)—OR bonds in the  $[\text{M}(\text{OR})_4(\text{ROH})]_2$  solvates [16]. The increased bond order of the terminal Hf—O bonds is reflected in the widening of the corresponding HfOC bond angles, which is even more pronounced in complex **I** [ $\text{Hf}(1)\text{—O}(3)\text{—C}(7) 177.4(7)^\circ$ ] than in the  $\text{Hf}(\text{OR})_4 \cdot \text{ROH}$  structure, wherein the relevant HfOC angles span the range of  $167.3\text{--}177.6^\circ$ . The regular increase of the O—C bond lengths and simultaneous decrease of the HfOC bond angles are observed in molecule **I** on going from terminal  $[\text{O}(3)\text{—C}(7) 1.377(9)$  Å] to bridging OR groups  $[\text{O}(1)\text{—C}(1) 1.454(8)$ ,  $\text{O}(2)\text{—C}(4) 1.450(6)$  Å,  $\text{Hf}(1)\text{—O}(1)\text{—C}(1) 126.3(5)$ ,  $\text{Hf}(1)\text{—O}(2)\text{—C}(4) 127.9(4)^\circ]$ .

Analogous geometrical differences are found in the coordination environment of the Al atoms. The Al—O and C—O bond lengths both terminal  $[\text{Al}(1)\text{—O}(4) 1.689(5)$ ,  $\text{O}(4)\text{—C}(10) 1.379(9)$  Å and

Table 4. The results of the indexing of X-ray powder diffraction patterns for **I** and **II** (DRON-3M, Co-K $\alpha$ ) using the cell parameters determined in the single crystal X-ray study of **I**

<i>I</i>	Al <sub>2</sub> Hf(OR) <sub>10</sub> ( <b>I</b> )			Al <sub>2</sub> Zr(OR) <sub>10</sub> ( <b>II</b> )		
	<i>d</i> <sub>exp</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>exp</sub>	
5	10.1	10.01	110	32	10.7	
5	9.25	9.07	$\bar{1}$ 10	20	9.64	
100	8.74	8.39	002	100	8.86	
40	7.96	8.19	111	85	8.12	
				60	7.97	
50	7.79	7.76	$\bar{2}$ 02	30	7.56	
10	6.25	6.23	310	15	6.15	
14	6.09	6.10	112	10	6.07	
15	5.45	5.47	311	—	—	
15	5.39	5.36	$\bar{4}$ 02	—	—	
10	5.01	5.00	220	12	5.10	
10	4.97	4.95	$\bar{2}$ 21	—	—	
15	4.56	4.56	312	10	4.58	
5	4.21	4.20	402	20	4.13	
5	4.08	4.10	222	5	3.97	
8	3.88	3.88	$\bar{4}$ 04	30	3.81	
20	3.79	3.81	$\bar{5}$ 13	10	3.76	
10	3.55	3.56	131	—	—	
5	3.36	3.36	422	—	—	
13	3.30	3.30	$\bar{1}$ 15	10	3.31	
5	3.26	3.20	331	7	3.26	
10	3.14	3.13	$\bar{1}$ 33	12	3.13	

Al(1)—O(5) 1.667(6), O(5)—C(13) 1.288(12) Å\*] and bridging [Al(1)—O(1) 1.803(5) and Al(1)—O(2) 1.787(4) Å], as well as the terminal and bridging AlOC bond angles [Al(1)—O(4)—C(10) 138.5(6), Al(1)—O(5)—C(13) 160.19(12)° and Al(1)—O(1)—C(1) 128.7(5), Al(1)—O(2)—C(4) 129.8(4)° respectively] are quite close to those observed earlier in the structures of [Al(OR)<sub>3</sub>]<sub>4</sub> [13] and Al<sub>3</sub>(OR)<sub>4</sub>Cl<sub>5</sub> [12]. The sums of the bond angles at the bridging oxygen atoms are approximately equal to 360°, which indicates that these atoms are evidently *sp*<sup>2</sup>-hybridized.

The results of the indexing of the powder diffraction pattern of **I** and **II** using the unit cell parameters, found in the single-crystal X-ray study of **I** (*vide infra*), are listed in Table 4.

