The alkoxides of zirconium and hafnium: direct electrochemical synthesis and mass-spectral study. Do "$M(OR)_4$", where M = Zr, Hf, Sn, really exist?

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The direct electrochemical synthesis of zirconium (**1a**) and hafnium (**1b**) alkoxides, $M(OPr^i)_4 \cdot Pr^iOH$, $Zr(OBu^i)_4 \cdot Bu^iOH$ (**4a**) and $M(OR)_4$, where R = Et (**2a,b**), Bu^n (**3a**), Bu^s (**5a**), C_2H_4OMe (**6a,b**) has been carried out by anodic oxidation of metals in anhydrous alcohols in the presence of LiCl as a conductive additive to give quantitative yields. The solubility polytherms and dissociation pressure of **1a,b** have been investigated. It has been proved by means of chemical analysis, X-ray powder, and IR spectral studies that the desolvation of **1a,b** and $Sn(OPr^i)_4 \cdot Pr^iOH$ (**1c**) is accompanied by the formation of amorphous oxocompounds $M_3O(OPr^i)_{10}$. On the basis of ^1H NMR data it has been proved that the structure of the latter is analogous to that of known triangular cluster molecules $M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6$, where M = Mo, W, U. Mass-spectral data and the determined physicochemical characteristics of **1—5** permit to conclude that the samples of composition $M(OR)_4$, where M = Zr, Hf, and **2**, **3**, **5** contain tri- and tetranuclear oxocomplexes $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$, respectively, along with $Zr(OR)_4$ oligomers of different molecular complexity.

Key words: oxoalkoxides, zirconium and hafnium alkoxides, electrochemical synthesis, mass-spectra, IR-, NMR-spectral, X-ray powder analysis.

Interest in zirconium and hafnium alkoxides has recently increased due to their increasing application as molecular precursors of inorganic oxide materials in sol-gel technology.[1,2] The isopropoxides of these metals are the best known and most widely used members of the corresponding homological series. They can be separated and purified much more easily than the other homologs due to the poor solubility of the $M(OPr^i)_4 \cdot D$ monosolvates that they form with donor ligands D, such as isopropanol, pyridine and THF.[3,4] They are formed during the interaction of MCl_4 or $(PyH)_2MCl_6$ with NH_3 in isopropanol[3,5,6]. According to the X-ray single crystal data the corresponding solvates with alcohols $[M(OPr^i)_4 \cdot Pr^iOH]_2$ (m.p. 138—141, M = Zr[3], and 135—137 °C, M = Hf[7]) possess binuclear structures, in which two octahedra share a common edge and alcohol molecules occupy axial positions on different sides of the equatorial plane and form hydrogen bonds with the oxygen atoms of the OR-groups attached to the neighboring metal atoms.[8] Their desolvation occurs at ~120 °C (0.5—1 Torr) with the formation of $M(OPr^i)_4$ — viscous liquids or glassy solids with b.p. ~170 °C (0.3 Torr), readily soluble in ether, CS_2, THF, and hydrocarbons, forming trimeric or tetrameric aggregates in benzene solutions (according to cryoscopic measurements).[9,10]

The reactions used for the preparation of other $M(OR)_4$ derivatives were either reactions of $(PyH)_2MCl_6$ with alcohols or esters in the presence of NH_3, or interchange reactions of $M(OEt)_4$ or $M(OPr^i)_4$ with alcohols or esters as well as the alcoholysis of the corresponding dialkylamides, $M(NR_2)_4$. The ethoxides exist as powders with m.p. 171 °C (M = Zr) and 180 °C (M = Hf), which can be sublimed at $T \geq 180$ °C (0.1 torr),[3,5,6,11–14] while the butoxides are waxy solids that can be distilled *in vacuo*. $Zr(OBu^s)_4$ can be isolated from the *sec*-butanol solution as the monosolvate (m.p. 80 °C with decomp.).[3,5,9,11] The patents[15–17] refer mainly to the abovementioned routes of $M(OR)_4$ preparation, based on reactions of MCl_4 or $(PyH)_2MCl_6$* with alcohols and

†Deceased.

* Pyridinium complexes are formed in these reactions as intermediates in the course of the action of HCl and Py on $MOCl_2 \cdot 8H_2O$ (with the subsequent removal of water in the form of its azeotrope with benzene or xylene by distillation).

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NH_3. These methods are usually rather labor-consuming, requiring large volumes of solvents and offering comparatively low yields. At the same time, in 1972 an electrochemical synthesis of $Zr(OEt)_4$ (along with alkoxide derivatives of many other metals) was reported in a patent publication devoted to the anodic oxidation of metals in alcohols in the presence of NH_4Cl as a conductive additive.[18]

The present paper reports the application of the latter method for the preparation of other homologs of $Zr(OR)_4$ series and hafnium alkoxides. Some physicochemical properties of these derivatives essential for their separation and purification, such as solubility in alcohols and hydrocarbons and molecular complexity in the gas phase (on the basis of mass-spectral data) have been investigated. The problem of the molecular composition of the "$M(OR)_4$" samples, where M = Zr, Hf, Sn, has also been considered.

Experimental

All the manipulations were carried out in a dry argon atmosphere using the Schlenk technique or in a dry box. The alcohols were purified by distillation over $Al(OR)_3$ and zeolites under argon; the final water content determined by Fischer titration was in 0.01—0.03 % range. Zr and Hf metals of 99.9 % purity (refined *via* chemical transport of iodides) were used. IR spectra of nujol and hexachlorobutadiene mulls were registered with a Perkin-Elmer 580-1p instrument, and proton NMR spectra were recorded with a Varian VXR-400 spectrometer. Mass spectra were obtained on AEI MS-30 and MI-1201 spectrometers (direct introduction, 70 eV) at 120—150 °C. The *m/z* values are given for ions based on ^{90}Zr, ^{180}Hf and ^{116}Sn. GLC-MS studies were carried out with a MAT-311 A Varian device (the sample evaporation temperature was 200 °C, SE-30 column).

The electrochemical synthesis was carried out in a cell in which the cathodic and anodic space was not separated. The cell was equipped with a reflux condenser and a water cooling jacket. A rod of Zr or Hf metal ~2 cm in diameter and 6—7 cm high was used as the anode, and the cathode was made of a platinum or stainless steel plate with an area of ~10 cm^2. LiCl (dried *in vacuo* prior to use at 80—100 °C) or Bu_4NBr * were used as conductive additives as 0.05—0.10 *N* solutions in the corresponding alcohols (100—200 mL). Dissolution was carried out at constant voltage (110 V), with an average current of 0.20—0.05 A, and an average current density of 0.05 A cm^{-2} in refluxing electrolyte, and was accompanied by intense evolution of hydrogen on the cathode.[19,20] When the electrolysis finished (in 10—20 h), the ROH was evaporated *in vacuo* (R = Et, Bu, C_2H_4OMe) or removed by decantation from the crystals formed (R = Pr^i). The crude products thus obtained were then subjected to reflux with small amounts of hexane or toluene in order to separate them from the conductive additive and the metal powder precipitates insoluble in hydrocarbons. The sediments were then removed by centrifugation and the clear solutions obtained were evaporated *in vacuo*, yielding pure alkoxides as residues.

