Tantalum(v) oxoalkoxides. Synthesis and structure

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Anodic oxidation of tantalum in isopropyl alcohol or prolonged reflux of an alcohol solution of $Ta(OPr^i)_5$ afford crystalline oxoisopropoxide $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (**1**). In its molecule, two octahedra about Ta atoms are linked *via* the shared edge $[(OPr^i)O]$. Compound **1** is the first example of oxoalkoxide containing such a small number of metal atoms. Unlike the known polynuclear molecules $M_nO_m(OR)_p$, oxoalkoxide **1** is stable in solutions; on transition to the gas phase, this compound is desolvated to form a very stable molecule $Ta_2O(OPr^i)_8$ (apparently, consisting of two octahedra with a shared edge). According to the data of mass spectrometry, analogous molecules exist in the gas phase over $Ta(OAlk)_5$ (Alk = Me, Et, Pr^i, or Bu^n). When compound **1** is heated *in vacuo* (10^{-2}—10^{-3} Torr), $Ta(OPr^i)_5$ is sublimated. Crystals of $Ta_7O_9(OPr^i)_{17}$ (**2**) were formed upon prolonged storage of solutions of **1** in Pr^iOH. Heptanuclear molecule **2** consists of two $[Ta_4]$ tetrahedra with a shared vertex. These tetrahedra are additionally linked together *via* one μ_3-oxo and two μ_2-OPr^i groups. Complex **2** is a representative of heptameric oxoalkoxides of a new structural type.

Key words: tantalum oxoalkoxides, electrochemical synthesis, X-ray structural analysis; mass spectrometry.

In the works devoted to tantalum(v) alkoxides, data on oxo complexes, which are very typical of analogous elements (vanadium and niobium),[1,2] are unavailable. It may be associated, in particular, with the substantially lower stability of initial $TaOCl_3$ compared to that of $VOCl_3$ or $NbOCl_3$. However, recently, oxoalkoxides have attracted particular interest, mainly because their oligomeric molecules have new (often very unexpected) structures.[3,4] It has also been established that compounds of this class are direct molecular precursors of oxide phases in sol—gel technology of oxide materials.[5]

In this work, synthesis, properties, and structures of two tantalum oxoisopropoxides are described, and an attempt was made to obtain oxo complexes of other members of the homologous series.

Experimental

Chemically pure isopropyl alcohol was dehydrated by boiling with $Al(OPr^i)_3$ for 6—8 h; hydrocarbons were dehydrated with metallic sodium and then with zeolite NaA. Concentrations of tantalum in solid samples and solutions were determined by weighing in the form of Ta_2O_5 (calcination of the hydrolysis product at 900 °C).

Tantalum oxoisopropoxide $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (1). *A.* Compound **1** was obtained by anodic dissolution of metallic tantalum in isopropyl alcohol. The process was carried out in an undivided cell equipped with a cooling jacket and a condenser. A tantalum cylinder was used as an anode (the diameter was 2 cm, the height was 6—7 cm); Pt plate or stainless-steel plate (the area was 10 cm²) was used as a cathode. A solution of LiCl (0.05—0.10 *N* solution in Pr^iOH) was used as a conductive additive; a direct current was maintained within 0.20—0.05 A (the voltage was 110 V); the average current density was ~0.05 A cm^{-2}. Electrolysis was attended by evolution of hydrogen on the cathode and by boiling of the electrolyte. When the process was completed (after 10—15 h), alcohol was removed *in vacuo*; alkoxide was extracted from the residue with hexane (in this case, LiCl remained in the precipitate). After evaporation of the solvent, a glassy greenish product was obtained (the current yield was 95 %); this product was dissolved at room temperature in a minimum amount of Pr^iOH. At −10 °C, colorless crystals of **1** were deposited from the solution; these crystals readily lose crystallization alcohol even at room temperature and rapidly decompose at 80—90 °C.

B. A solution of $Ta(OPr^i)_5$ in isopropyl alcohol was refluxed; for several hours, the initial isopropoxide quantitatively decomposed to form compound **1**. Found (%): Ta, 40.2; C, 35.4; H, 7.3. $C_{27}H_{57}Ta_2O_{10}$. Calculated (%): Ta, 39.8; C, 35.6; H, 7.0. IR, ν/cm⁻¹: 3350 br.m, 2970 s, 2930 s, 2865 s, 1462 m, 1378 s, 1362 s, 1330 m, 1170 v.s, 1135 v.s, 1015 v.s, 960 s, 820 s, 740 s, 682 s, 637 s, 584 v.s, 465 v.s (differs from the spectrum of $Ta(OPr^i)_5$ (*cf.* Ref. 6) only by the presence of the broad band corresponding to the stretching

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[†] Deceased in 1995.

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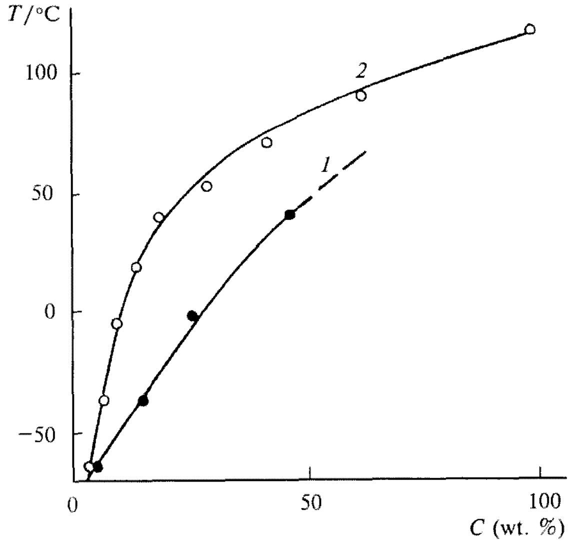

Fig. 1. Solubility polytherms of $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (**1**) and $Ta(OPr^i)_5$ (**2**).

vibrations of the OH group and the band at 637 cm^{-1} corresponding, apparently, to νTa—O(oxo)). Chromato-mass-spectrometric analysis of the electrolyte evidenced the presence of Pr^i_2O.