Solubility studies of the Al(OR)<sub>3</sub>-M(OR)<sub>4</sub>·ROH-ROH (M = Hf, Zr) systems at 20°C (Fig. 1, Tables 1 and 2) lead to the conclusion that in each case there exists the only one complex, *viz.* complex Al<sub>2</sub>M(O-Pr)<sub>10</sub> (M = Hf(**I**), Zr(**II**)) with the 2:1 composition. Both complexes are sufficiently stable and crystallize in a broad range of concentrations on both sides of

Table 5. Mass spectra of Al<sub>2</sub>M(OR)<sub>10</sub>, M = Hf (**I**) and Zr (**II**)<sup>a</sup>

<b>I</b>		<b>II</b> <sup>s</sup>		Interpretation
<i>m/z</i>	<i>I</i>	<i>m/z</i>	<i>I</i>	
765	100	675	100	Al <sub>2</sub> M(OR) <sub>9</sub> <sup>+</sup>
664	32	574	87	Al <sub>2</sub> MO(OR) <sub>7</sub> <sup>+</sup>
650	10	560	25	Al <sub>2</sub> MO(OR) <sub>6</sub> (OEt) <sup>+</sup>
620	7	530	12	AlM(OR) <sub>7</sub> <sup>+</sup>
621	7	531	12	Al <sub>2</sub> MO <sub>2</sub> (OR) <sub>8</sub> <sup>+</sup>
605	7	515	25	Al <sub>2</sub> MO(OR) <sub>8</sub> <sup>+</sup>
561	11	471	100	AlM(OR) <sub>6</sub> <sup>+</sup>
				Al <sub>2</sub> MO <sub>2</sub> (OR) <sub>8</sub> <sup>+</sup>
547	—	457	—	AlM(OR) <sub>5</sub> (OEt) <sup>+</sup>
518	4.7	428	18	AlMO(OR) <sub>5</sub> <sup>+</sup>
503	4.7	413	18	Al <sub>2</sub> MO <sub>2</sub> (OR) <sub>4</sub> <sup>+</sup>
502	10	412	18	AlM(OR) <sub>5</sub> <sup>+</sup>
475	5	—	—	Al <sub>2</sub> MO <sub>2</sub> (OR) <sub>3</sub> (OMe) <sup>+</sup>
459	3.5	369	—	AlMO(OR) <sub>4</sub> <sup>+</sup>
401	2	311	37	Al <sub>2</sub> MO <sub>3</sub> (OR) <sub>2</sub> <sup>+</sup>

<sup>a</sup>Along with the listed ions in both mass-spectra the ions corresponding to the products of the [Al(OR)<sub>3</sub>]<sub>*n*</sub> (*n* = 3, 4) fragmentation are present: 757 [Al<sub>4</sub>(OR)<sub>7</sub>]<sub>1</sub><sup>+</sup>, 553 [Al<sub>3</sub>(OR)<sub>6</sub>]<sub>1</sub><sup>+</sup>, 349 [Al<sub>2</sub>(OR)<sub>5</sub>]<sub>1</sub><sup>+</sup>.

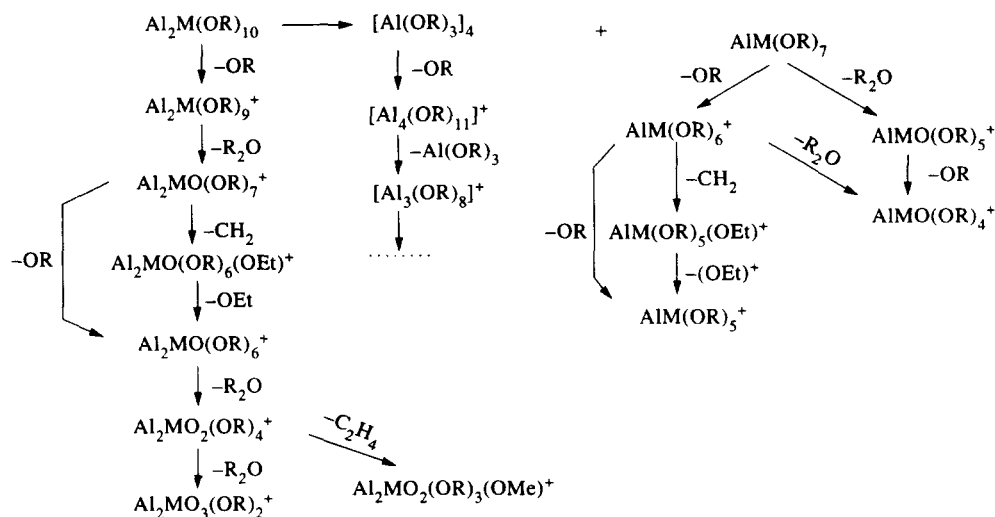
the 2:1 section. According to the mass-spectroscopic data, these complexes are also present in the vapour phase (Fig. 3, Table 5). Mass-spectroscopic study of **I** and **II** shows that the complexes exhibit two main fragmentation pathways on electron impact, *viz.*, (1) the consecutive elimination of OR, R<sub>2</sub>O and CH<sub>2</sub> groups; and (2) the abstraction of Al(OR)<sub>3</sub> with the formation of AlM(OR)<sub>7</sub> and subsequent fragmentation of the latter, proceeding similarly to the decomposition of molecule **I** to **II**.