The solubility polytherms of $M(OPr^i)_4 \cdot Pr^iOH$ (**1a,b**) [M = Zr (**a**), Hf (**b**)] were studied by chemical analysis methods. The zirconium content in the solutions analyzed was determined by complexometric titration with xylenol orange as the indicator, the hafnium content was determined gravimetrically in the form of HfO_2 (obtained by the thermal decomposition of the samples). The solubility at temperatures higher than 60 °C was determined in special ampulae, supported with appendices for sampling.

$M(OPr^i)_4 \cdot Pr^iOH$ (1a,b). Only Bu_4NBr was used in the preparation of **1b** because of the rapid extinction of the process in the presence of LiCl. The crystallization of the solvates occured already during the course of the anodic dissolution of the metal in accordance with the data on their solubility in alcohols (Table 1). The yields of the products were practically quantitative with respect to the metal amounts consumed, while the electric current yields varied in the range of 70—90 %. **1a**. Found (%): Zr, 23.5; C, 46.1; H, 9.3. Calculated (%): Zr, 23.5; C, 46.5; H, 9.3. $C_{15}H_{36}O_5Zr$. IR (ν/cm^{-1}): 3400 s, 2970 vs, 2930 s, 2865 m, 1460 w, 1380 m, 1340 sh, 1165 vs, 1130 sh, 1020 s, 950 m, 840 m, 820 m, 580 m, 550 vs, 460 m, 430 sh. **1b.** Found (%): Hf, 37.6; C, 37.8; H, 7.6. Calculated (%): Hf, 37.5; C, 37.9; H, 7.6. $C_{15}H_{36}O_5Hf$. The IR spectrum of **1b** is very close to that of **1a**, and for $\nu < 1340$ cm^{-1} it practically coincides with that described in the literature.[8] The melting points of the crystals determined by rapid heating are equal to ~140 °C for the Zr complex and 150—153 °C for that of Hf. The latter value is nearly 15 °C higher than that reported earlier.[7] However the partial desolvation of both complexes takes place at room temperature. The dissociation pressure for **1a** varies with temperature in the following way [*T*/°C, (*p*/Torr)]: 20 (2); 37 (5); 66 (12); 70 (13); 73 (15); 80 (16); 85 (18); 90 (22); 95 (28). In the 20—95 °C temperature range it can be described by the following equation:

$$\log(p/\text{mm}) = 5.36 - 1460/T.$$

The solubilities of the complexes in Pr^{i}OH at temperatures from 20 °C up to their melting points are given in Table 1. **1a,b** are also soluble in benzene, hexane, and THF.
Mass-spectra of the solvates coincide with those of "$M(OPr^i)_4$" (Table 2); their X-ray powder patterns (Co-Kα-radiation) can be indexed using the parameters obtained for their single

Table 1. Solubility of $M(OPr^i)_4 \cdot Pr^iOH$ (**1a,b**) in Pr^{i}OH (wt. %)

T/°C	1a	1b
0	0.9	1.0
20	1.5	1.9
40	3.6	3.0
50	5.5	—
60	6.9	4.4
70	9.9	—
80	12.0	6.2
90	14.8	9.0
100	15.3	12.5
110	19.5	18.5
115	23.2	26.6
125	28.3	43.0

* Special experiments demonstrated that if the salts of the NH_4^+ cation (proposed earlier for this purpose[18]) are used the process slows down and can stop after the passage of 0.6—2.0 A · h of electricity through the solution.

Table 2. Mass-spectra of "$M(OR)_4$"

"$Zr(OEt)_4$"	"$Hf(OEt)_4$"	"$Zr(OPr^i)_4$"	"$Hf(OPr^i)_4$"	"$Sn(OPr^i)_4$"		"$Zr(OBu)_4$"			Interpretation
		m/z (I (%))			m/z	I (%)			
						3a	**4a**	**5a**	
—	—	—	—	—	1455	—	—	—	$[M_4(OR)_{15}]^+$
1006(12)	—	—	—	—	1398	50	—	—	$[M_4O(OR)_{14}]^+$
961(100)	1324(100)	—	—	—	1325	75	100	—	$[M_4O(OR)_{13}]^+$
—	—	—	—	—	1283	5	5	—	$[M_4O(OR)_{12}(OMe)]^+$
—	—	—	—	—	1269	2	0.5	—	$[M_4O(OR)_{12}(OH)]^+$
916(0.5)	1276(20)	—	—	—	626(++)	70	—	—	$[M_4O(OR)_{12}]^+$
887(40)	1247(30)	—	—	—	1195	6	12	—	$[M_4O_2(OR)_{11}]^+$
873(8)	—	—	—	—	1153	2	10	—	$[M_4O_2(OR)_{10}(OMe)]^+$
—	300.5(20)	—	—	—	—	—	—	—	$[M_4O_2(OR)_{10}]^{++}$
—	—	—	—	—	1080	0.5	2	—	$[M_4O_2(OR)_9(OMe)]^+$
—	—	—	—	—	1032	3	1	—	$[M_4O_2(OR)_8(OMe)_2]^{++}$
—	—	—	—	—	982	7	1	—	$[M_4O_2(OR)_7(OMe)_2(OH)]^+$
813(20)	1173(50)	—	—	—	1065	100	3	—	$[M_4O_3(OR)_9]^+$
739(10)	1099(25)	—	—	—	—	—	—	—	$[M_4O_4(OR)_7]^+$
—	—	978(0.5)	—	—	—	—	—	—	$[M_3(OR)_{12}]^+$
—	—	963(0.5)	—	—	—	—	—	—	$[M_3(OR)_{11}(OC_2H_4)]^+$
765(80)*	—	919(0.2)	—	—	—	—	—	—	$[M_3(OR)_{11}]^+$
—	—	905(10)	—	—	—	—	—	—	$[M_3(OR)_{10}(OEt)]^+$
—	—	890(15)	—	—	—	—	—	—	$[M_3(OR)_{10}(OCH_2)]^+$
736(5)	1006(80)	876(8)	1146(10)	—	1016	—	—	4	$[M_3O(OR)_{10}]^+$
—	—	862(1)	—	—	1002	—	—	10	$[M_3O(OR)_9(OR^-CH_2)]^+$
—	—	848(0.5)	—	—	987	—	—	5	$[M_3O(OR)_9(OR^-C_2H_4)]^+$
—	—	—	—	—	973	—	—	10	$[M_3O(OR)_9(OCH_2)]^+$
691(50)	961(15)	817(100)	1087(100)	895(70)	943	30	100	100	$[M_3O(OR)_9]^+$
—	—	803(4)	1073(70)	—	915	3	15	22	$[M_3O(OR)_8(OEt)]^+$
		401.5	536.5						$[M_3O(OR)_8(OEt)]^{++}$
—	—	—	—	—	901	3	8	20	$[M_3O(OR)_8(OMe)]^+$
—	—	758(1)	1028(10)	—	870	1	1	1	$[M_3O(OR)_8]^+$
		379(20)	514(80)						$[M_3O(OR)_8]^{++}$
—	—	—	999(40)	—	—	—	—	—	$[M_3O(OR)_7(OCH_2)]^+$
—	—	372(1)	—	—	—	—	—	—	$[M_3O(OR)_7(OEt)]^{++}$
—	—	—	—	—	887	—	6	12	$[M_3O_2(OR)_8]^+$
—	—	—	—	—	859	0.5	2	1	$[M_3O_2(OR)_7(OEt)]^+$
617(25)	887(30)	715(15)	985(46)	793(1)	813	10	1	10	$[M_3O_2(OR)_7]^+$
—	—	—	—	—	799	—	—	9	$[M_3O_2(OR)_6(OPr)]^+$
—	—	701(4)	971(15)	779(100)	785	1	—	10	$[M_3O_2(OR)_6(OEt)]^+$
—	—	—	—	—	771	5	12	5	$[M_3O_2(OR)_6(OMe)]^+$
543(10)	813(25)	613(70)	883(100)	691(10)	683	3	10	30	$[M_3O_3(OR)_5]^+$
—	—	598(4)	868(21)	676(5)	—	—	—	—	$[M_3O_3(OR)_4(OC_2H_4)]^+$
—	—	568(5)	838(42)	—	—	—	—	—	$[M_3O_3(OR)_2(OC_2H_4)_3]^+$
498(5)	768(3)	—	—	—	610	4	1	1	$[M_3O_3(OR)_4]^+$
—	—	495(50)	765(21)	—	—	—	—	—	$[M_3O_3(OR)_3]^+$
—	—	467(10)	737(41)	545(50)	—	—	—	—	$[M_3O_3(OR)_2(OMe)]^+$
469(1)	739(15)	511(20)	781(53)	589(10)	553	2	—	50	$[M_3O_4(OR)_3]^+$
—	—	452(10)	722(11)	530(5)	480	1	—	—	$[M_3O_4(OR)_2]^+$
495(2)	—	593(10)	—	—	691	3	90	1	$[M_2(OR)_7]^+$
421(40)	601(70)	491(15)	671(10)	543(50)	561	25	40	20	$[M_2O(OR)_5]^+$
393(10)	—	—	—	—	505	20	5	10	$[M_2O(OR)_4(OH)]^+$
348(12)	528(15)	—	—	—	—	—	—	—	$[M_2O(OR)_3(OH)]^+$
347(10)	527(15)	389(1)	—	441(1)	431	1	10	100	$[M_2O_2(OR)_3]^+$
—	—	—	—	—	382	2	20	10	$[M(OR)_4]^+$
—	—	325(7)	—	—	367	—	27	10	$[M(OR)_3(OC_3H_6)]^+$
—	—	311(100)	—	337(10)	—	—	—	—	$[M(OR)_3(OC_2H_4)]^+$
—	—	—	—	—	339	22	100	1	$[M(OR)_3(OCH_2)]^+$
255(30)	—	267(70)	—	293(2)	309	10	100	1	$[M(OR)_3]^+$
—	—	265(50)	—	291(1)	—	—	—	—	$[M(OR)(OC_3H_6)_2]^+$
—	—	253(30)	—	—	281	1	31	10	$[M(OR)_2(OEt)]^+$
—	—	251(20)	—	—	—	—	—	—	$[M(OR)(OC_3H_6)(OC_2H_4)]^+$

