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Modification of yttrium alkoxides: β-Ketoesterate-substituted yttrium alkoxo/hydroxo/oxo clusters

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ABSTRACT

Reaction of $Y_5O(OiPr)_{13}$ ("yttrium iso-propoxide") with one molar equivalent of isopropyl acetoacetate ($i$prac) per Y resulted in the formation of $Y_9O(OH)_9(OiPr)_8(i$prac$)_8$, a rare example of an yttrium alkoxo/hydroxo/oxo cluster. Reaction in a 1:3 molar ratio gave $Y_4(OH)_2(i$prac$)_{10}$ and $Y_6(OH)_6(i$prac$)_{12}$ instead. A fourth cluster, $Y_9O(OH)_9(i$prac$)_{16}$, structurally closely related to $Y_9O(OH)_9(OiPr)_8(i$prac$)_8$, was obtained upon recrystallization of $Y_4(OH)_2(i$prac$)_{10}$ from $CDCl_3$.

1. Introduction

The chemistry of yttrium alkoxide derivatives was studied to a much smaller extent [1–5] than that of other metal alkoxides, e.g. alkoxides of titanium, zirconium or aluminum [6–8]. Yttrium has a high tendency to form oxo-alkoxides instead of homoleptic alkoxides. For example, "yttrium iso-propoxide" is in fact $Y_5O(OiPr)_{13}$ (Fig. 1). The structure of this compound is also due to the high tendency of yttrium for coordination expansion, with coordination numbers up to nine. Both features result in a very complex structural chemistry of yttrium alkoxides and their derivatives.

Little is known about the modification of yttrium alkoxides [9–11]. The only derivative prepared by substitution of alkoxo groups, which bears alkoxo groups as well as other ligands, is $Y_8O_2(OH)_4(OEt)_6(aaa)_{10}$ (aaa = allyl acetoacetate) [9]. This compound was obtained upon reaction of $Y_5O(OiPr)_{13}$ with aaa-H and subsequent crystallization from an ethanol/toluene-mixture. The latter step causes exchange of the remaining OiPr against OEt groups. Reaction of $Y_5O(OiPr)_{13}$ with three molar equivalents of 2,2,6,6-tetramethyl-3,5-heptandione (thd-H) per yttrium gave $Y(thd)_3$, showing that the Y_5O core can be degraded upon coordination [10]. Reaction of $Y_5O(OiPr)_{13}$ with acetylacetone (acac-H) showed that substitution of OiPr groups by β-diketonates is not necessarily straightforward. This reaction yielded dimeric $Y_2(acetate)_2(acac)_4(H_2O)_2$, the acetate ligands being formed by cleavage of acetylacetonate ligands [9].

Some other examples of homo-metallic yttrium compounds with alkoxo groups and additional organic ligands have been reported, but were prepared either by reaction of an yttrium salt [12] or by ligand exchange starting from another coordination compound [13].

Four new yttrium alkoxo/hydroxo/oxo complexes with isopropyl acetoacetate ($i$prac) ligands are presented in this contribution. The complexes were obtained by reaction of $Y_5O(OiPr)_{13}$ with $i$prac-H in varying stoichiometric ratios and under varying conditions. $i$prac-H was chosen as β-ketoester to avoid undesired transesterification reactions between the β-ketoester and the alkoxo groups of the yttrium alkoxide and/or liberated alcohol molecules, as reported in literature for related yttrium compounds [14]. This article does not intend to provide a comprehensive picture on the substitution chemistry of $Y_5O(OiPr)_{13}$ with β-ketoesters or related compounds. The reported structures are instead additional motifs to complement the structural manifold of yttrium oxo derivatives.

2. Results and discussion

Reaction of *one molar equivalent* of $i$prac-H per yttrium atom with $Y_5O(OiPr)_{13}$ in toluene gave a colorless powder, which was recrystallized from toluene. Single crystal structure analysis revealed that the composition was $Y_9O(OH)_9(OiPr)_8(i$prac$)_8$ [**1** = $Y_9(\mu_5$-O$)(\mu_4$-OH$)(\mu_3$-OH$)_8(\mu$-OiPr$)_8(i$prac$)_8$] (Fig. 2).

Compound **1** is one of the rare examples of homometallic yttrium clusters with both alkoxo and bidentate organic ligands. Other compounds besides $Y_8O_2(OH)_4(OEt)_6(aaa)_{10}$ (see above) are $Y_2(tmp)_4(OEt)_2$ and $Y_2(tmp)_4(OEt)(OBu)$ (tmp = 2,2,6,6-tetramethylpiperidinate) prepared from YCl_3, or $Y_3(OC_2H_4OMe)_5(acac)_4$, obtained as a by-product in the reaction of $[Y(OC_2H_4OMe)_3]_{10}$ with $Cu(acac)_2$.