A solubility of compound **1** in Pr^iOH is substantially lower than that of $Ta(OPr^i)_5$ (Fig. 1.). The solubility polytherm was studied using different ways of reaching equilibrium between crystals and solution: by isothermal saturation, by heating followed by cooling of the concentrated solution, and by partial evacuation of the solvent. At 70 °C, crystal decomposed over the solution and, hence, it was impossible to extend the solubility isotherm of **1** toward higher temperatures. The desolvation product of oxoalkoxide **1** is an amorphous white compound, which decomposes without melting at temperatures >200 °C.

The mass spectrum of compound **1** (Table 1) pointed to the presence of $Ta_2O(OPr^i)_8$ molecules in the gas phase. However, the $Ta(OPr^i)_4^+$ ion has the maximum intensity, which is indicative of disproportionation of **1**:

$$5\ Ta_2O(OPr^i)_8 \cdot Pr^iOH \xrightarrow[-Pr^iOH]{} 8\ Ta(OPr^i)_5 + Ta_2O_5.$$

Actually, when oxoalkoxide **1** was heated to the temperature >200 °C *in vacuo* (10^{-1}—10^{-2} Torr), $Ta(OPr^i)_5$ sublimated in a yield of 84 % (which is in agreement with the above-given equation).

Tantalum oxoisopropoxide $Ta_7O_9(OPr^i)_{17}$ (2) crystallized upon prolonged storage of mother solutions, which were obtained after separation of crystals of **1**. Found (%): Ta, 52.7; C, 25.4; H, 4.7. $C_{51}H_{119}Ta_7O_{26}$. Calculated (%): Ta, 52.5; C, 25.4; H, 4.9. The large colorless crystals of **2** are insoluble at room temperature in Pr^iOH and other solvents; when heated in a tube, these crystals decompose without melting at ~150 °C. A set of interplanar distances in the X-ray diffraction pattern of **2** were indexed using the parameters determined from X-ray diffraction study of the single crystal, *d* (*I*; *hkl*): 13.68 (44; 002), 10.69 (100; 200), 6.77 (8; 020), 6.31 (8; 310), 4.32 (10; 314), 3.71 (8; $\bar{2}26$), 3.55 (8; $\bar{4}21$), 3.357 (13; 041), 3.336 (14; $\bar{1}18$), 3.059 (13; $\bar{5}17$), 2.819 (21; 516), 2.693 (17; $\bar{7}16$).

Table 1. Mass spectrum of $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (**1**)

m/z	I_{rel} (%)	Interpretation
834	10	$Ta_2(OPr^i)_8^+$
806	7	$Ta_2(OPr^i)_7(OMe)^+$
792	40	$Ta_2(OPr^i)_7(OH)^+$
732	5	$Ta_2O(OPr^i)_6^+$
690	10	$Ta_2O(OPr^i)_5(OH)^+$
648	3	$Ta_2O(OPr^i)_4(OH)_2^+$
630	5	$Ta_2O_2(OPr^i)_4^+$
606	5	$Ta_2O(OPr^i)_3(OH)_3^+$
588	6	$Ta_2O_2(OPr^i)_3(OH)^+$
564	2	$Ta_2O(OPr^i)_2(OH)_4^+$
546	2	$Ta_2O_2(OPr^i)_2(OH)_2^+$
522	2	$Ta_2O(OPr^i)(OH)_5^+$
504	7	$Ta_2O_2(OPr^i)(OH)_3^+$
480	10	$Ta_2O(OH)_6^+$
462	30	$Ta_2O_2(OH)_4^+$
417	100	$Ta(OPr^i)_4^+$
375	6	$Ta(OPr^i)_3(OH)^+$
366	3	$Ta_2O(OPr^i)_6^{2+}$
358	2	$Ta(OPr^i)_3^+$
345	2	$Ta_2O(OPr^i)_5(OH)^{2+}$
333	8	$Ta(OPr^i)_2(OH)_2^+$
316	5	$Ta(OPr^i)_2(OH)^+$
303	2	$Ta_2O(OPr^i)_3(OH)_3^{2+}$
291	5	$Ta(OPr^i)(OH)_3^+$
274	5	$Ta(OPr^i)(OH)_2^+$
249	8	$Ta(OH)_4^+$
232	6	$Ta(OH)_3^+$

Oxoalkoxides of the series of $Ta_2O(OR)_8$ (R = Me, Et, and Bu^n) were synthesized by the action of an excess of ROH on a solution of compound **1** in hexane or by refluxing $Ta(OR)_5$ solutions. In the case R = Me, after the removal of MeOH *in vacuo*, a white amorphous precipitate of composition $Ta_2O(OMe)_8$ (**3**) was obtained. Found (%): Ta, 57.0; C, 15.5; H, 3.9. $C_8H_{24}Ta_2O_9$. Calculated (%): Ta, 57.8; C, 15.3; H, 3.8. An analogous product was formed when a $Ta(OMe)_5$ solution in toluene was boiled for 3 h. This compound was isolated (the yield was ~15 %) after evaporation of the solvent and extraction of excess methoxide with hexane. Compound **3** is soluble in THF and toluene and insoluble in hexane and methanol. The IR spectrum of **3** differs from that of $Ta(OMe)_5$ only in the frequency region <600 cm^{-1} (520 v.s.br, 365 w, 275 w). Powdered **3** does not melt and does not transform to the gas phase under conditions of mass-spectrometric study. The reaction of compound **1** with EtOH and Bu^nOH in toluene afford viscous products. The composition of oxoethoxide is close to $Ta_2O(OEt)_8$ (**4**). Found (%): Ta, 51.0; C, 27.6; H, 4.4. $C_{16}H_{40}Ta_2O_9$. Calculated (%): Ta, 49.0; C, 26.0; H, 5.4. Under the same conditions, the product of deeper decomposition, $TaO(OBu^n)_3$ (**5**), is formed in butanol. Found (%): Ta, 42.6; C, 35.0; H, 6.5. $C_{12}H_{27}TaO_4$. Calculated (%): Ta, 43.5; C, 34.6; H, 6.5.