Table 2. (Continued)

$Zr(OEt)_4$	$Hf(OEt)_4$	$Zr(OPr^i)_4$	$Hf(OPr^i)_4$	$Sn(OPr^i)_4$	$Zr(OBu)_4$				Interpretation
m/z (I (%))					m/z	I (%)			
						3a	**4a**	**5a**	
—	—	—	—	—	267	2	100	1	$[M(OR)_2(OMe)]^+$
—	—	—	—	—	253	1	50	1	$[M(OR)_2(OH)]^+$
180 (2)	—	—	—	—	236	1	25	5	$[M(OR)_2]^+$

* The ion is present only in the spectra of the samples not subjected to sublimation.

Note. m^*/z (metastable ions):

$Zr(OEt)_4$. 818: 961→887; 672: 813→739; 538: 1006→736; 456: 543→498; 496: 961→691; 358: 495→421; 313: 393→348; 286: 421→347; 256: 691→421.

$Hf(OEt)_4$. 1029: 1173→1099; 818: 961→887; 699: 1321→961.

$Zr(OPr^i)_4$. 785: 978→876; 762: 876→817; 625: 817→715; 525: 715→613; 425: 613→511; 295: 817→491.

$Zr(OBu)_4$. 1206: 1455→1325; 701: 943→813; 671: 1325→943; 604: 1252→870; 574: 813→683; 447: 683→553; 455: 691→561; 331: 561→431.

crystals[8] [given are d/Å (relative intensity(%)), hkl]. **1a.** 10.07 (40) $10\bar{1}$; 9.87 (45) $1\bar{1}1$; 9.51 (35) 101; 8.89 (100) 200; 8.78 (60) 210; 8.42 (70) $11\bar{1}$; 8.32 (90) $1\bar{1}\bar{1}$; 7.15 (30) 021; 6.47 (20) 130; 5.95 (30) $2\bar{2}0$; 002; 5.66 (<10) $31\bar{1}$; 5.34 (10) 131; 5.104 (10) 311; 4.821 (15) $3\bar{1}1$; 4.77 (20) 202; $13\bar{2}$; 4.323 (<10) $3\bar{2}1$; $3\bar{2}\bar{1}$; 4.270 (<10) 331; $2\bar{2}1$; 4.219 (<10) 222; 4.111 (<10) $33\bar{2}$; 3.994 (<20) 312; $11\bar{3}$; 3.793 (70) $1\bar{1}3$; 322; $3\bar{3}1$; 3.651 (60) $3\bar{2}\bar{2}$; 3.599 (<10) $35\bar{1}$; 3.425 (15) $30\bar{3}$; 3.376 (10) 511. a = 18.262, b = 19.883, c = 12.067 Å; α = 98.59, β = 96.26, γ = 77.49°, space group $P\bar{1}$ (see Ref. 8). **1b.** 10.90 (10) $01\bar{1}$; 9.87 (30) 011; 9.67 (40) 020; 9.49 (90) 101; 8.60 (100) 111; 8.22 (100) $1\bar{1}\bar{1}$; 7.11 (20) 021; 6.36 (<10) $2\bar{1}1$; 5.85 (60) $11\bar{2}$; 5.59 (12) 320; 5.28 (15) $21\bar{2}$; 5.05 (10) $3\bar{1}\bar{1}$; 4.95 (<10) 140; 4.75 (15) $33\bar{1}$; 202; 4.241 (15) 331; 4.202 (15) $2\bar{2}\bar{2}$; 4.072 (15) $1\bar{4}\bar{1}$; 3.934 (30) $3\bar{1}2$; 3.753 (50) 341; 3.662 (20) $3\bar{2}2$; 3.612 (30) 151; 3.392 (20). a = 18.32, b = 19.92, c = 12.11 Å; α = 97.64, β = 96.72, γ = 78.30°, space group $P\bar{1}$ (see Ref. 8).