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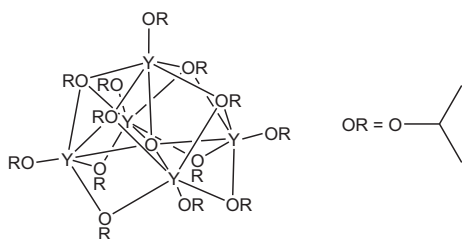E-mail address: uschuber@mail.zserv.tuwien.ac.at (U. Schubert).

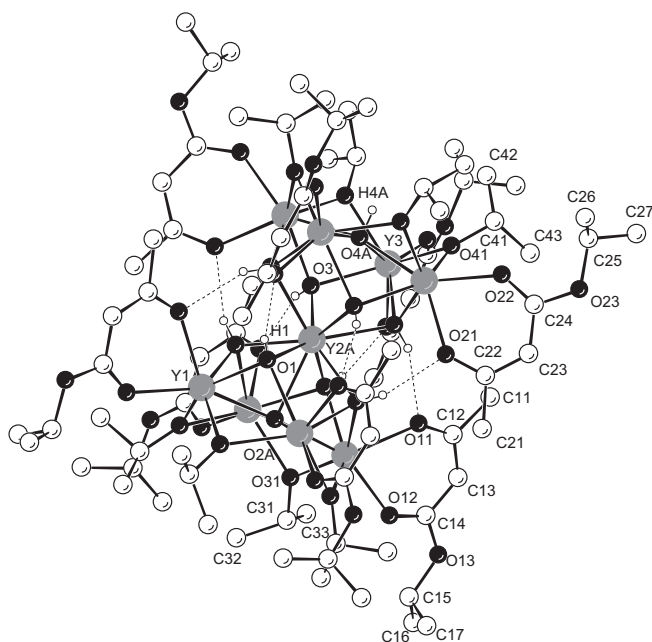**Fig. 1.** Schematic representation of $Y_5O(OiPr)_{13}$.

Fig. 2. Molecular structure of $Y_9O(OH)_9(OiPr)_8(iprac)_8$ (**1**).

The structure of **1** has an Y_9 core (Fig. 3), similar to that of $[Na(EtOH)_6][Y_9O_2(OH)_8(etac)_{16}]$ (etac = ethyl acetoacetate). This cluster core is also known for related lanthanide complexes [15]. In contrast to anionic $[Y_9O_2(OH)_8(etac)_{16}]^-$ [14], cluster **1** is neutral because one of the μ_5-O is protonated, resulting in a μ_4-OH group, and thus has a lower symmetry.

The structure of **1** can be described by two Y_5 square pyramids sharing the yttrium atom at the vertex (Y(2A), Fig. 3). The basal planes of the two pyramids are rotated by 45° with respect to each other. The eight yttrium atoms of the basal planes are each
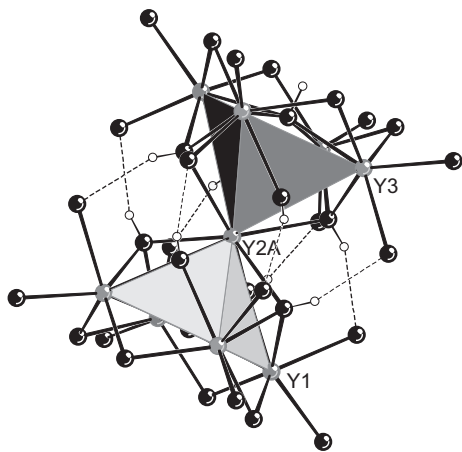

Fig. 3. Y_9 core structure of $Y_9O(OH)_9(OiPr)_8(iprac)_8$ (**1**).

seven-coordinated by one chelating iprac, two μ-OiPr, two μ_3-OH and one μ_5-O or μ_4-OH groups. Their coordination geometry can be described as capped trigonal prismatic. The central yttrium atom is coordinated by eight μ_3-OH groups in a square antiprismatic geometry and one μ_5-O atom that caps one of the base planes of the prism.

In the crystal structure of **1**, the cluster core was disordered over two positions (70:30), where the two halves of the cluster are mirrored. Two positions were only found, however, for the atoms located on the 4-fold axis, that is the μ_5-O [O(2)] and μ_4-OH [O(4)] groups as well as the central metal atom Y(2). The disordered positions of the other atoms were not resolved.

The structural motif of the square-pyramidal Y_5 arrangement with an oxygen atom in the centre of the square base is also found in the structure of $Y_5O(OiPr)_{13}$, the starting compound for the preparation of **1**. This reflects the stability of this structural motif.