Tantalum oxoethoxide and tantalum oxobutoxide are soluble in alcohols and hydrocarbons. Upon prolonged storage, further elimination of ethers occurred (the concentration of carbon substantially decreased, and a liquid was evolved from product **5**; according to chromato-mass spectrometric data, it is Bu^n_2O). When compound **4** was heated to 300 °C, ions typical of $Ta(OEt)_5$ appeared in the mass spectrum; these ions were, apparently, formed as a result of thermal destruction of **4**

Table 2. Crystallographic data and parameters of X-ray diffraction studies

Parameter	Complex **1**	Complex **2**
Empirical formula	$Ta_2O_{10}C_{27}H_{64}$	$Ta_7O_{26}C_{51}H_{119}$
Mol. wt.	910.7	2415
a/Å	9.408(2)	21.413(9)
b/Å	12.052(3)	13.698(5)
c/Å	17.298(4)	27.421(9)
α/deg	94.43(2)	90.00
β/deg	95.95(2)	99.73(2)
γ/deg	97.57(2)	90.00
V/Å^3	1925.5(8)	7927(5)
d_{calc}/g cm^{-3}	1.571	2.024
Z	2	4
Space group	$P\bar{1}$	$C\ 2/c$
F(000)	904	4576
T/K	161	185
$2\theta_{max}$/deg	50.0	40.0
μ/cm^{-1}	57.2	96.8
Absorption correction	DIFABS (min 0.510, max 1.550)	DIFABS (min 0.805, max 1.349)
F_{obs}	4179	4352
R	0.0519	0.0485
R_w	0.0572	0.0686

(ethoxide transformed to the gas phase under the conditions of the mass-spectrometric study at ~100 °C).

X-ray structural study of crystals of **1** and **2** was carried out on an automated Siemens P3/PC diffractometer (graphite monochromator, Mo-Kα radiation, λ = 0.71073 Å, $\theta/2\theta$ scanning technique). Crystallographic data and characteristics of X-ray structural study for both compounds are given in Table 2. The structures were solved by the direct method and refined by the least-squares method first with isotropic temperature factors and then with anisotropic temperature factors. The H atoms of isopropyl groups in the structures of **1** and **2** were placed in calculated positions and were included in the refinement with a common refinable anisotropic temperature factor (U_{iso} = 0.24(2) and 0.12(1) Å^2 for **1** and **2**, respectively). All calculations were carried out on an IBM PC computer with the use of the SHELXTL PLUS program (Version PC).[7] Atomic coordinates for the structures of **1** and **2** are given in Tables 3 and 4; the bond lengths and bond angles are listed in Tables 5 and 6, respectively.

Results and Discussion

Formation of tantalum oxoalkoxides, which we observed in this work, occurs as a result of elimination of ethers from alkoxides of the *ortho* series according to the following scheme:

$$Ta(OAlk)_5 \rightarrow TaO_n(OAlk)_{5-2n} + Alk_2O.$$

Table 3. Atomic coordinates (×10^4) and equivalent isotropic temperature factors (×10^3) in the structure of **1**

Atom	x	y	z	U_{eq}/Å^2
Ta(1)	7378(1)	−3509(1)	7755(1)	49(1)
Ta(2)	8136(1)	−926(1)	7358(1)	58(1)
O(1)	8777(8)	−2167(7)	7872(5)	43(3)
O(2)	6348(8)	−2218(7)	7250(4)	38(3)
O(3)	6604(10)	−3255(10)	8700(5)	69(4)
O(4)	5821(10)	−4652(8)	7362(6)	60(4)
O(5)	8669(11)	−4431(8)	8161(6)	66(4)
O(6)	8121(10)	−3763(7)	6676(5)	56(3)
O(7)	7530(14)	−210(9)	8238(7)	92(5)
O(8)	9985(12)	−12(8)	7463(7)	78(5)
O(9)	8662(11)	−1763(8)	6348(6)	64(4)
O(10)	7113(12)	−61(8)	6664(6)	71(4)
C(1)	4900(15)	−2157(14)	6880(9)	66(6)
C(2)	3790(18)	−2480(16)	7410(11)	96(9)
C(3)	4681(18)	−2640(16)	6072(9)	93(8)
C(4)	6375(31)	−3200(34)	9464(15)	206(21)
C(5)	4966(34)	−3329(36)	9636(17)	315(37)
C(6)	7459(37)	−2660(33)	10013(15)	249(26)
C(7)	4788(20)	−5457(16)	7511(12)	103(9)
C(8)	5389(19)	−6333(14)	8007(11)	93(8)
C(9)	3706(20)	−5931(16)	6876(12)	107(9)
C(10)	10018(29)	−4527(22)	8446(16)	166(14)
C(11)	10277(27)	−5722(19)	8423(14)	155(14)
C(12)	10760(27)	−3893(23)	9064(18)	182(17)
C(13)	8290(16)	−4824(12)	6256(8)	59(6)
C(14)	7273(21)	−5048(16)	5522(11)	102(9)
C(15)	9853(21)	−4853(18)	6129(11)	108(10)
C(16)	7377(36)	367(30)	8854(19)	225(21)
C(17)	5919(31)	395(31)	9031(22)	260(27)
C(18)	8182(32)	1420(23)	9109(17)	212(19)
C(19)	11337(24)	159(35)	7777(16)	253(23)
C(20)	11656(26)	−149(22)	8570(16)	161(15)
C(21)	12226(26)	1061(26)	7559(15)	226(19)
C(22)	9274(14)	−1288(13)	5683(9)	61(6)
C(23)	10816(19)	−1524(17)	5688(11)	102(9)
C(24)	8345(20)	−1764(19)	4923(10)	108(10)
C(25)	6654(26)	834(18)	6462(18)	157(15)
C(26)	5326(27)	910(19)	6041(14)	146(13)
C(27)	7799(24)	1823(14)	6518(14)	123(12)

Presently, this process is well known for alkoxides of Nb,[2] Mo,[8] W,[9] Zr,[10] *etc.* The tendency to eliminate ethers is typical of all compounds of the $Ta(OAlk)_5$ type not only in the condensed phase but in the gas phase as well. In the latter case, the major products are very stable molecules of composition $Ta_2O(OAlk)_8$ * (in which two octahedra, apparently, are linked *via* a shared edge), which are unknown for alkoxides of other metals. The $Ta_2O(OR)_n^+$ ions are substantially more stable than $Ta_2(OR)_9^+$ dimers (judging from intensities of their peaks in the mass spectra).