In the X-ray powder diffraction pattern for the samples of "AlZr(OR)<sub>7</sub>" only those diffraction lines which may be attributed to complex **II** were present; the same is, by the way, true for the hafnium derivatives. It may be, therefore, assumed that the excess of the zirconium alkoxide is found in the sample in the form of amorphous thermolysis product Zr(OR)<sub>4</sub>·ROH [6] (this fact may account for the variations of the solubility values of the samples having the 1:1 composition).

The mass-spectrum of the "AlZr(OR)<sub>7</sub>" samples, reported earlier [5] may find more natural interpretation in the assumption of the presence of both complex **II** and the Zr(OR)<sub>4</sub>·ROH solvate in these samples. It may, therefore, be concluded that alkoxozirconates and -hafnates of the 1:1 composition do not exist.

The study of the interaction of Al and Hf ethoxides is of particular interest, taking into account, that in this case both components contain oxo groups. Thus, according to the preliminary results of the X-ray diffraction study the Hf(OEt)<sub>4</sub> samples contain the [Hf<sub>3</sub>O(OEt)<sub>10</sub>(EtOH)]<sub>2</sub> species [18]. The reaction of complex formation with polymer aluminium ethoxide

\* The Al—O bond lengths in the almost regular tetrahedron in the structure of [C<sub>6</sub>H<sub>11</sub>NH<sub>3</sub>]<sup>+</sup>[Al(OR)<sub>4</sub>]<sup>−</sup> are equal to 1.73–1.76 Å [17].

Fig. 3. Fragmentation scheme for complexes  $\text{Al}_2\text{M}(\text{OR})_{10}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ).Table 6. Mass spectrum of  $\text{Al}_2\text{Hf}(\text{OEt})_{10}^+$ 

$m/Z$	$I$	Interpretation
686	17	$\text{Al}_2\text{Hf}(\text{OEt})_{10}^+$
670	19	$\text{Al}_2\text{Hf}(\text{OEt})_9(\text{OCH}_3)^+$
643	100	$\text{Al}_2\text{Hf}(\text{OEt})_9^+$
569	20	$\text{Al}_2\text{HfO}(\text{OEt})_7^+$
521	7	$\text{AlHf}(\text{OEt})_7^+$
499	4	$\text{Al}_2\text{HfO}_2(\text{OEt})_5^+$
477	5	$\text{AlHf}(\text{OEt})_6^+$
419	10	$\text{Al}_2\text{HfO}_3(\text{OEt})_3^+$
403	5	$\text{AlHfO}(\text{OEt})_4^+$
345	10	$\text{Al}_2\text{HfO}_4(\text{OEt})^+$

"The ions corresponding to the fragmentation of  $[\text{Al}(\text{OEt})_3]_n$  (973  $[\text{Al}_6(\text{OEt})_{18}]^+$ , 779  $[\text{Al}_5(\text{OEt})_{14}\text{CH}_2]^+$ , 691  $[\text{Al}_5(\text{OEt})_{12}\text{O}^+]$ , 529  $[\text{Al}_4(\text{OEt})_9\text{O}^+]$ , 442  $[\text{Al}_3(\text{OEt})_6^+]$ , 323  $[\text{Al}_2(\text{OEt})_3^+]$ ) and "hafnium ethoxide" ions (956  $[\text{Hf}_3\text{O}(\text{OEt})_7^+]$ , 817  $[\text{Hf}_2\text{O}_3(\text{OEt})_5^+]$ ) are also present.