The two different halves of the cluster structure, i.e. the one containing the μ_5-O group [O(2A) or O(2B)] and the other with the μ_4-OH group [O(4A) or O(4B)] in the centre of the basal plane of the square pyramids, can clearly be distinguished by means of bond distances and angles. The Y(2A)–O(2A) and Y(2B)–O(2B) distances [248.3(11) and 247.6(16) pm] are significantly shorter than that of Y(2A)–O(4A) and Y(2B)–O(4B) [319.7(11) and 320.0(17) pm]. While O(2A) and O(2B) thus form bonds to the central yttrium atom, O(4A) and O(4B) do not. This is also reflected by the fact, that the positions of O(2A) and O(2B) slightly deviate from the basal plane of the symmetry-related Y(1) atoms, lying "inside" the Y_5 pyramid, whereas O(4A) and O(4B) are clearly positioned "outside" the pyramid. In the structurally analogous compound $[Y_9O_2(OH)_8(etac)_{16}]^-$, the corresponding Y–O distances [289(2) and 294(2) pm] are in between the values found in **1**. The same influence is seen for the Y–Y distances in the two different pyramids: the μ_5-O- and μ_4-OH-pyramid [Y(2A)–Y(1) and Y(2B)–Y(3) 349.9(4) and 351.6(6) versus Y(2A)–Y(3) and Y(2B)–Y(1) 374.9(4) and 373.4(6) pm], This comparison shows that the formation of the Y(2)–O(2) bond leads to a contraction of the whole $Y_5(\mu_5$-O) pyramid compared with the $Y_5(\mu_4$-OH) pyramid, again with shorter distances for the μ_5-O side and longer distances for the μ_4-OH side compared to $[Y_9O_2(OH)_8(etac)_{16}]^-$ [366.9(3)–368.0(3) pm] [14]. This contraction is also reflected in shorter Y(1)–Y(1)* distances of 337.71(8) pm compared to 342.43(8) pm for Y(3)–Y(3)*, but both being shorter than in $[Y_9O_2(OH)_8(etac)_{16}]^-$ [356.0(3)–359.3(3) pm]. An analogous influence is also observed for the Y-(μ_3-OH) and Y-(μ-OiPr) distances. However, it has to be kept in mind that the positions of Y(1) and Y(3) both contain a 30% influence of the other pyramid and the Y–Y distances are therefore not purely that of one pyramid type.

As expected, the Y–O$_{ester}$ bond distances [232.6(2) and 230.1(2) pm] are slightly longer than the Y–O$_{keto}$ distances (230.0(2) and 228.3(2) pm). The bite angles of the chelating iprac ligands are 73.67(8)° [Y(1)) and 73.92(8)° (Y(3)), respectively.

As can be expected for steric reasons, the ester OR groups of the iprac ligands are directed away from the centre of the structure. The cluster is further stabilized by the formation of eight hydrogen bonds between the μ_3-OH groups and the keto carbonyl oxygen atoms of the iprac ligands [217(2) pm for O(11)···H(3) and 220(2) pm for O(21)···H(1)] (see Figs. 2 and 3). The hydrogen bonds also determine the orientation of the β-ketoesterate ligands, since hydrogen bonds are preferentially formed to the keto carbonyl oxygen.