$Sn(OPr^i)_4 \cdot Pr^iOH$ (1c) was prepared by metathesis of $SnCl_4$ with NH_3 and Pr^iOH in benzene.[21]

$M(OEt)_4$ (2a,b) [M = Zr (**a**), Hf (**b**)]. The electrical conductivity of the solutions remains stable during the course of the electrochemical preparation of ethoxides for very long periods of time, which makes it possible to obtain electrolytes with 40—50 % weight concentration of **2a,b**. The evaporation of alcohols gives waxy foam-like residues with practically quantitative current yields. Extraction with hexane and subsequent evaporation of the solvent (the residual amounts of which are very hard to remove) gives white amorphous powders. **2a.** Found (%): Zr, 33.6; C, 35.6; H, 7.2. Calculated (%): Zr, 33.6; C, 35.4; H, 7.4. $C_8H_{20}O_4Zr$. IR (ν/cm^{-1}): 2980 vs, 2930 s, 2860 s, 1470 m, 1380 vs, 1360 sh, 1170 vs, 1150 sh, 1100 m, 1080 m, 1060 m, 1040 m, 925 vw, 895 vw, 520 m, 470 m. **2b.** Found (%): Hf, 50.3; C, 28.6; H, 5.5. Calculated (%): Hf, 49.7; C, 26.8; H, 5.5. $C_8H_{20}O_4Hf$. The IR spectrum is analogous to that of **2a** and practically coincides with that described earlier[22] (for ν <1170 cm^{-1}).

The melting points of **2a,b** vary over a wide range of temperatures, and are dependent on the heating rate and sample isolation procedure (separation from solutions in alcohol or sublimation *in vacuo*): 90—120 °C (**2a**) and 150—180 °C (**2b**). Both ethoxides are more soluble when heated in hexane than in aromatic hydrocarbons. The solubility of **1a** in EtOH at 20 °C achieves 10—15 % on saturation, but the residual solid which remains after the "extraction" turns out to be practically insoluble in alcohol. At the same time on heating to 40—50 °C the above-mentioned samples dissolve quantitatively (up to 30—50 % concentration), and on cooling of the solutions prepared no precipitation can be observed.

The mass-spectra of **2a,b** are given in Table 2.

$Zr(OBu^n)_4$ (3a), $Zr(OBu^i)_4 \cdot Bu^iOH$ (4a), $Zr(OBu^s)_4$ (5a). The anodic dissolution of Zr in butanols proceeds at a rather lower speed than in the case of lighter homologs (in pure Bu^tOH no dissolution takes place at all, while in the presence of MeCN the evolution of hydrogen takes place on both the cathode and the anode, and the carbon content in the product obtained is nearly 1.5 times lower than that calculated for tetraalkoxide formulation).

Liquid **3a** and **5a** were purified from LiCl by extraction with hexane and then benzene. The solvate **4a** was twice recrystallized from Bu^iOH. The microanalysis data for the products dried *in vacuo* at 80—100 °C were in good agreement with the theory. **3a.** Found (%): Zr, 23.4; C, 49.5; H, 9.2. Calculated (%): Zr, 23.8; C, 50.1; H, 9.4. $C_{16}H_{36}O_4Zr$. IR (ν/cm^{-1}): 2970 vs, 2930 s, 2878 vs, 2860 vs, 1465 s, 1380 s, 1232 m, 1140 vs, 1107 vs, 1065 s, 1045 s, 1000 m, 972 m, 955 m, 902 m, 865 m, 750 m, 727 w, 558 s, 503 s, 483 s.

5a. Found (%): Zr, 24.6; C, 48.7; H, 9.2. IR (ν/cm^{-1}): 2972 vs, 2930 s, 2880 s, 2855 sh, 1475 s, 1372 s, 1345 m, 1168 s, 1148 s, 1105 m, 1052 s, 1008 m, 938 m, 920 m, 830 w, 757 w, 722 w, 620 s, 563 s, 490 s.

Freshly prepared **3a** and **5a** were, in accordance with literature,[3,5] viscous colorless liquids that solidified slowly to solids penetrated by thin crystalline needles. Their liquification temperatures slowly increase on storage and achieve ~100 °C* in 3—5 months.

4a. Found (%): Zr, 19.3; C, 52.7; H, 9.8. Calculated (%): Zr, 19.9; C, 52.5; H, 9.2. $C_{20}H_{46}O_5Zr$. IR (ν/cm^{-1}): 3375 vs, 2958 vs, 2928 s, 2872 s, 2860 m, 1378 s, 1365 sh, 1152 vs, 1112 vs, 1070 vs, 1038 vs, 962 m, 945 m, 822 m, 728 m, 612 s, 542 w, 465 m, 427 w, 413 w. The X-ray powder pattern of **4a** [Co-Kα-radiation, d/Å (relative intensity(%))]: 10.1 (100); 7.57 (5); 7.23 (4); 6.71 (9); 5.20 (5); 5.03 (29); 4.27 (7); 4.16 (17);

* We did not succeed in isolating the crystalline solvate **5a**, described earlier.[3] The alcohol adduct of 1 : 1 composition was formed only by **4a**.

3.99 (5); 3.77 (5); 3.69 (5); 3.35 (3); 3.25 (2); 3.06 (5); 2.74 (2); 2.62 (2). The crystals of **4a** melt with decomposition at 145—150 °C and lose solvating alcohol *in vacuo* at $T > 100$ °C.

The alcohol interchange reaction of **1a** with the corresponding BuOH[22] was also used as a source of **4a** and **5a** in addition to the electrochemical techniques described above. The mass-spectra of **3—5** are given in Table 2.

$M(OC_2H_4OMe)_4$ (6a,b). The 2-methoxyethoxides were prepared according to the standard techniques of electrochemical synthesis. These are colorless liquids infinitely soluble in common organic solvents. On storage a few single crystals, which unfortunately were not suitable for X-ray investigation, precipitated from the liquid samples of **6a**. The mass spectra of **6a,b** (Table 3) indicate the presence of trimeric molecules in the gas phase (in **6b** only the dimeric ions could be observed because of the limited resolution of the device). Nevertheless the purification of **6a,b** by distillation can not be achieved under preparative conditions (~10^{-3} Torr) because of the partial decomposition of the samples. **6a.** Found (%): Zr, 23.0; C, 36.2; H, 7.2. Calculated (%): Zr, 23.3; C, 36.8; H, 7.1. $C_{12}H_{28}O_8Zr$. **6b.** Found (%): Hf, 36.8; C, 30.2; H, 6.0. Calculated (%): Hf, 37.3; C, 30.1; H, 5.8. $C_{12}H_{28}O_8Hf$. IR for **6a,b** (ν/cm^{-1}): 2935 vs, 2880 s, 2830 w, 1460 s, 1380 w, 1240 m, 1200 m, 1125 vs, 1080 vs, 1025 s, 965 w, 835 s, 625 s, 570 s, 510 s, 475 m.

Desolvation of 1a,b,c. The process was carried out by heating *in vacuo* at 120 °C (10^{-1} Torr). During the first minutes, evolution of gas from the melt occured. After cooling to room temperature the melts crystallized in about 24 hours. The composition of the products subjected to this treatment for 10—15 min corresponded to "$M(OPr^i)_4$" and then remained unchanged even if the heating continued for 1 additional hour. Nevertheless the IR spectra of such samples revealed a strong ν(OH) band at ~3400 cm^{-1}, while the X-ray powder pattern and the mass spectra coincided with those described above for **1a,b**. When recrystallized from ether solutions, single crystals of **1a,b** were obtained. Increasing both the time and the temperature of heating to 150—160 °C caused a decrease in both the intensity of ν(OH) and the carbon content in the samples. The main characteristics of the products prepared are summarized in the Tables 4 and 5. It should be mentioned that the composition of the "$M(OPr^i)_4$" distillation products is close to $M_3O(OPr^i)_{10}$.