proceeds only after prolonged refluxing with the solution of " $\text{Hf}(\text{OEt})_4$ " in ethanol, which probably increases the concentration of oxo ligands. Nevertheless, it is possible to isolate from the concentrated solutions (in rather low yields) the crystals of  $\text{Al}_2\text{Hf}(\text{OEt})_{10}$  (**III**). Mass-spectrum of **III**, and that of the foam-like sample, formed after evaporation of the solvent from the 2:1 aluminium and hafnium ethoxide solution *in vacuo*, turned out to be identical and their fragmentation scheme (Table 6) was similar to that of **I** and **II**. It means, therefore, that molecules of **III** exist also in the vapour phase, and the ions of the  $\text{Al}_2\text{HfO}_n(\text{OR})_{9-n}^+$  type ( $n = 1-4$ ) are formed only in the process of the elimination of ether from **III**.

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## REFERENCES

1. R. C. Mehrotra and A. Mehrotra, *Inorg. Chim. Acta Rev.* 1971, 127.
2. D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London (1978).
3. R. C. Mehrotra and J. Singh, *J. Indian Chem. Soc.* 1977, **54**, 109.
4. R. C. Mehrotra and A. Mehrotra, *J. Chem. Soc.* 1972, 1203.
5. N. Ya. Turova, S. I. Kucheiko and N. I. Kozlova, *Soviet J. Coord. Chem.* 1983, **9**, 513 (English).
6. E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, A. I. Belokon', D. V. Berdyev, V. G. Kessler and Yu. K. Grishin, *Russ. Chem. Bull.* 1995, 734 (English).
7. V. A. Kozunov and N. Ya. Turova, *Russ. J. Inorg. Chem.* 1978, **23**, 680 (English).
8. E. P. Turevskaya, N. Ya. Turova, A. V. Korolev, A. I. Yanovsky and Yu. T. Struchkov, *Polyhedron* 1995, **14**, 1531.
9. T. V. Rogova, N. Ya. Turova and N. I. Kozlova, *Soviet J. Coord. Chem.* 1986, **12**, 440 (English).
10. E. P. Turevskaya, M. I. Yanovskaya, V. K. Limar and N. Ya. Turova, *Russ. J. Inorg. Chem.* 1993, **38**, 563 (English).
11. E. P. Turevskaya, D. V. Berdyev, N. Ya. Turova and I. M. Yanovskaya, *Russ. J. Inorg. Chem.* 1995, **40**, 1527 (English).
12. A. I. Yanovsky, V. A. Kozunov, N. Ya. Turova, N. G. Furmanova and Yu. T. Struchkov, *Doklady Chem. Proc. Acad. Sci. USSR* 1979, **244**, 26 (English).
13. N. Ya. Turova, V. A. Kozunov, A. I. Yanovsky, N. G. Bokiy, Yu. T. Stuchkov and V. L. Tar-nopolsky, *J. Inorg. Nucl. Chem.* 1979, **41**, 5.
14. K. Folting, W. E. Streib, K. G. Cauton, O. Pon-celet and L. G. Hubert-Pfalzgraf, *Polyhedron* 1991, **10**, 1639.
15. M. Wijk, R. Norrestam, M. Nygren and G. Westin, *Inorg. Chem.* 1996, **35**, 1077.
16. B. A. Vaartstra, J. C. Huffman, P. S. Gradeff, J. C.

- Daran, S. Parraud, K. Yunlu and K. G. Caulton, *Inorg. Chem.* 1990, **29**, 3126.
17. B. Beagley, K. Jones, P. Parkes and R. G. Pritchard, *Synth. React. Inorg. Met. Org. Chem.* 1988, **18**, 465.
18. Z. A. Starikova, A. I. Yanovsky, E. P. Turevskaya, N. Ya. Turova and D. V. Berdyev (unpublished results).