In the reaction of $Y_5O(OiPr)_{13}$ with three molar equivalents of iprac-H per yttrium atom, a mixture of two different types of colorless crystals was obtained directly from the reaction solution. They were identified as $Y_4(OH)_2(iprac)_{10}$ [**2** = $Y_4(\mu_3$-OH)$_2(\mu$-iprac)$_6(iprac)_4$] (Fig. 4) and $Y_6(OH)_6(iprac)_{12}$ [**3** = $Y_6(\mu_3$-OH)$_6(\mu$-iprac)$_6(iprac)_6$] (Fig. 5) by single crystal structure analyses. Because
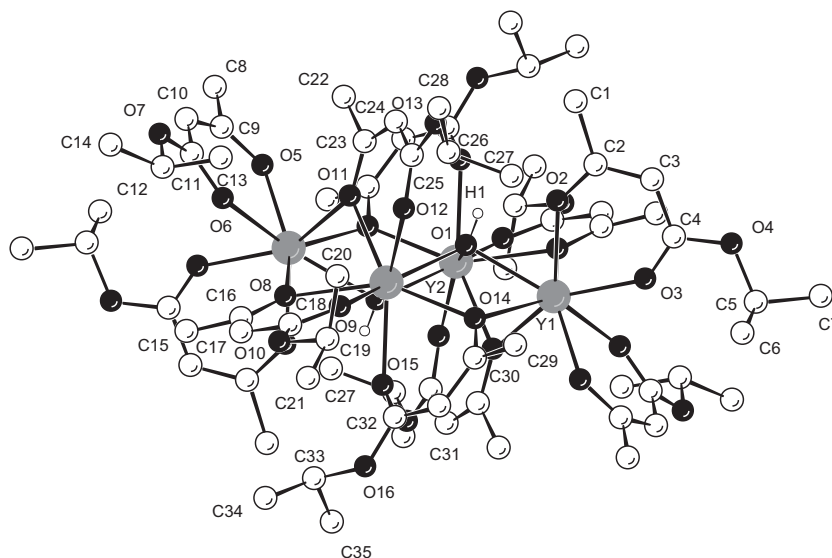
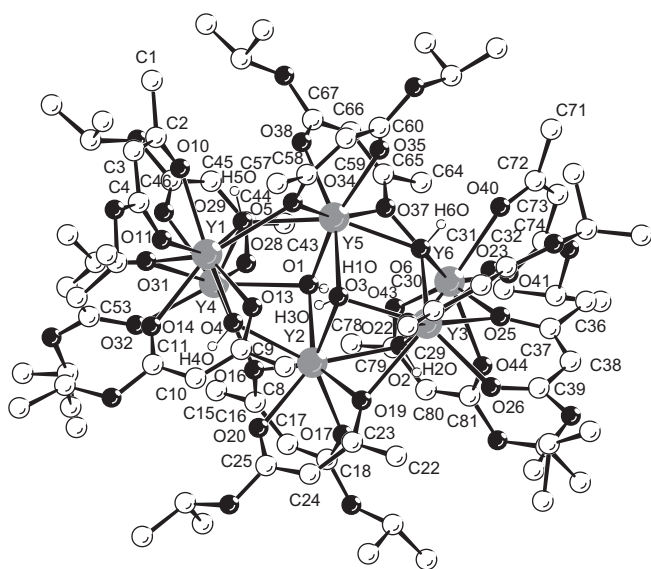**Fig. 4.** Molecular structure of $Y_4(OH)_2(iprac)_{10}$ (**2**).

Fig. 5. Molecular structure of $Y_6(OH)_6(iprac)_{12}$ (**3**).

of the higher iprac-H:Y ratio, neither the OiPr groups nor the μ_5-O atom of the parent $Y_5O(OiPr)_{13}$ is retained in **2** and **3**, and the yttrium atoms are only substituted by β-ketoesterate or hydroxo ligands. Complex **2** was also obtained by performing the reaction under slightly different conditions (extended reaction time).

The centrosymmetric structure of **2** has a planar Y_4 core with two crystallographically independent eight-coordinate yttrium atoms. Two of the yttrium atoms [Y(1)] are coordinated by two chelating iprac ligands each. The other six iprac ligands are bridging–chelating, where bridging occurs exclusively through the keto carbonyl groups. In addition to the two chelating iprac ligands, Y(1) is coordinated by a μ_3-OH group and the bridging oxygen atoms of three bridging–chelating iprac ligands in a distorted dodecahedral coordination geometry. The other yttrium centers [Y(2)] are coordinated by two μ_3-OH groups and chelated by three bridging–chelating iprac ligands. The coordination geometry around Y(2) is better described as a distorted square antiprism. Each μ_3-OH group is capping an Y_3 triangle, one being located above and one below the Y_4 plane. The Y–Y distances are 372.2(1) pm for Y(2)–Y(2), and 358.9(1) and 387.8(1) pm for Y(1)–Y(2).

The Y–O bond distances for the different ligands are compared in Table 1. They show the expected lengthening for the bridging compared to the terminal keto groups as well as slightly longer distances for the ester groups compared to the (terminal) keto groups. The average Y-(μ-O_{keto}) distances are longer for Y(1) (244.0 ± 1.2 pm) than for Y(2) (239.3 ± 2.0 pm). The two non-bridging iprac ligands are nearly planar. Two bridging iprac ligands are also nearly planar, with the Y(1)–Y(2) axis being approximately coplanar. The third iprac ligand [coordinated through O(14) and O(15)] has an envelope conformation and is strongly twisted with respect to the Y(1)–Y(2) axis.

Comparison of this structure with the analogous compound $Y_4(OH)_2(acac)_{10}$ shows that both structures have the same

Table 1
Comparison of Y–O bond distances (pm) of **1–4**.