The GLC-MS analysis of the volatile products of desolvation (condensed in a trap) reveals the presence of a complex mixture of compounds containing Pr^iOH, Me_2O, Et_2O, PrOMe, PrOEt, acetone, MeCHO, and saturated and unsaturated hydrocarbons (C_6H_{14}, C_7H_{12}). These data are considerably different from those reported earlier,[26] where the formation of only two volatile products — Pr^iOH and C_3H_6, was detected in the course of the decomposition of **1a**.

Results and Discussion

Electrochemical synthesis

In the present work we established that direct electrochemical synthesis can be efficiently used for the preparation of a large variety of zirconium and hafnium alkoxides. In comparison with the known chemical routes of their preparation it appeares to be rather simple and productive (the $M(OR)_4$ yields with respect to the metal consumed are nearly quantitative). The products isolated directly from electrolytes and sometimes also those obtained after the first step of purification (extraction by hydrocarbons) contain a ~0.5 % admixture of the conductive additive LiCl in the form of volatile and hydrocarbon soluble bimetallic alkoxide chlorides. Thus the mass spectra of ethoxides contain fragments of $LiM(OEt)_4Cl$ molecules, where M = Zr and Hf. In this respect the crystalline **1a,b** appear to be the most advantageous derivatives due to their poor solubility at 20 °C, which increases greatly on heating to ~80 °C (see Table 1). The recrystalization of **1a,b** from isopropyl alcohol makes it possible to diminish the Li and Cl contents to practically trace amounts (≤0.01 %). High purity samples of other homologs can be prepared from isopropoxides *via* the alcohol interchange reaction.

It should be noted that the conventionally used reaction of metal halides with ammonia offers, according to the literature,[3] samples of alkoxides more contaminated with impurities than the crude products of electrolysis. The vacuum distillation usually recommended for their purification leads, as has been shown above, to further decomposition of "$M(OR)_4$" accompanied by the formation of oxoalkoxides. Thus the distilla-

Table 3. Mass spectra of $M(OC_2H_4OMe)_4$ (**6a,b**), m/z (I (%))

6a	6b	Interpretation
795 (8)	—	$[M_3(OR)_7]^+$
781 (10)	—	$[M_3(OR)_6(OC_2H_4OH)]^+$
765 (<1)	—	$[M_3(OR)_6(OEt)]^+$
751 (<1)	—	$[M_3(OR)_6(OMe)]^+$
737 (<1)	1007 (1)	$[M_3(OR)_5(OC_2H_4OH)(OMe)]^+$
721 (<1)	991 (10)	$[M_3(OR)_6(OEt)(OMe)]^+$
705 (10)	885 (15)	$[M_2(OR)_7]^+$
—	841 (3)	$[M_2(OR)_6(OMe)]^+$
630 (10)	810 (1)	$[M_2(OR)_6]^+$
—	797 (1)	$[M_2(OR)_5(OMe)_2]^+$
586 (70)	766 (20)	$[M_2(OR)_5(OMe)]^+$
555 (11)	735 (10)	$[M_2(OR)_5]^+$
511 (25)	—	$[M_2(OR)_4(OMe)]^+$
490 (10)	—	$[M_2(OR)_4]^+$
436 (50)	—	$[M_2(OR)_3(OMe)]^+$
361 (1)	541 (1)	$[M_2(OR)_2(OMe)]^+$
315 (100)	405 (100)	$[M(OR)_3]^+$
299 (42)	389 (2)	$[M(OR)_2(OPr)]^+$
285 (31)	375 (2)	$[M(OR)_2(OEt)]^+$
271 (41)	361 (50)	$[M(OR)_2(OMe)]^+$
255 (26)	345 (2)	$[M(OR)(OMe)(OPr)]^+$
227 (31)	317 (20)	$[M(OR)(OMe)_2]^+$
212 (100)	302 (5)	$[M(OC_2H_4O)(OMe)_2]^+$
196 (29)	287 (10)	$[M(OR)(OMe)]^+$
183 (100)	273 (55)	$[M(OMe)_3]^+$
181 (28)	—	$[M(OMe)(OCH_2)_2]^+$
167 (17)	257 (13)	$[M(OCH_2)_2(OH)]^+$
151 (15)	241 (9)	$[M(OMe)(OCH_2)]^+$
137 (14)	227 (8)	$[M(OMe)O]^+$
123 (40)	213 (2)	$[M(OH)O]^+$

Note. m^*/z (metastable ions): **6a.** 636: 781 → 705; 565: 705 → 630; 233: 315 → 271. **6b.** 321: 405 → 361; 272: 361 → 317; 235: 317 → 273.

Table 4. Characterization of the desolvatation products of $M(OPr^i)_4 \cdot Pr^iOH$ (**1a,b**)

M	№ of the sample	The duration of the process	Found / Calculated (%) M	C	H	ν(OH)	Composition of the product
Zr	*1*	10 min	28.0 / 27.9	43.5 / 44.0	8.3 / 8.5	~3440 vs	"$Zr(OR)_4$"
	2	1.5 h	28.6 / 27.9	42.8 / 44.0	8.2 / 8.5	~3440 w	"$Zr(OR)_4$"
	3	4 h	31.2 / 31.0	39.5 / 40.9	8.5 / 8.8	—	$Zr_3O(OR)_{10}$
	4	6 h	35.2 / 35.6	35.8 / 36.2	7.1 / 7.1	—	$ZrO_{0.7}(OR)_{2.6}$
Hf	*1*	10 min	43.1 / 43.1	34.7 / 34.7	6.7 / 6.7	~3440 s	"$Hf(OR)_4$"
	2	1.5 h	44.4 / 43.1	33.1 / 34.7	6.4 / 6.7	~3440 w	"$Hf(OR)_4$"
	3	4 h	47.0 / 46.9	32.6 / 31.5	6.5 / 6.1	—	$Hf_3O(OR)_{10}$

Table 5. Chemical shifts (δ) and intensities of the signals (%, in brackets) in the ^1H NMR spectra of $M(OPr^i)_4 \cdot Pr^iOH$ (**1a,b**), the products of their desolvation (C_6D_{12}, 25 °C), and $W_3O(OPr^i)_{10}$ and $Th_3O(OBu^t)_{10}$