The rate of decomposition of tantalum isopropoxide is particularly high: under conditions of electrochemical synthesis, compound **1** is formed in quantitative yield (upon boiling of a solution in alcohol). For other homolog, this reaction proceeds substantially more slowly,

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* It is interesting to note that elimination of ether from the $Ta(OC_2H_4OMe)_4^+$ ion, unlike $Ta(OAlk)_4^+$, affords the fragment of mononuclear oxoalkoxide $TaO(OC_2H_4OMe)_2^+$ (see Ref. 6).

Table 4. Atomic coordinates ($\times10^4$) and equivalent isotropic temperature factors ($\times10^3$) in the structure of **2**

Atom	x	y	z	U_{eq}/Å^2
Ta(1)	0	3482(1)	2500(0)	33(1)
Ta(2)	89(1)	989(1)	3077(1)	31(1)
Ta(3)	1053(1)	2881(1)	3755(1)	37(1)
Ta(4)	565(1)	3144(1)	1539(1)	34(1)
O(1)	0	1975(8)	2500(0)	34(5)
O(2)	−321(4)	3380(6)	1782(4)	35(3)
O(3)	796(5)	3394(7)	2232(4)	45(4)
O(4)	784(5)	1576(6)	3449(3)	34(3)
O(5)	535(4)	1708(7)	1675(4)	34(3)
O(6)	−170(4)	2852(7)	952(4)	40(4)
O(7)	0	4846(9)	2500(0)	45(5)
O(8)	49(5)	−190(7)	3425(4)	46(4)
O(9)	−570(5)	387(7)	2465(4)	42(4)
O(10)	1474(5)	2199(8)	4312(4)	49(4)
O(11)	1172(5)	4108(8)	4061(4)	47(4)
O(12)	1682(5)	3044(9)	3365(4)	51(4)
O(13)	654(5)	4431(8)	1318(4)	43(4)
O(14)	1329(5)	2825(8)	1319(50	56(5)
C(1)	−134(8)	2561(12)	448(5)	42(5)
C(2)	44(10)	1531(16)	440(8)	73(8)
C(3)	325(9)	3240(13)	228(7)	61(7)
C(4)*	−47(25)	5708(24)	2731(16)	81(18)
C(5)*	−743(25)	6021(34)	2358(29)	117(33)
C(6) *	489(38)	6474(26)	2615(21)	109(31)
C(7)	−117(17)	−1124(18)	3593(11)	111(14)
C(8)	−667(15)	−1019(24)	3883(11)	137(17)
C(9)	498(21)	−1521(29)	3896(18)	223(29)
C(10)	−1217(7)	125(12)	2493(6)	46(6)
C(11)	−1657(8)	1034(15)	2365(8)	72(8)
C(12)	−1422(11)	−720(17)	2149(9)	85(9)
C(13)	1671(10)	1268(15)	4462(7)	65(7)
C(14)	1787(14)	1157(16)	5011(8)	91(11)
C(15)	2216(11)	953(17)	4242(9)	90(10)
C(16)	1031(8)	4912(11)	4315(7)	54(6)
C(17)	1018(14)	5765(16)	4048(12)	121(14)
C(18)	1511(12)	5016(20)	4759(8)	95(11)
C(19)	2145(10)	3514(15)	3164(10)	76(9)
C(20)	2158(15)	4513(18)	3196(15)	159(21)
C(21)	2776(12)	3103(25)	3317(15)	158(20)
C(22)	1142(8)	5049(14)	1188(8)	66(8)
C(23)	1610(10)	5246(20)	1643(8)	89(10)
C(24)	865(10)	5927(14)	926(10)	85(10)
C(25)	1801(8)	2078(17)	1324(7)	64(8)
C(26)	1962(11)	1921(22)	803(9)	105(12)
C(27)	2373(8)	2388(17)	1675(9)	82(9)

* Atoms are disordered at two sites related by the twofold axis and were refined with occupancies G = 0.5.