	1	2	3	4
Y-(μ_5-O)	238.91(6)–248.3(11)			254.3(1)[c]
Y-(μ_4-OH)	241.1(2)–244.4(1)			254.3(1)[c]
Y-(μ_3-OH)	228.8(2)–249.4(5)	227.5(2)–236.5(3)	229.2(3)–242.2(4)	228.2(5)–242.4(4)
Y-$O_{keto,t}$ [a]	228.3(2)–230.0(2)	227.5(2)–232.5(2)	224.7(3)–232.0(3)	227.4(5)
Y-(μ-O_{keto})	226.5(2)–229.0(2)[b]	237.2(3)–245.2(2)	237.7(3)–256.7(3)	239.0(5)–240.0(5)
Y-$O_{ester,t}$ [a]	230.1(2)–232.6(2)	233.2(2)–234.7(2)	232.0(3)–240.0(3)	233.7(5)
Y-$O_{ester,b}$ [a]		229.8(2)–234.3(2)	227.7(3)–235.8(4)	235.4(5)

[a] t and b indicate bridging and terminal binding of the iprac ligands.
[b] Y-(μ-OiPr) instead of Y-$O_{keto,t}$.
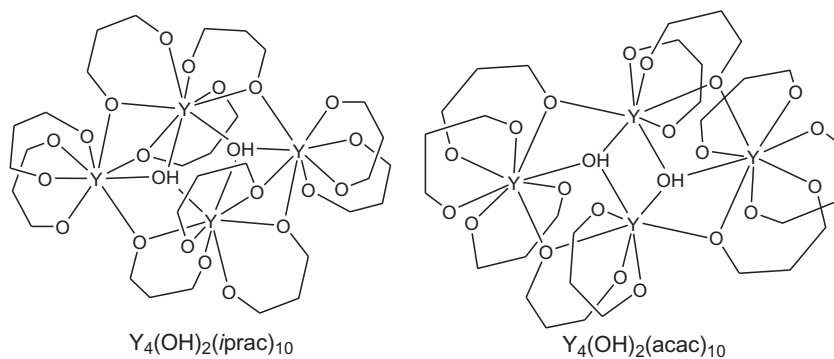[c] Average value for Y-(μ_5-O) and Y-(μ_4-OH) because of disorder.

Fig. 6. Schematic representations of **2** (left) and $Y_4(OH)_2(acac)_{10}$ (right) (methyl and ester groups omitted for clarity).
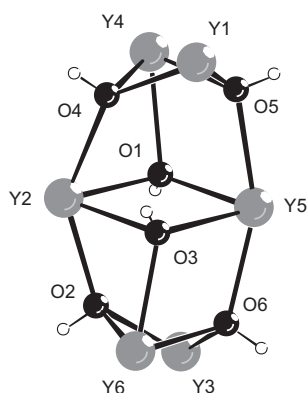

Fig. 7. $Y_6(OH)_6$ core of **3**.

$Y_4(OH)_2$ core [16]. Whereas **2** has four terminal and six bridging iprac ligands, $Y_4(OH)_2(acac)_{10}$ has six terminal and four bridging iprac ligands. This results in a higher average coordination number of the yttrium atoms in **2** (Fig. 6). Both cluster structures are very similar to that of $Zr_4O_2(methacrylate)_{12}$, where the zirconium atoms are seven-coordinated and the carboxylate ligands are either chelating or bridging [17,18]. The Y_4 structural motif of **2** can also be found in $Y_8O_2(OH)_4(OEt)_6(aaa)_{10}$ (*vide supra*), which is assembled from two $Y_4(\mu_4\text{-}O)(aaa)_5(\mu\text{-}OEt)_2$ units through μ_3-OH and OEt ligands.