The initial sample	CH3: OR terminal		CH3: **1** + +M(OR)4	CH3: μ-OR	CH3: μ_3-OR	CH: μ_3-OR	CH: OR terminal		CH: μ-OR	CH: **1** + +M(OR)4	OH	The composition of the sample
"$Zr(OR)_4$", sample №*1*	1.216 (18)	1.234 (18)	1.303 (168)	1.373 (18)	1.434 (6)	4.25 (1)	4.28 (3)	4.29 (3)	4.49 (3)	4.51 (28)	—	$\frac{[\mathbf{1a}+Zr(OR)_4]}{[Zr_3O(OR)_{10}]} = \frac{5.6}{1}$
"$Zr(OR)_4$", sample №*2*[a]	1.216 (18)	1.234 (18)	1.303 (102)	1.373 (18)	1.434 (6)	4.25 (1)	4.28 (3)	4.29 (3)	4.49 (3)	4.512 (17)	—	$\frac{[\mathbf{1a}+Zr(OR)_4]}{[Zr_3O(OR)_{10}]} = \frac{3.4}{1}$
1a	—	—	1.262 (60)	—	—	—	—	—	—	4.413 (10)	5.0 (2)	**1a**
1a (C_7D_8, 25 °C)[b]	—	—	1.36 (60)	—	—	—	—	—	—	4.54 (10)	6.3 (2)	**1a**
"$Hf(OR)_4$"	1.18 (36)		1.27 (72)	1.33 (18)	1.40 (6)	4.38 (1)	4.50 (6)		4.64 (3)	4.82 (12)	—	$\frac{[\mathbf{1b}]}{[Hf_3O(OR)_{10}]} = \frac{2.4}{1}$
1b ($CDCl_3$, 25 °C)[b]		—	1.23 (60)	—	—	—	—		—	4.51 (10)	6.15 (2)	**1b**
$W_3O(OR)_{10}$[c]	1.59 (18)	1.32 (18)	—	1.01 (18)	1.09 (6)	3.98 (1)	5.57 (3)	5.12 (3)	4.55 (3)	—	—	$M_3O(OR)_{10}$
$Th_3O(OBu^t)_{10}$[d]	1.45 (3)	1.46 (3)	—	1.74 (3)	1.80 (1)	—	—	—	—	—	—	$M_3O(OR)_{10}$

[a] It seems strange that in the proton NMR spectrum of the product prepared earlier under analogous conditions[25] only two signals at δ 1.43 and 4.61 (in C_6D_6) have been observed. [b] See Ref. 8. [c] See Ref. 23. [d] See Ref. 24.

tion of **2a** leads to complete elimination of the ions corresponding to $[Zr(OR)_4]_3$ in its mass spectrum (see Table 2).

Desolvation of $M(OPr^i)_4 \cdot Pr^iOH$ (**1a—c**)

The view that the thermal decomposition of **1a—c** *in vacuo* (or the recrystallization of **1b** from cyclohexane) proceeds *via* simple elimination of a solvating alcohol molecule and leads to the formation of $M(OPr^i)_4$, which can be distilled *in vacuo* without any change in composition, has become common in the literature.[3,6,8] However, the results of microanalytical, X-ray powder, and IR spectral analysis of the desolvation products of composition "$M(OPr^i)_4$", where M = Zr, Hf, Sn, permit one to draw the conclusion that they consist of initial **1a—c** and an oxoalkoxide (Table 4). The microanalysis data and X-ray pattern for the product of recrystallization of **1b** coincide with those for the initial solvate [while the observed intensity of ν(OH) in its IR spectrum was slightly lower]. In the mass spectra of **1a—c** or their desolvation products (see Table 2) the ions corresponding to the fragmentation patterns of $M_3O(OPr^i)_{10}$

oxoalkoxides that give the most intense peaks. The latter are formed presumably in the course of the radical decomposition of **1a—c,** which can be seen by the presence of a large number of volatile decomposition products isolated along with Pr^iOH. The easy formation of oxoalkoxides *via* a variety of reaction pathways has been already emphasized in the literature.[27]

Taking into account the composition of the oxocomplexes present in the gas phase it would be logical to suppose that products of the same composition could contaminate the solid samples obtained by desolvation. The results of microanalysis of the first decomposition products of **1a,b** (see Table 4, sample *1*) correspond to an equimolar mixture of **1** and $M_3O(OPr^i)_{10}$, the latter becoming the main products after 4 h of heating (sample *3*). The same composition can be attributed to the products of the sublimation or distillation of "$M(OPr^i)_4$".

Oxoalkoxides of quadrivalent metals

The molecular structures of $M_3^{IV}O(OR)_{10}$, where $R = Pr^i$, Bu^t, were investigated[23,28] for the derivatives of Mo, W, U. These are $M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6$ cluster molecules, where the metal atom triangle is capped by an oxogroup on one side and an OR group on the other. We achieved no success in isolating single crystals of Zr and Hf oxocomplexes, and therefore we used ^{1}H NMR* for their identification. The spectrum of $W_3O(OPr^i)_{10}$ reported earlier in the literature[23] was used for the attribution of the signals. The data presented in the Table 5 show that the spectra of "$M(OPr^i)_4$" samples (and those of the products of further decomposition) contain the signals of the initial solvates and those of molecules whose structure is analogous to that of tungsten oxoisopropoxide. A comparison of the microanalysis data and the integral intensities of the signals in the ^{1}H NMR spectrum of "$Zr(OPr^i)_4$" leads to the conclusion that the samples should also contain some amount of free unsolvated zirconium isopropoxide along with **1a** and $Zr_3O(OPr^i)_{10}$. This conclusion is supported also by the data of the mass spectrometric study — the spectra of "$Zr(OPr^i)_4$" display the fragmentation patterns of the *ortho*-$Zr(OPr^i)_4$ monomer and trimer along with ions corresponding to the above-mentioned trinuclear oxocomplex. In contrast, the samples of "$Hf(OPr^i)_4$" contain only **1b** and $Hf_3O(OPr^i)_{10}$; no ions corresponding to *ortho*-derivative were found in the mass spectrum. Unfortunately, it was not possible to identify the free $Zr(OPr^i)_4$ from the NMR data because of the rapid exchange of alkoxygroups and solvating Pr^iOH molecules (in the structure of **1a**), resulting in the presence of only one signal for both CH_3- and CH-protons in the spectrum.[10]

It should be stated therefore that in contrast to the data earlier reported in the literature, the desolvation of $M(OPr^i)_4 \cdot Pr^iOH$, where M = Zr, Hf, Sn (and probably Ce^{IV}, which forms an isopropoxide with a structure and composition analogous to those of **1a—c**), does not lead to formation of individual $M(OPr^i)_4$ derivatives. The results of desolvation studies of some metal alkoxide solvates, such as, for example, $Nd(OPr^i)_3 \cdot Pr^iOH$ and $Ba(OR)_2 \cdot 4ROH$, which were recently described in the literature,[29,30] permit one to draw the conclusion that the elimination of the solvating alcohol molecule very often leads to simultaneous partial decomposition of $M(OR)_n$ accompanied by the formation of oxocomplexes. From this point of view, the presence of $Zr_3O(OPr^i)_{10}$ and $Zr_4O(OBu^i)_{14}$ in the products of **1a** and **4a** desolvation seems quite natural. The observed similarities in the mass spectra of **1a,b**, the products of their desolvation and the other Zr and Hf alkoxides, which have no tendency to form solvates such as ethoxides, and *n*- and *sec*-butoxides (whether they were prepared by electrochemical techniques or by metathesis reactions) were completely unexpected. The only exception was provided by **6a,b**, whose mass spectra contained only the fragmentation patterns of the *ortho*-forms — $[M(OR)_4]_n$, where $n = 2$ and 3 (see Table 3), and by the monomeric molecules of $M(OC_5H_{11}{}^t)_4$ and $M[OCH(CF_3)_2]_4$ (see Ref. 21). The data presented in the Table 2 show that the formation of trimeric oxocomplexes is characteristic of both primary and secondary alkoxide derivatives, while the tetranuclear complexes are characteristic of only primary alkoxide derivatives. For the latter one can propose a molecular structure analogous to that observed for $Zr_4(\mu_4\text{-}O)(OPr^i)_{10}(acac)_4$ or $Ce_4(\mu_4\text{-}O)(OPr^i)_{13}(Pr^iOH)$, where the central oxygen atom is tetrahedrally coordinated.[31,32] Such highly symmetric molecules should be rather stable and be more easily transferred into the gas phase or into solution than those of $M(OR)_4$, which appear to form large and strong aggregates. The main pathway of oxocomplex formation in the samples of

Table 6. Comparison of average molecular complexity x for the alkoxides of Zr, Hf and Sn in the gas phase (according to the mass-spectral data) and in solution

Sample	x in the gas phase*	x in solution[9—11,21]
"$Zr(OEt)_4$"	3.2	3.6
"$Zr(OPr^i)_4$"	3.2	3.6
"$Zr(OBu^n)_4$"	3.2	3.4
"$Zr(OBu^i)_4$"	1.7	—
"$Zr(OBu^s)_4$"	2.3	2.4
"$Hf(OPr^i)_4$"	3—4	3.3
"$Sn(OPr^i)_4$"	2.8	3.1

* The data of the present work.