and the products of this reaction are not pure compounds. Apparently, these products are compounds of variable composition $TaO_n(OR)_{5-2n}$, a number of oxo groups increasing with time, which affords amorphous compounds of the polymeric nature (this can be judged from a decrease in solubility of the samples). Crystalline oxoalkoxide of the individual composition **1** occurs only in the case of isopropoxide. A particular stability of binuclear solvates of isopropoxides $[M(OPr^i)_4(Pr^iOH)]_2$ has been already reported for M = Zr and Hf; alkoxides "$M(OR)_4$" with all other radicals are not pure compounds but contain oxo complexes $[MO_n(OR)_{4-2n}]_x$[10] Their molecules consist of two octahedra linked *via* a shared edge.[11] In the molecule of $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (**1**), one OPr^i group and one oxo group act as bridges. The molecule of Pr^iOH is one of the terminal ligands (Fig. 2). The lengths of terminal and bridging Ta—OPr^i bonds in **1** are virtually identical to the corresponding distances in alkoxides of tantalum and niobium (in methoxide, isopropoxide,[6,12,13] Cellosolve chloride,[14] *etc.*). The relation between Ta—OPr^i distances is typical of dimeric molecules $[M(OR)_5]_2$ (M = Nb and Ta; R = Me and Pr^i). Thus, the sums of the axial bond lengths at the Ta(1) and Ta(2) atoms (3.952 and 3.957 Å, respectively) are substantially smaller than the sums of the lengths of equatorial bonds (4.005 and 4.036 Å),* apparently, because of the different contribution of π bonding to the Ta—O interaction. This is also evidenced by the value of the Ta—O—C bond angles at the corresponding oxygen atoms: the angles at the O(3) and O(7) axial atoms [164(2)° and 169(2)°, respectively] are substantially larger than the bond angles at the equatorial O(4), O(5), O(8), and O(10) atoms [148(1)°, 148(1)°, 148(2)°, and 154(1)°, respectively]. Substantially smaller values of the bond angles at two other axial atoms, O(6) and O(9) (128.1(8) and 128.7(8)°, respectively) are, apparently, attributable to the fact that one of this atoms belongs to the alcohol molecule (rather than to the OPr^i group). The short O(6)...O(9) contact [2.52(2) Å] corresponds to a very strong O—H...O hydrogen bond. A substantial (almost by 0.2 Å) elongation of the Ta(1)—O(6) [2.07(1) Å] and Ta(2)—O(9) [2.09(1) Å] bonds compared to the Ta—O bonds with the participation of the terminal OPr^i groups (1.87—1.92 Å) is also in agreement with this interpretation. Even the C—O bond lengths at the O(9) and O(6) atoms [1.46(2) Å] are substantially larger than the distances for other terminal groups [1.26(3)—1.34(3) Å] and are equal to the C(1)—O(2) bond length in the bridging Pr^iO group. Naturally, the bridging Ta—O(oxo) bonds [Ta(1)—O(1), 1.929(7) Å and Ta(2)—O(1), 1.930 Å] are much shorter than the Ta—μ-OPr^i distances [Ta(1)—O(2), 2.134(8) Å and Ta(2)—O(2), 2.120 Å]. The same Ta—O(oxo) distances were observed, for example, in the molecule $[ZrTa_2I(\mu_3\text{-}O)(\mu\text{-}O)(OR)_7]_2$ studied recently[15]; these lengths are close to the known Ta—O bond lengths for octahedral Ta atoms in the structures of its inorganic derivatives.

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* By the axial bonds in molecules of the $[M(OR)_5]_2$ type we mean the bonds whose vectors are approximately normal to the plane of the four-membered cycle $[M_2O_2]$; vectors of equatorial bonds lie in this plane or form small angles with this plane.

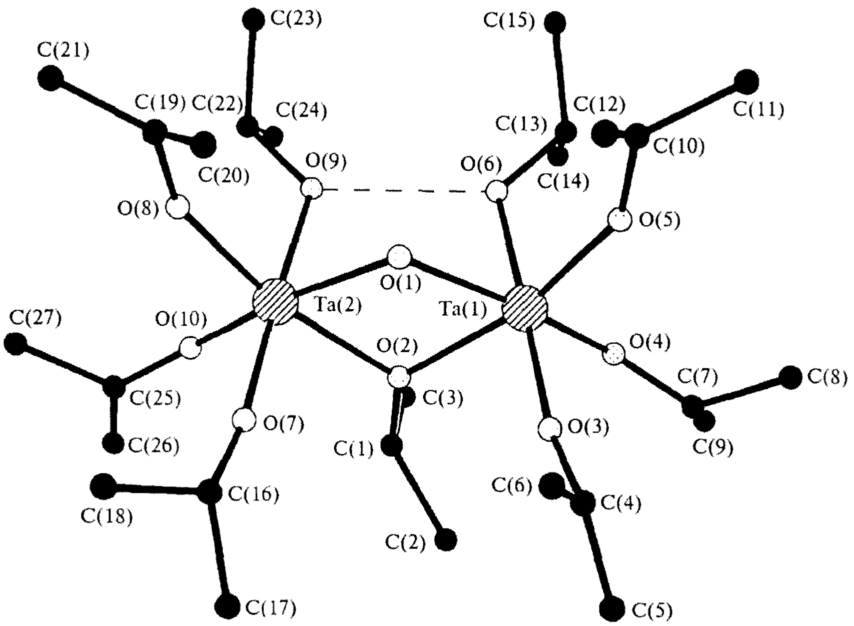

Fig. 2. Molecular structure of $Ta_2O(OPr^i)_8 \cdot Pr^iOH$ (**1**).

In the IR spectrum of compound **1**, a band at 637 cm^{-1} corresponds to the Ta—O(oxo) stretching vibrations; this band is located in a higher-frequency region compared to $\nu Ta—OPr^i$ and is absent in the spectrum of $Ta(OPr^i)_5$ (*cf.* Ref. 6). In the known structures of isopropoxide solvates $[M(OPr^i)_4(Pr^iOH)]_2$, where M = Zr, Hf, Sn, or Ce,[11,16,17] analogous intramolecular $Pr^iOH...OPr^i$ contacts occur above and below the planes of the $[M_2(OPr^i)_2]$ cycles, which cause no substantial distortion of the octahedral coordination about metal atoms. At the same time, two axial ligands of molecule **1** are pulled together only on one side of the plane of the $[M_2O_2]$ cycle, which results in pushing apart of the O(3) and O(7) atoms that are in *trans*-positions with respect to the first two atoms. As a result, the O(1)—Ta(1)—O(6), O(1)—Ta(2)—O(9), O(2)—Ta(1)—O(6), and O(2)—Ta(2)—O(9) bond angles [83.9(3)°, 84.8(4)°, 79.8(2)°, and 84.5(3)°, respectively] are substantially smaller than the O(1)—Ta(1)—O(3), O(1)—Ta(2)—O(7), O(2)—Ta(1)—O(3), and O(2)—Ta(2)—O(7) angles [97.1(4)°, 98.7(3)°, 91.9(4)°, and 92.1(4)°, respectively].