The $Y_6(\mu_3\text{-}OH)_6$ core of **3** (Fig. 7) can be described as a distorted double cube of alternating eight-coordinate Y atoms and μ_3-OH groups, with two open edges. The Y atoms of the centre square [Y(2) and Y(5)] are thus coordinated to four μ_3-OH groups; the coordination sphere is completed by two chelating μ-iprac ligands. Y(3) and Y(4) of the upper and lower, butterfly-shaped four-membered rings are coordinated by two μ_3-OH groups, one chelating (non-bridging) iprac, one bridging–chelating μ-iprac, and the keto oxygen atom of one additional bridging μ-iprac ligand. Y(1) and Y(6) at the open edges of the upper and lower four-membered ring are coordinated by two μ_3-OH groups, two (non-bridging) chelating iprac and the keto oxygen atoms of two μ-iprac ligands. Y(1)
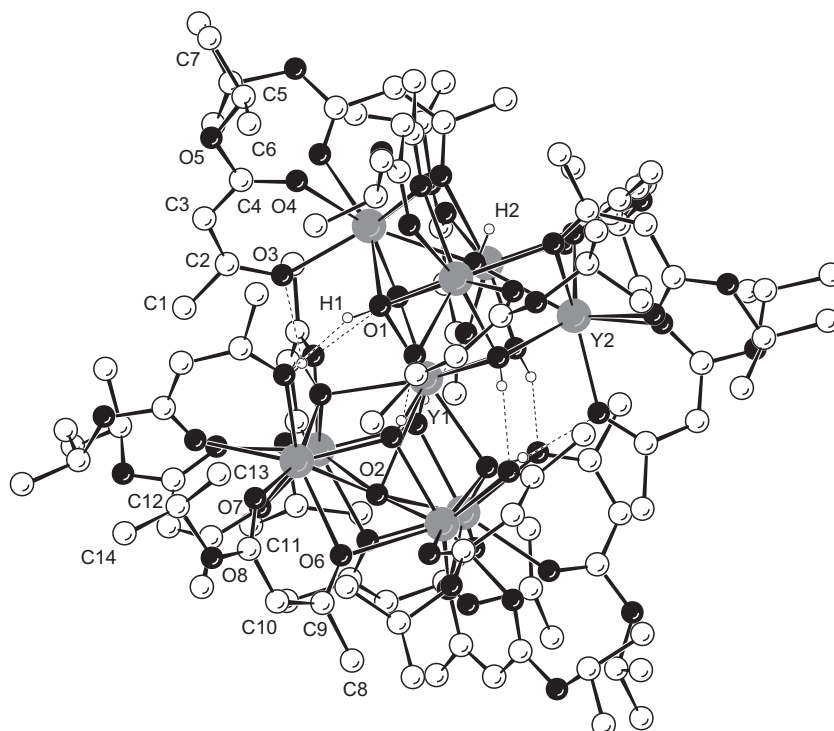

Fig. 8. Molecular structure of $Y_9O(OH)_9(iprac)_{16}$ (**4**).

Table 2
Crystallographic and structural parameters of **1–4**.

	1 · 4 Toluene	**2**	**3** · 2 Toluene	**4** · 4 CHCl₃
Empirical formula	$C_{108}H_{185}O_{42}Y_9$	$C_{70}H_{112}O_{32}Y_4$	$C_{98}H_{154}O_{42}Y_6$	$C_{116}H_{185}Cl_{12}O_{58}Y_9$
Formula weight	2955.75	1821.24	2537.67	3733.23
Crystal system	tetragonal	monoclinic	triclinic	cubic
Space group	$P4/n$	$P2_1/n$	$P\bar{1}$	$Pn{-}3n$
a (pm)	2076.9(4)	1417.2(5)	1436.25(10)	3109.91(12)
b (pm)		2004.8(7)	1699.42(12)	
c (pm)	1497.9(6)	1656.9(6)	2547.26(18)	
α (°)			88.1240(10)	
β (°)		114.755(5)	75.7180(10)	
γ (°)			77.8340(10)	
V (pm³) · 10⁶	6461(3)	4275(3)	5888.6(7)	30078(2)
Z	2	2	2	6
ρ (g cm⁻³)	1.52	1.42	1.43	1.24
μ (mm⁻¹)	4.068	2.766	3.002	2.796
Crystal size (mm)	$0.27 \times 0.05 \times 0.04$	$0.15 \times 0.14 \times 0.11$	$0.20 \times 0.20 \times 0.20$	$0.47 \times 0.44 \times 0.29$
Θ range (°)	2.39–28.28	1.59–28.31	1.23–25.00	2.62–23.99
Reflections collected/unique	44 166/7977	56 717/10 612	60 690/20 728	139 939/3955
Data/parameters	7977/414	10 612/526	20 728/1412	3955/300
Goodness-of-fit (GOF) on F^2	1.002	1.109	0.735	1.118
R [$I > 2\sigma(I)$]	0.036	0.036	0.044	0.061
wR_2	0.078	0.083	0.083	0.182
Largest difference in peak and hole (e Å⁻³)	0.896/−0.660	0.851/−1.218	0.721/−1.145	1.846/−0.578

and Y(6) show a distorted dodecahedral coordination geometry whereas the other four yttrium centers are better described to have a distorted square antiprismatic coordination. A similar cluster core has been found for $Ti_4Y_2(\mu_3\text{-}O)_4(\mu_2\text{-methacrylate})_{12}(\mu_1\text{-meth-acrylate})_2L_2$ (L = $MeOCH_2CH_2OH$ or methacrylic acid), with octahedrally coordinated titanium and dodecahedrally coordinated yttrium, where the "outer" [TiO_6] octahedra, corresponding to Y(1) and Y(6), are less condensed (because of the lower coordination number of Ti) [19].

The average Y–O bond lengths follow the same trends and range as for the other complexes [Y–$O_{keto,t}$ < Y–$O_{ester,b}$ < Y–$O_{ester,t}$ < Y-(μ-OH) < Y-(μ-O_{keto}), see Table 1]. All μ_3-OH groups have relatively short distances to neighboring carbonyl oxygen atoms, indicating stabilization by hydrogen bond interactions.