* Recently a product of analogous composition — $Th_3O(OBu^t)_{10}$ — was obtained[24] by decomposition of $Th_2(OBu^t)_8 \cdot Bu^tOH$. Its proton NMR spectrum (Table 6) in the region corresponding to the chemical shifts of the methyl protons is almost analogous to that observed for $M_3O(OPr^i)_{10}$, where M = Zr, Hf, W.

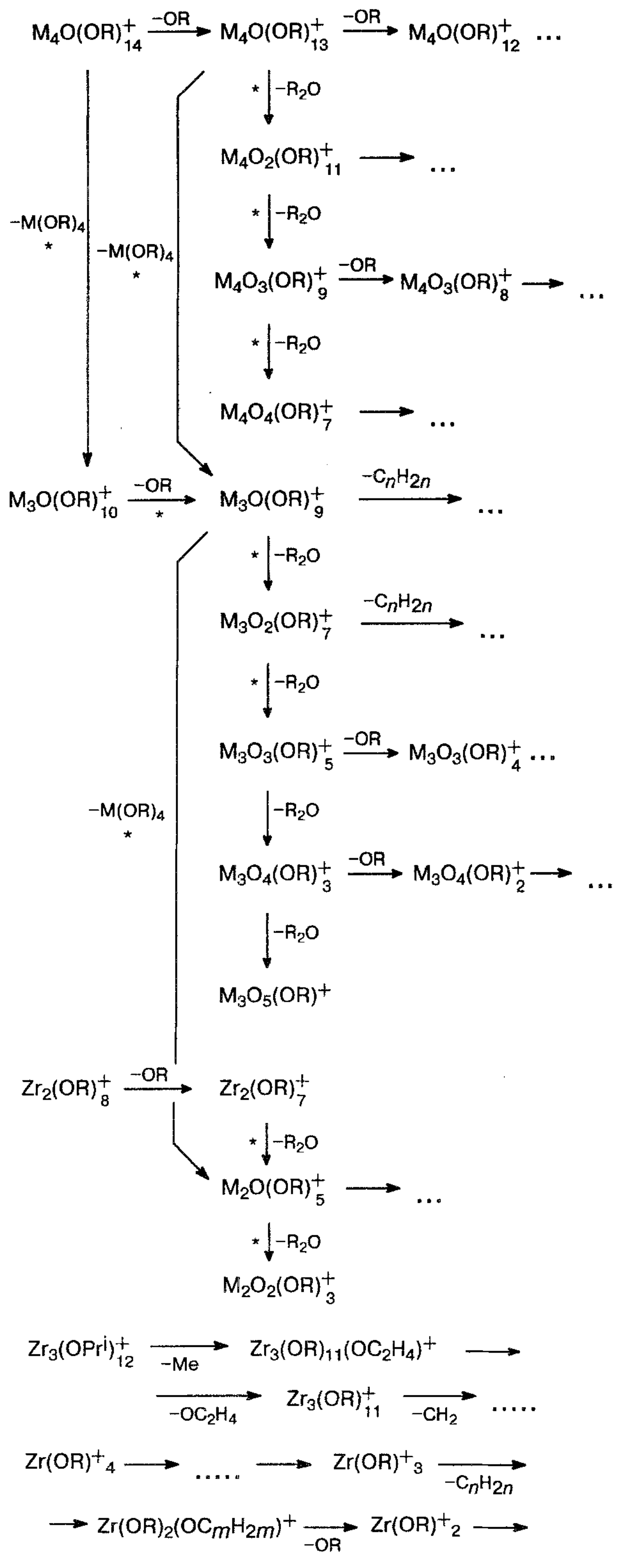

Fig. 1. General fragmentation scheme in the mas-spectra of $M(OR)_4$ (M = Zr, Hf). The transitions supported by the observed metastable ions are marked by*.

"$M(OR)_4$" is apparently low-temperature thermolysis of the alkoxides. This specific kind of decomposition is now well known for derivatives of Mo, W and Nb and proceeds *via* ether elimination.[33,34] This process is accelerated by any factor influencing this system, such as thermal treatment, microhydrolysis or electron impact. The main pathways of "$M(OR)_4$" fragmentation in the mass spectra are also associated with the elimination of R_2O and the formation of new oxogroups in the resulting ions. The elimination of "$M(OR)_4$" monomeric molecules is also revealed in the spectra of butoxides and isopropoxides along with the above-mentioned processes. Each ion thus formed then gives rise to a separate fragmentation series which is formed by elimination of a number of smaller particles such as OR, C_nH_{2n}, MeOH, *etc.* (Fig. 1).

Molecular composition of $M(OR)_4$ samples

It should be mentioned that the use of direct introduction mass spectrometry for the determination of molecular composition in the condensed phase is usually questioned in the literature. However the good correlation of the mass spectra of the majority of the metal alkoxide aggregates with the results of their single crystal X-ray study led us to the conclusion that usually the size (and probably the structure) of such aggregates does not significantly vary in the gas phase from that observed in the solid phase.[35] Even in the mass spectrum of the decanuclear molecules of $Al_{10}O_4(OEt)_{22}$ was observed its own fragmentation pattern.[36] Therefore the high intensity of $M_3O(OR)_9{}^+$ or $M_4O(OR)_{13}{}^+$ ions in the mass spectra of "$M(OR)_4$" can be considered as additional proof of the existence of the corresponding Zr and Hf oxoalkoxides.

It is of interest that the average size of the oligomeric aggregates (the total number of metal atoms) calculated on the basis of mass spectral data* is usually in good agreement with their molecular complexity in solution[9—11,21] (Table 6). Taking this fact into consideration it is possible to assume that the samples whose general composition corresponds to "$M(OR)_4$" are in reality complex mixtures containing tri- and tetranuclear oxoalkoxide molecules along with $[M(OR)_4]_x$ where x is also a variable value.

