Synthesis and Characterization of Tantalum–Zinc Oxoisopropoxides. Molecular Structure of $[ZnTa_2I(\mu_3\text{-}O)(\mu\text{-}O)(\mu\text{-}OPr^i)_3(OPr^i)_4]_2$ containing an Unprecedented Tantalum Oxoalkoxide Anion

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A tantalum–zinc oxoisopropoxide is prepared and its crystal structure described.

Electronic ceramics are largely based on perovskite derivatives, thus involving large divalent elements such as barium, lead, zinc, and early transition metals such as titanium, niobium or tantalum.[1] Sol–gel routes are crucial for the obtaining of some of these,[2] and on the other hand, the formation of perovskite *vs.* pyrochlore is generally favoured by chemical routes based on alkoxides as precursors.[3] One attractive feature of metal alkoxides is their ability to form, generally quite easily, mixed-metal species.[4] However, while zinc is involved in the composition of capacitors such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) or $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN).[5] $Pb_2Zn_2(OAc)_4(OC_2H_4OMe)_4$[6] remains the only structurally characterized mixed-metal species based on zinc. The compound $ZnNb_2(OEt)_{12}$ has been mentioned but no characterization or even analysis has been reported.[7]

Many mixed-metal alkoxides result from Lewis acid–base reactions between alkoxides. Zinc alkoxides based on classical OR groups such as ethoxides or isopropoxides are polymeric, insoluble derivatives. In contrast, with other polymeric divalent metal isopropoxides such as lead, no reaction was observed between isolated $[Zn(OPr^i)_2]_\infty$ (suspensions of particles of 5000 nm) and $[M(OPr^i)_5]_2$ M = Nb, Ta even in toluene–isopropyl alcohol (up to 130 equiv. of ROH with respect to Zn) at reflux for 48 h. Different means such as controlled microhydrolysis were investigated to overcome this lack of reactivity. The use of the colloidal suspensions of $Zn(OPr^i)_2$ resulting either from the alcoholysis of $Zn[N(SiMe_3)_2]_2$ in toluene with an excess of isopropyl alcohol or from ultrasonic activation of isolated zinc isopropoxide in toluene–isopropyl alcohol (transluscent suspensions with particles of 100–300 nm size) appears as an alternative for group 5 metal alkoxides. Indeed, a facile reaction, at room temperature becomes possible with $Ta(OPr^i)_5$ giving a compound **1**, whose analytical data account for the presence of the two metals in a $ZnTa_2$ stoichiometry and suggest the formation of an oxo species of empirical formula $ZnTa_2O_2(OPr^i)_8$.

The same compound **1** is obtained by metathesis between ZnI_2 and $KTa(OPr^i)_6$ (1:2 stoichiometry) in THF at room temp. However, no crystals suitable for X-ray structure determination could be grown for compound **1**. Metathesis reaction between ZnI_2 and $KTa(OPr^i)_6$ (1:1) in refluxing toluene over 24 h offers a compound **2**,† soluble in common organic solvents except hydrocarbons, containing zinc and tantalum, as well as iodine. Colourless, crystalline needles of compound **2** suitable for X-ray diffraction studies‡ were obtained from the reaction medium in the presence of isopropyl alcohol at 10 °C.

Complex **2** (Fig. 1) is a centrosymmetric dimer composed of two triangular $Ta_2Zn(\mu_3\text{-}O)(\mu\text{-}OPr^i)_3I$ units linked by two oxo bridges, involving the two tantalum centres of both units. These Ta–O–Ta oxo bridges are nearly linear (175.30°), the distances between the metals Ta(1) and Ta(1′) being 3.811(9) Å. The tantalum atoms are six-coordinate with substantial departure from an ideal octahedral geometry. Zinc has a distorted tetrahedral geometry with iodide as the only terminal ligand. The Ta–O bond lengths range from 1.83(1) to 2.12(1) Å. These values fall in the range of those found in a variety of siloxide[8] or aryloxide[9] derivatives. As expected, terminal isopropoxide bonds are the shortest, the general variation being Ta–OR < Ta–μ_2-O < Ta–μ_3-O < Ta–μ-OR. Zinc oxygen bond distances vary from 1.95(1) for the bridging isopropoxides to 2.10(1) Å for the oxo bond. These values are comparable with the data observed for other zinc alkoxide or aryloxide derivatives.[10] The terminal Ta–O–C angles are large, 146.7° (av.) and 157.15° (av.) for Ta(1) and Ta(2), respectively, as usually observed for early transition metal alkoxides. The zinc iodide bond distance of 2.481(2) Å is quite long.[11]