Another Y cluster was obtained by slow evaporation of the solvent from a solution of **2** in CDCl₃. Since the clusters **2** and **3** cannot be distinguished by their ¹H or ¹³C chemical shifts, we cannot totally rule out that the sample of **2** used for this experiment did also contain some **3**. Single crystal XRD of the cubic crystals showed that the new cluster had the composition $Y_9O(OH)_9(iprac)_{16}$ (**4**) (Fig. 8).

The structure of **4** has the same Y₉ core as **1**, but the O*i*Pr groups are replaced by additional *i*prac ligands. These *i*prac ligands are bridging chelating, as in **2** and **3**. The ester carbonyl oxygen atoms of the eight μ-*i*prac ligands coordinate to one of the eight outer yttrium atoms each. The yttrium atoms therefore increase their coordination number from seven to eight compared to **1**. This leads to a distorted dodecahedral coordination geometry, whereas the central yttrium atom is nine-coordinate with a capped tetragonal antiprismatic coordination geometry, as in **1**.

Compound **4** is disordered, with respect to the μ_5-O and μ_4-OH groups, with 50% occupancy for both groups. This leads to a higher symmetry for the average structure in the crystalline state (D_{4d}) and indistinguishable Y₅ square pyramids. The average Y(1)–O(2) (μ_5-O/μ_4-OH) distance is 287.1(9) pm and hence shorter than in $[Y_9O_2(OH)_8(etac)_{16}]^-$ [14], but quite similar to the average distance in **1**. The Y–Y distances [367.84(7) pm for Y(1)–Y(2) and 358.47(9) pm for Y(2)–Y(2)] are longer than for **1** [362.1(6) pm and 340(2) pm], most probably caused by the increase of the coordination number of the yttrium atoms from seven to eight. This is in accordance with the similarity to the analogous Y–Y distance of $[Y_9O_2(OH)_8(etac)_{16}]^-$ [356.0(3)–359.2(3) pm] [14]. The Y–O bond

distances of the *i*prac ligands increase in the same order as observed for the other compounds (Table 1).

The μ-*i*prac ligands are strongly twisted with respect to the basal plane, as observed for one type of μ-*i*prac ligands in **2** and the etac ligand in $[Y_9O_2(OH)_8(etac)_{16}]^-$. They show an envelope-like conformation with respect to the chelated yttrium centre, as it is also observed for the terminal *i*prac ligands.

The structure of **4** is stabilized by eight hydrogen bonds between the μ_3-OH groups and the keto carbonyl oxygen atoms of the terminal *i*prac ligands (see Fig. 8), similar to **1**.

3. Conclusions

Four new clusters, viz. $Y_9O(OH)_9(OiPr)_8(iprac)_8$ (**1**), $Y_4(OH)_2(iprac)_{10}$ (**2**), $Y_6(OH)_6(iprac)_{12}$ (**3**), and $Y_9O(OH)_9(iprac)_{16}$ (**4**) were obtained by reaction of $Y_5O(OiPr)_{13}$ ("yttrium iso-propoxide") with the β-ketoester isopropyl acetoacetate, some of them having new structural motifs for yttrium oxo complexes. Compound **1** is one of rare examples of an yttrium alkoxide modified by an organic ligand. While an equimolar amount of *i*prac results in partial substitution of the iso-propoxo groups of the starting metal alkoxide, i.e. in the formation of **1**, all OR groups were substituted with a 3-fold excess of *i*prac-H. The easy substitution of the OR groups by β-ketoesters was previously also observed for aluminum alkoxides, although the products had simpler compositions and structures [20].

Formation of $Y_9O(OH)_9(OiPr)_8(iprac)_8$ (**1**) from $Y_5O(OiPr)_{13}$ cannot be a process with a simple mechanism because oxo/hydroxo groups are formed concomitant with the substitution of the O*i*Pr groups. The same is true for the transformation of **2** to **4** which proceeds easily at room temperature. The *i*prac/Y ratio decreases from 2.5 to 1.78 and correspondingly the proportion of O/OH groups increases until the same composition is reached as in the 1:1 reaction of $Y_5O(OiPr)_{13}$ and *i*prac-H. This indicates that the organic ligand could be involved in the O/OH-forming reaction. The non-hydrolytic formation of oxo derivatives from metal alkoxides is not uncommon for some elements such as Y, Nb, Ta, Mo, W and others [e.g. formation of $Y_5O(OiPr)_{13}$ instead of $Y(OiPr)_3$] [21]. The O or OH groups are often formed by alkene elimination from OR ligands. Such a reaction was recently also observed upon reaction of $Al(OEt)_3$ with diethylmalonate [22]. The possibility that the O

and OH groups are formed by reaction of *i*prac-H with cleaved alcohol, as it often occurs in the reaction of metal alkoxides with carboxylic acids, is less likely [23].