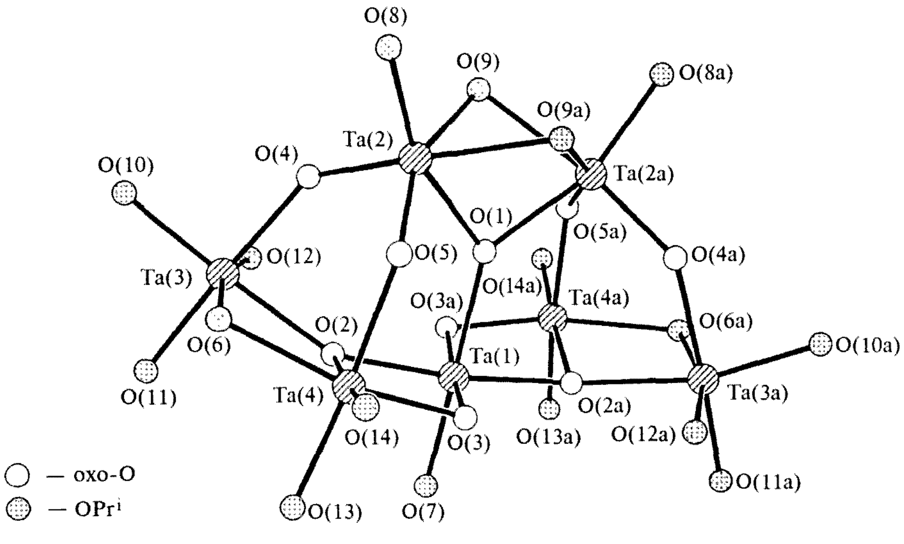

Fig. 3. Molecular structure of $Ta_7O_9(OPr^i)_{17}$ (**2**).

Table 5. Principal bond lengths (d) and bond angles (ω) in the structure of **1**

Bond	d/Å	Bond	d/Å
Ta(1)—O(1)	1.929(7)	Ta(2)—O(10)	1.916(11)
Ta(1)—O(2)	2.134(8)	O(2)—C(1)	1.457(16)
Ta(1)—O(3)	1.878(10)	O(3)—C(4)	1.359(28)
Ta(1)—O(4)	1.904(9)	O(4)—C(7)	1.339(21)
Ta(1)—O(5)	1.871(10)	O(5)—C(10)	1.336(29)
Ta(1)—O(6)	2.074(10)	O(6)—C(13)	1.456(17)
Ta(2)—O(1)	1.930(9)	O(7)—C(16)	1.258(35)
Ta(2)—O(2)	2.120(7)	O(8)—C(19)	1.314(25)
Ta(2)—O(7)	1.870(12)	O(9)—C(22)	1.461(18)
Ta(2)—O(8)	1.916(10)	O(10)—C(25)	1.273(26)
Ta(2)—O(9)	2.087(10)		

Angle	ω/deg	Angle	ω/deg
O(1)—Ta(1)—O(2)	72.7(3)	O(1)—Ta(2)—O(9)	84.8(4)
O(1)—Ta(1)—O(3)	97.1(4)	O(2)—Ta(2)—O(9)	84.5(3)
O(2)—Ta(1)—O(3)	91.9(4)	O(7)—Ta(2)—O(9)	176.0(5)
O(1)—Ta(2)—O(4)	163.1(4)	O(8)—Ta(2)—O(9)	89.2(4)
O(2)—Ta(1)—O(4)	93.1(4)	O(1)—Ta(2)—O(10)	162.5(3)
O(3)—Ta(1)—O(4)	92.4(4)	O(2)—Ta(2)—O(10)	91.5(4)
O(1)—Ta(1)—O(5)	95.0(4)	O(7)—Ta(2)—O(10)	92.5(5)
O(2)—Ta(1)—O(5)	166.9(4)	O(8)—Ta(2)—O(10)	98.2(4)
O(3)—Ta(1)—O(5)	94.2(5)	O(9)—Ta(2)—O(10)	85.6(4)
O(4)—Ta(1)—O(5)	98.2(4)	Ta(1)—O(1)—Ta(2)	114.3(4)
O(1)—Ta(1)—O(6)	83.9(3)	Ta(1)—O(2)—Ta(2)	99.4(3)
O(2)—Ta(1)—O(6)	85.2(3)	Ta(1)—O(2)—C(1)	134.4(8)
O(3)—Ta(1)—O(6)	176.6(4)	Ta(2)—O(2)—C(1)	126.1(8)
O(4)—Ta(1)—O(6)	85.9(4)	Ta(1)—O(3)—C(4)	163.8(17)
O(5)—Ta(1)—O(6)	89.0(4)	Ta(1)—O(4)—C(7)	148.3(11)
O(1)—Ta(2)—O(2)	73.0(3)	Ta(1)—O(5)—C(10)	147.8(13)
O(1)—Ta(2)—O(7)	96.2(4)	Ta(1)—O(6)—C(13)	128.1(8)
O(2)—Ta(2)—O(7)	92.1(4)	Ta(2)—O(7)—C(16)	168.6(17)
O(1)—Ta(2)—O(8)	96.3(4)	Ta(2)—O(8)—C(19)	148.1(19)
O(2)—Ta(2)—O(8)	168.0(4)	Ta(2)—O(9)—C(22)	128.7(8)
O(7)—Ta(2)—O(8)	94.6(5)	Ta(2)—O(10)—C(25)	154.0(14)

Table 6. Principal bond lengths (d) and bond angles (ω) in the structure of **2**