The trinuclear Ta_2Zn units correspond to isosceles triangles with Zn···Ta and Ta···Ta distances of 3.14 (av.) and 3.31 Å, respectively. They are capped by a triply bridging oxo ligand O(1) having a pyramidal stereochemistry (sum of the angles 311.1°), while the different metals are connected by isopropoxide bridges, symmetrical between the two tantalums, unsymmetrical between tantalum and zinc. Each triangular unit can be viewed as resulting from two TaO_6 octahedra sharing a common edge further connecting a ZnO_3I tetrahedron *via* an apex and two faces. The overall metallic framework of compound **2** bears some similarity with that of the hexameric titanium oxoacetoalkoxide $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2\text{-}(OBu)_8(OAc)_8$[12] although the triply bridging oxo ligands of **2** are trigonal instead of planar for the titanium aggregate.

Room temperature ^1H NMR spectra of **2** show three types of magnetically non-equivalent methine groups between δ 5.30 and 4.72 in a 1:2:4 ratio. Although a 1:2:2:2 ratio is expected on the basis of the solid-state structure, these data are consistent with the retention of the structure of the heterometallic cluster in solution if the methine resonances of the terminal alkoxide ligands are accidentally degenerate.

$[ZnTa_2I(\mu_3\text{-}O)(\mu\text{-}O)(\mu\text{-}OPr^i)_3(OPr^i)_4]_2$ is obtained in high yield (96%). The peripheral positions of the iodide ligands, the lability of the Zn–I bonds allow further substitution and **2** may thus act as an interesting synthon. Indeed, **2** reacts at room temp. in toluene–isopropyl alcohol with 2 equiv. of potassium isopropoxide, giving a compound whose analytical

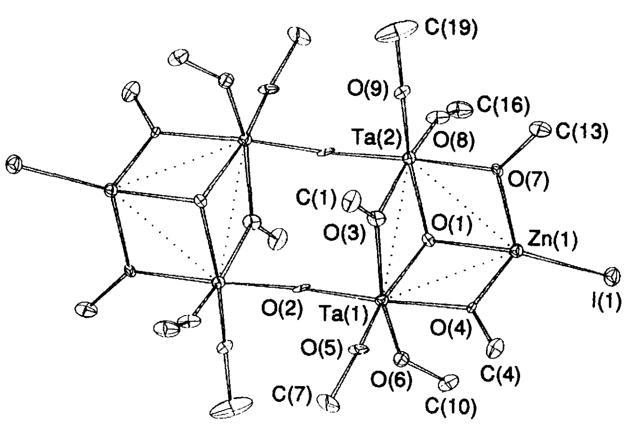

Fig. 1 ORTEP view of the molecular structure of $[ZnTa_2I(\mu_3\text{-}O)(\mu\text{-}O)(\mu\text{-}OPr^i)_3(OPr^i)_4]_2$ showing the atom-labelling scheme (methyl groups have been omitted for clarity). Selected bond lengths (Å) and angles (°) (av.): Ta–OR(terminal) 1.87(1); Ta–μ_2-OR 2.11(1): Ta–μ_2-O 1.90(1); Ta–μ_3-O 2.01(1); Zn–1 2.481(2), Zn–μ_3-O, 2.10(1), Zn–μ_2-OR, 1.96(1), <Ta–O(2)–Ta 175.3(5)°.

and spectral data are similar to those of compound **1**.[§] The ^1H NMR spectra of **1** are characterized by a shift to higher frequencies (δ 5.10 to 4.59) with only two types of methine groups at room temperature in a 7 : 1 ratio. Compound **1** is actually a fluxional molecule although only broad and poorly resolved spectra could be obtained at low temperature. **1** is obtained either by substitution of the remaining halides in **2** or by direct reaction between $Ta(OPr^i)_5$ and colloidal $Zn(OPr^i)_2$, the analytical and spectral data support its formulation as a mixed-metal oxoisopropoxide whose structure is derived from that of compound **2**. This conclusion is also supported by the niobium analogue of **1**, compound **3**. The chemical exchange, fast on the NMR timescale for tantalum, is slown down for compound **3** and low-temperature ^1H NMR spectra (−40 °C) display four types of magnetically non-equivalent methine groups between δ 4.85–4.44 in a 2 : 1 : 4 : 1 ratio, in accordance with $Nb_4Zn_2(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OPr^i)_6(OPr^i)_{10}$ and with the accidental degenerency of the resonances of the methine groups of the terminal Nb–OR linkages.