The inhomogeneity in the molecular composition of "$M(OR)_4$" is also indirectly proved by their reluctance to crystallize and by the fact that the reproducibility of their melting points depends on the heating rate, the sample storage time, *etc.*, as has been often mentioned in the literature. In conclusion, let us consider the interaction of "$M(OR)_4$" with alcohols. It has been

* The "stability" of a single oligomer was taken to be the ratio of the sum of the intensities of all the ions of its fragmentation pattern to the sum of intensities of all the ions observed in the spectrum (%). The average size of the aggregates (the number of metal atoms they contain) was calculated taking into consideration the stability of this oligomer in the spectrum.

stated earlier that the liquid samples of "$Zr(OPr^i)_4$" — in contrast to **1a** — display very high solubility (up to 40—50 % at 20 °C). Within several days the crystallization of a product with the same "$Zr(OR)_4$" composition takes place from these solutions. In the present study it was found that this product, as well as the products obtained by desolvation, are mixtures of crystals of **1a** and oxoalkoxide absorbed on their surface (the solubility of the latter is practically infinite). It should be emphasized that the lower the initial "$Zr(OR)_4$" concentration (and thus the lower the oxoalkoxide content in the sample) the higher the melting point of the sample. After prolonged storage, the concentrations of the solutions slowly decrease presumably due to the solvolysis of the oxocomplex and solvation of its products to form **1a**:

$$Zr_3O(OR)_{10} + ROH \rightarrow [Zr(OR)_4 \cdot ROH]_2 + ZrO_n(OR)_{4-2n},\ n \geq 1/3.$$

As has been mentioned above, the solubility of the samples of **2a** in EtOH also never reaches equilibrium values which also supports the possibility of the "extraction" of more soluble forms by alcohol.

The presence of oxocomplexes in "$M(OR)_4$" samples should significantly affect their complex formation with other alkoxides, because the stoichiometry usually observed for bimetallic oxocomplexes differs substantially from that of $M_nM'_m(OR)_p$ (see Refs. 37,38). Taking into account the fact that it is the bimetallic oxoalkoxides that are true molecular precursors of complex oxides,[27,38] the results reported in the present paper seem to be of considerable importance for the sol-gel preparation of zirconates, hafnates, *etc.* The other factor which can be used in the preparation of solutions for subsequent hydrolysis is provided by the possibility of varying the solubility of alkoxides in alcohols, varying the oxoalkoxide content in their samples.

References

1. D. C. Bradley, *J. Organomet. Chem.*, 1982, **239**, 17.
2. N. Ya. Turova and M. I. Yanovskaya, *Bull. Acad. Sci. USSR, Div. Inorg. Mat.*, 1983, **19**, 615 (Engl. Transl.).
3. D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 1951, 280.
4. N. I. Kozlova and N. Ya. Turova, *Zh. Neorg. Khim.*, 1980, **25**, 2145 [*Russ. J. Inorg. Chem.*, 1980, **25**, 1188 (Engl. Transl.)].
5. D. C. Bradley, W. Wardlaw, F. M. Abd-el Halim, and E. A. Sadek, *J. Chem. Soc.*, 1952, 2032.
6. D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 1953, 1634.
7. N. Yoshino, M. Sohma, and T. Yoshino, *J. Chem. Soc. Jpn., Chem. and Ind.*, 1974, 1712.
8. B. A. Vaarstra, J. C. Huffman, P. S. Gradeff, L. G. Hubert-Pfalzgraf, J. Daran, S. Parraud, K. Yunlu, and K. G. Caulton, *Inorg. Chem.*, 1990, **29**, 3126.
9. D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 1952, 5020.
10. D. C. Bradley and C. E. Holloway, *J. Chem. Soc., A*, 1968, 1316.
11. D. C. Bradley, R. C. Mehrotra, J. D. Swanwick, and W. Wardlaw, *J. Chem. Soc.*, 1953, 2025.
12. R. C. Mehrotra, *J. Am. Chem. Soc.*, 1954, **76**, 2266.
13. S. K. Anand, J. J. Singh, R. K. Multani, and B. D. Jain, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 554.
14. D. C. Bradley, in *Preparative Inorganic Reactions*, Ed. W. L. Jolly, 1965, **2**.
15. Eur. Pat. Appl. 299, 171, 1989; *Chem. Abstrs.*, **111**, 38866.
16. Jap. Pat. 60'258.132, 1985; *Chem. Abstrs.*, **105**, 26611.
17. Jap. Pat. 172.390, 1989; *Chem. Abstrs.*, **112**, 76386.
18. Fr. Pat. 2091.229; Ger. offen Pat. 2 121732; *Chem. Abstrs.*, 1972, **77**, 96297; 4885.
19. V. A. Shreider, E. P. Turevskaya, N. I. Kozlova, and N. Ya. Turova, *Inorg. Chem. Acta*, 1981, **53**, 73.
20. N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, N. I. Kozlova, and A. I. Belokon', *Zh. Neorg. Khim.*, 1992, **37**, 50 [*Russ. J. Inorg. Chem.*, 1992, **37**, 26 (Engl. Transl.)].
21. J. C. Mair, *Ann. Chim.*, 1961, **6**, 969.
22. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978.
23. M. H. Chisholm, K. Folting, J. C. Huffman, and E. M. Cober, *Inorg. Chem.*, 1985, **24**, 241.
24. D. L. Clark and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 1766.
25. B. A. Vaarstra, J. C. Huffman, W. E. Streib, and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 3068.
26. M. K. Dongare and A. P. Sinha, *Nat. Acad. Sci. Lett.*, 1979, **2**, 13.
27. N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, and M. I. Yanovskaya, *J. Sol-Gel Sci. and Technol.*, 1994, **2**, 17.
28. F. A. Cotton, D. O. Marler, and W. Schwotzer, *Inorg. Chim. Acta*, 1984, **85**, 207.
29. G. Helgesson, S. Jagner, O. Poncelet, and L. G. Hubert-Pfalzgraf, *Polyhedron*, 1991, **10**, 1559.
30. N. Ya. Turova, E. P. Turevskaya, M. I. Yanovskaya, N. M. Kotova, and R. R. Shifrina, *Zh. Neorg. Khim.*, 1993, **38**, 1137 [*Russ. J. Inorg. Chem.*, 1993, **38**, 1055 (Engl. Transl.)].
31. Toledano, M. In, and C. Sanchez, *C. r. Acad. Sci.*, Ser. 2, 1990, 1161.
32. K. Yunlu, P. S. Gradeff, N. Edelstein, W. Kot, G. Shalimoff, W. E. Streib, B. A. Vaarstra, and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 2317.
33. N. Ya. Turova, V. G. Kessler, and S. I. Kucheiko, *Polyhedron*, 1991, **10**, 2617.
34. V. G. Kessler, N. Ya. Turova, A. I. Yanovsky, A. I. Belokon', and Yu. T. Struchkov, *Zh. Neorg. Khim.*, 1991, **36**, 1662 [*Russ. J. Inorg. Chem.*, 1991, **36**, 938 (Engl. Transl.)].
35. N. I. Kozlova, N. Ya. Turova, and Yu. S. Nekrasov, *Koord. Khim.*, 1980, **6**, 221 [*Sov. J. Coord. Chem.*, 1980, **6**, 124 (Engl. Transl.)].
36. A. I. Yanovsky, N. Ya. Turova, N. I. Kozlova and Yu. T. Struchkov, *Koord. Khim.*, 1987, **13**, 242 [*Sov. J. Coord. Chem.*, 1987, **13**, 149 (Engl. Transl.)].
37. K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
38. E. P. Turevskaya, M. I. Yanovskaya, V. K. Lymar' and N. Ya. Turova, *Zh. Neorg. Khim.*, 1993, **38**, 609 [*Russ. J. Inorg. Chem.*, 1993, **38**, 563 (Engl. Transl.)].

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