Bond	d/Å	Bond	d/Å
Ta(1)—O(1)	2.064(11)	Ta(4)—O(2)	2.141(10)
Ta(1)—O(2)	1.977(10)	Ta(4)—O(3)	1.912(11)
Ta(1)—O(3)	1.971(11)	Ta(4)—O(5)	2.006(9)
Ta(1)—O(7)	1.869(13)	Ta(4)—O(6)	2.090(9)
Ta(2)—O(1)	2.065(7)	Ta(4)—O(13)	1.884(10)
Ta(2)—O(4)	1.838(9)	Ta(4)—O(14)	1.888(12)
Ta(2)—O(5)	1.877(10)	O(6)—C(1)	1.454(19)
Ta(2)—O(8)	1.884(10)	O(7)—C(4)	1.353(38)
Ta(2)—O(9)	2.166(10)	O(8)—C(7)	1.425(29)
Ta(2)—O(9A)	2.116(11)	O(9)—C(10)	1.445(19)
Ta(3)—O(2)	2.077(9)	O(10)—C(13)	1.384(23)
Ta(3)—O(4)	2.018(8)	O(11)—C(16)	1.362(21)
Ta(3)—O(6)	2.177(11)	O(12)—C(19)	1.372(26)
Ta(3)—O(10)	1.885(10)	O(13)—C(22)	1.436(22)
Ta(3)—O(11)	1.877(11)	O(14)—C(25)	1.436(24)
Ta(3)—O(12)	1.869(12)		

Angle	ω/deg	Angle	ω/deg
O(1)—Ta(1)—O(2)	86.0(3)	O(2)—Ta(4)—O(3)	75.9(4)
O(1)—Ta(1)—O(3)	86.5(3)	O(2)—Ta(4)—O(5)	91.8(4)
O(2)—Ta(1)—O(3)	78.6(4)	O(2)—Ta(4)—O(6)	71.1(4)
O(2)—Ta(1)—O(7)	94.0(3)	O(2)—Ta(4)—O(13)	95.9(4)
O(2)—Ta(1)—O(2A)	171.9(5)	O(2)—Ta(4)—O(14)	175.2(4)
O(3)—Ta(1)—O(7)	93.5(3)	O(3)—Ta(4)—O(5)	90.0(4)
O(1)—Ta(2)—O(4)	95.7(3)	O(3)—Ta(4)—O(6)	146.5(4)
O(1)—Ta(2)—O(5)	87.4(3)	O(3)—Ta(4)—O(13)	97.4(4)
O(1)—Ta(2)—O(8)	160.3(4)	O(3)—Ta(4)—O(14)	105.5(5)
O(1)—Ta(2)—O(9)	73.1(3)	O(5)—Ta(4)—O(6)	84.9(4)
O(1)—Ta(2)—O(9A)	72.0(3)	O(5)—Ta(4)—O(13)	170.4(4)
O(4)—Ta(2)—O(5)	97.4(4)	O(5)—Ta(4)—O(14)	83.7(5)
O(4)—Ta(2)—O(8)	101.4(4)	O(6)—Ta(4)—O(13)	92.1(4)
O(4)—Ta(2)—O(9)	96.7(4)	O(6)—Ta(4)—O(14)	106.9(5)
O(4)—Ta(2)—O(9A)	162.9(4)	O(13)—Ta(4)—O(14)	88.5(5)
O(5)—Ta(2)—O(8)	99.8(5)	Ta(1)—O(1)—Ta(2)	98.3(5)
O(5)—Ta(2)—O(9)	156.9(4)	Ta(1)—O(2)—Ta(3)	145.4(5)
O(5)—Ta(2)—O(9A)	93.9(4)	Ta(1)—O(2)—Ta(4)	98.3(4)
O(8)—Ta(2)—O(9)	95.2(4)	Ta(3)—O(2)—Ta(4)	109.4(4)
O(8)—Ta(2)—O(9A)	89.1(4)	Ta(1)—O(3)—Ta(4)	106.7(4)
O(9)—Ta(2)—O(9A)	68.7(5)	Ta(2)—O(4)—Ta(3)	140.0(5)
O(2)—Ta(3)—O(4)	82.4(3)	Ta(2)—O(5)—Ta(4)	129.0(5)
O(2)—Ta(3)—O(6)	70.7(4)	Ta(3)—O(6)—Ta(4)	107.6(5)
O(2)—Ta(3)—O(10)	159.7(4)	Ta(3)—O(6)—C(1)	123.0(8)
O(2)—Ta(3)—O(11)	93.0(4)	Ta(4)—O(6)—C(1)	129.1(9)
O(2)—Ta(3)—O(12)	94.9(4)	Ta(1)—O(7)—C(4)	151(2)
O(4)—Ta(3)—O(6)	86.1(4)	Ta(2)—O(8)—C(7)	165(1)
O(4)—Ta(3)—O(10)	87.9(4)	Ta(2)—O(9)—Ta(2A)	93.7(4)
O(4)—Ta(3)—O(11)	170.8(4)	Ta(2)—O(9)—C(10)	124.0(9)
O(4)—Ta(3)—O(12)	92.9(5)	Ta(2A)—O(9)—C(10)	136.0(9)
O(6)—Ta(3)—O(10)	91.1(4)	Ta(3)—O(10)—C(13)	141(1)
O(6)—Ta(3)—O(11)	84.9(4)	Ta(3)—O(11)—C(16)	158(1)
O(6)—Ta(3)—O(12)	165.5(4)	Ta(3)—O(12)—C(19)	158(1)
O(10)—Ta(3)—O(11)	94.1(5)	Ta(4)—O(13)—C(22)	138(1)
O(10)—Ta(3)—O(12)	103.4(5)	Ta(4)—O(14)—C(25)	144(1)
O(11)—Ta(3)—O(12)	95.3(5)		

Among all oxoalkoxides currently known,* complex **1** contains the smallest number of metal atoms. Apparently, it is the reason of an unusually high stability of compound **1**; unlike other compounds of the $M_nO_m(OR)_p$ type,[2] complex **1** does not decompose in alcohol solutions (the values of the solubility of compound **1** are equilibrium) or in the gas phase. It is very interesting that under these conditions, dimeric molecules $[Ta(OPr^i)_5]_2$ completely dissociate to give monomers.