The mixed-metal Zn_2Ta_4 species represent a new framework for heterometallic alkoxides based on a 2 : 4 stoichiometry. Classical examples involve divalent metals (Mg, Ba, Cd) associated to tetravalent ones, titanium or zirconium, the typical structure being illustrated by that of $Ba_2Zr_4(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_{10}(OR)_8$[4] based on the $Zr_2(OR)_9^-$ moiety and in which all metals are hexacoordinated. In the case of group 5 metal alkoxides, a similar structure would lead to seven-coordinated niobium or tantalum, and thus to a coordination number disfavoured for the alkoxides of these elements. The spontaneous generation of oxo ligands allows tantalum to return to its most usual coordination number, namely six. Compound **2** can formally be considered as resulting from ZnI^+ and $Ta_2O_2(OR)_7^-$ fragments, the later being the first example of a complex oxoalkoxide anion based on tantalum. In the novel Ta–Zn and Nb–Zn species reported, this anion acts as a tetradentate ligand.

Hydrolysis experiments of compounds **1** and **2** in THF offer amorphous powders whose thermal treatment leads to crystalline Ta_2ZnO_6 and to Ta_2ZnO_6 with traces of $Ta_2Zn_3O_8$ and Ta_2O_5, respectively.

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Footnotes

[†] $[ZnTa_2IO_2(OPr^i)_7]_2$ **2**: satisfactory elemental analysis (C, H, Ta, Zn). *Selected spectral data*: IR (mineral oil, ν/cm^{-1}): 1367s, 1340m, 1168s, 1130sh, 1115vs, 1091s, 1039m, 1015vs, 960m, 939s, 858m, 820s: ν(M–OR) 607s, 584s, 565s, 523w, 461m: ^1H NMR (δ, C_7D_8, 25 °C): 5.30, 4.84, 4.72 (heptuplet, CH, *J*, 6 Hz, 1 : 2 : 4, 14H), 1.56, 1.46, 1.30 (d, CH_3, *J* 6 Hz, 12 : 6 : 24, 84H). $^{13}C\{^1H\}$: 77.57, 75.25, 70.63 (CH), 28.87, 27.73, 26.64 (CH_3).

[‡] *Crystal data* for $C_{42}H_{98}I_2O_{18}Ta_4Zn_2$ **2**: $M = 1998.6$, monoclinic, space group $P2_1/n$; $a = 10.497(5)$, $b = 23.684(9)$, $c = 12.964(4)$ Å, $\beta = 95.92(3)°$. $V = 3205(2)$ Å^3, $D_c = 2.07$ g cm^{-3}, for $Z = 2$, μ(Mo-Kα) = 84.7 cm^{-1}.

5050 data were collected at low temperature (−100 °C) on a Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Of 3932 unique reflections, 2856 with $I > 3\sigma(I)$ were used to solve and refine the structure: $R = 0.066$, $Rw = 0.078$, 494 variables. Computations were performned by using CRYSTALS[13] adapted on a Micro Vax II. The structure was solved by direct methods using the SHELXS 86 program[14] and subsequent Fourier maps. All atoms were anisotropically refined. Full-matrix least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. In the last stages of refinements each reflection was assigned a weight: $w = w'^*[1 - \{(F_o - [F_c])/6^*\sigma(F_o)\}^2]^2$ with $w' = \{1/[A_oT_o(x) + \cdots + A_iT_i(x) + \cdots + A_nT_n(x)]\}$ for which x is $F_o/F_{o\,\max}$ and A_i are the coefficients of the Chebyshev's series (8.87; 0.05; 6.31 respectively). Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in the final difference map. Empirical absorption corrections were made.[1,5]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] **1**: $[Ta_2ZnO_2(OPr^i)_8]m$; satisfactory elemental analysis (C, H, Ta, Zn) *Selected spectra data*, IR (mineral oil, ν/cm^{-1}): 1354s, 1281m, 1187m, 1164vs, 1129vs, 1031m, 991vs, 970m, 935m, 844s, 828s, 808sh, 612m; 575vs, 457s, 422m, 410m: ^1H NMR (δ, C_7D_8), 4.90, 4.39 (heptuplet, *J* 6 Hz, 7 : 1 : 8): 1.39, (d, *J* 6 Hz, 42H), 1.52 (d, *J* 6 Hz, 6 H).

[¶] $Nb_4Zn_2O_4(OPr^i)_{16}$ **3**: satisfactory elemental analysis (C, H, Nb, Zn). IR (Nujol, ν/cm^{-1}): 1323m, 1161m, 1180sh, 1161m, 1122m, 1014m, 986s, 953m, 845m, 827m, 808m; 577vs, 465m, 434m (νM–OR); ^1H NMR ($CDCl_3$, −40 °C): 4.85, 4.75, 4.64, 4.44 (heptuplet, *J* 6 Hz, 2 : 1 : 4 : 1, 16H): 1.3–1.1 overlapping of doublets, *J* 6 Hz. 96H: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): 77.26, 66.58 (CH), 29.25, 26.24 (CH_3).

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