One more crystalline oxo complex, $Ta_7O_9(OPr^i)_{17}$ (**2**), which is the product of further condensation of tantalum isopropoxide, was formed from alcohol solutions of compound **1** as a result of further elimination of ether or noncontrolled hydrolysis. In the crystal, heptanuclear molecules **2** occupy special positions, namely, twofold axes passing through the O(1), Ta(1), and O(7) atoms (Fig. 3) (the OPr^i group at the O(7) atom is disordered at two sites related by the twofold axis). Molecules **2** consist of two $[Ta_4]$ tetrahedra with a

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* Recently, trinuclear complex $[Ti_3O][OPr^i]_9(OMe)$, obtained by controlled hydrolysis of $Ti(OPr^i)_4$ in a solution of MeOH, was described. Its molecules, which have a triangular form, $Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu\text{-}OPr^i)_3(OPr^i)_6$, are stable in alcohol solutions but decompose upon heating or in a medium of hydrocarbons to give products of deeper condensation.[18]

shared Ta(1) vertex; these tetrahedra are additionally linked through three bridges (two μ_2-OPr^i and one μ_3-O). This is a new type of heptamer observed for alkoxides. Up to now, only complex $Ti_7O_4(OEt)_{20}$ was known; it is a highly symmetrical molecule, in which the metal atoms are located in a single plane; this structure consists of the central [TiO_6] octahedron connected with six other octahedra *via* shared edges.[19,20] The Ta—OPr^i bond lengths in molecule **2** are very close to those observed for **1** (1.87—1.88 Å for terminal bonds and 2.09—2.18 Å for bridging bonds) (see Table 6). However, the variety of functions of oxo groups in molecule **2** results in a much wider spread in the Ta—O(oxo) distances: 1.84—2.02 Å and 1.98—2.14 Å for the μ_2- and μ_3-bridging groups, respectively. The Ta(1)—μ_3-O(oxo) bonds at the Ta(1) atom shared by two tetrahedra have the shortest distances [Ta(1)—O(1), 2.06(1) Å and Ta(1)—O(2), 1.98(1) Å].

Complex **2** belongs to a large group of known crystalline polynuclear oxoalkoxides, the cluster molecules of which are formed by blocks consisting of several octahedra [$M(OR)_6$] linked together through isolated [MO_n] groups containing oxo groups of high dentation. These structures often resemble the structures of isopolyanions (many of them are formed upon hydrolysis). Clearly that upon transition into an alcohol solution, these molecules undergo solvation destruction, and in the gas phase, molecules $M(OR)_n$, which are formed as a result of disproportionation of oxo complexes, are present above the solution.

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References

1. E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, and V. G. Kessler, *Koord. Khim.* [*Coord. Chem.*], 1988, **14**, 926 (in Russian).
2. 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.)].
3. 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.)].
4. N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, A. I. Yanovsky, and Yu. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1993, 21.
5. N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, and M. I. Yanovskaya, *J. Sol-Gel Sci. and Technol.*, 1994, **2**, 17.
6. N. Ya. Turova, A. V. Korolev, D. E. Chebukov, A. I. Belokon', A. I. Yanovsky, and Yu. T. Struchkov, *Polyhedron*, 1996, in press.
7. W. Robinson and G. M. Sheldrick, *SHELX* in *Crystallographic Computing Techniques and New Technologies*, Eds. N. M. Isaacs and M. R. Taylor, Oxford. Univ. Press, Oxford, 1988, 366.
8. N. I. Kozlova, V. G. Kessler, N. Ya. Turova, and A. I. Belokon', *Koord. Khim.*, 1989, **15**, 1524 [*Sov. J. Coord. Chem.*, 1989, **15**, 867 (Engl. Transl.)].
9. S. I. Kucheiko, N. Ya. Turova, and N. I. Kozlova, *Koord. Khim.*, 1985, **11**, 1656, 945 [*Sov. J. Coord. Chem.*, 1985, **11** (Engl. Transl.)].
10. E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, A. I. Belokon', D. V. Berdyev, V. G. Kessler, and Yu. K. Grishin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 752 [*Russ. Chem. Bull.*, 1995, **44**, 734 (Engl. Transl.)].
11. B. A. Vaartstra, J. C. Huffman, P. Gradeff, L. G. Hubert-Pfalzgraf, J.-C. Daran, S. Parraud, K. Yun-Lu, and K. Caulton, *Inorg. Chem.*, 1990, **29**, 3126.
12. A. I. Yanovsky, E. P. Turevskaya, N. Ya. Turova, F. M. Dolgushin, A. P. Pisarevsky, A. S. Batsanov, and Yu. T. Struchkov, *Zh. Neorg. Khim.*, 1994, **39**, 1307 [*Russ. J. Inorg. Chem.*, 1994, **39**, 1246 (Engl. Transl.)].
13. A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, and J. G. Riess, *Inorg. Chem.*, 1976, **15**, 1196.
14. M. G. B. Drew and J. D. Wilkins, *Inorg. and Nucl. Chem. Lett.*, 1974, **10**, 549.
15. S. Boulmaâz, L. G. Hubert-Pfalzgraf, S. Halut, and J. C. Daran, *J. Chem. Soc., Chem. Commun.*, 1994, 60.
16. C. D. Chandler, G. D. Fallon, A. J. Koplick, and B. O. West, *Austral. J. Chem.*, 1987, **40**, 1427.
17. P. Toledano, F. Ribot, and C. Sanchez, *Acta Crystallogr., Sect. C*, 1990, **46**, 1419.
18. V. W. Day, T. A. Eberspacher, Y. Chen, J. Hao, and W. G. Klemperer, *Inorg. Chim. Acta*, 1995, **229**, 391.
19. K. Watenpaugh and C. N. Caughlan, *Chem. Commun.*, 1967, 76.
20. R. Schmid, A. Mosset, and J. Galy, *J. Chem. Soc., Dalton Trans*, 1991, 1999.

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