The observations that (i) **2** transforms into **4**, (ii) **2** and **3** were produced in the same reaction, and (iii) a cluster with another composition was isolated in the reaction of another keto ester (aaa-H – see Section 1) shows that several cluster species are similar in energy and can possibly interconvert. The structures of such yttrium oxo/hydroxo/alkoxo clusters must therefore be considered as structural "snapshots" of a complex chemical processes.

4. Experimental

All operations were carried out in moisture- and oxygen-free argon using standard Schlenk or glove box techniques. $Y_5O(OiPr)_{13}$ (Aldrich, 25% in toluene) and isopropyl acetoacetate (Alfa Aesar, 98%) were used as received. Toluene was dried and purified by standard techniques.

4.1. Synthesis of $Y_9O(OH)_9(OiPr)_8(iprac)_8$ (**1**)

An amount of 965 mg of a 25% solution of $Y_5O(OiPr)_{13}$ in toluene was diluted with toluene (2 mL). Isopropyl acetoacetate (0.15 mL, 148 mg, 1.023 mmol) was slowly added at room temperature under stirring. The reaction solution was stirred at 90 °C for 18 h. The volatiles were then removed *in vacuo*, and a white solid was obtained. Compound **1** was obtained as colorless crystals (95 mg, 34%) suitable for single crystal XRD after recrystallization from toluene at room temperature (the yield is based on the first crop of crystals. Because of the high solubility of **1** in toluene the actual yield is higher).

4.2. Synthesis of $Y_4(OH)_2(iprac)_{10}$ (**2**) and $Y_6(OH)_6(iprac)_{12}$ (**3**)

An amount of 960 mg of a 25% solution of $Y_5O(OiPr)_{13}$ in toluene was diluted with toluene (2 mL). Isopropyl acetoacetate (0.43 mL, 423 mg, 2.94 mmol) was slowly added at room temperature under stirring. The reaction solution was stirred 90 °C for 18 h. $Y_4(OH)_2$-$(iprac)_{10}$ (**2**) and $Y_6(OH)_6(iprac)_{12}$ (**3**) were obtained as colorless crystals suitable for single crystal XRD after recrystallization from the reaction solution at room temperature.

Compound **2** was also obtained following an alternative reaction procedure: an amount of 926 mg of a 25% solution of $Y_5O(OiPr)_{13}$ in toluene was diluted with toluene (2 mL). Isopropyl acetoacetate (0.38 mL, 374 mg, 2.59 mmol) was slowly added under stirring. After addition of additional toluene (2 mL), the reaction solution was stirred at room temperature for 6 d, giving a white precipitate. After stirring at 80 °C for additional 18 h, causing dissolution of the precipitate, $Y_4(OH)_2(iprac)_{10}$ (**2**) was obtained (102 mg, 24% based on the first crop of crystals. Because of the high solubility in toluene the actual yield is higher). Colorless crystals suitable for single crystal XRD were obtained from the reaction solution at room temperature.

4.3. Synthesis of $Y_9O(OH)_9(iprac)_{16}$ (**4**)

A solution of 51 mg (0.028 mmol) of **2** in $CDCl_3$ in a tube sealed with a cap and Parafilm® yielded colorless cubic crystals of **4** (32 mg, 80%), suitable for single crystal XRD, upon slow evaporation of the solvent at room temperature over a period of 1 week.

4.4. X-ray structure analyses

Crystals of **1** · 4 toluene, **2**, **3** · 2 toluene, and **4** · $CHCl_3$ were mounted on a Bruker AXS KAPPA diffractometer with an APEX II CCD area detector using graphite-monochromated Mo Kα radiation (λ = 71.073 pm). Crystal-to-detector distance was 55 mm. Data collection at 100 K in a nitrogen stream covered a hemisphere of the reciprocal space by recording three sets of exposures, each of them exhibiting a different Φ angle. Each exposure covered 0.3° in ω (Table 1). The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structures were solved with direct methods (SHELXS97) and refinement to convergence was carried out with the full-matrix least squares method based on F^2 (SHELXL97) with anisotropic structure parameters for all non-hydrogen atoms. The hydrogen atoms bonded to carbon were placed on calculated positions and refined riding on their parent atoms. Selected bond lengths and angles are compared in Table 1. Crystallographic and structural parameters are summarized in Table 2.

The cluster core of **1** was disordered over two positions (70:30), leading to two positions of atoms located on the 4-fold axis (Y2, O2 and O4). Two voids in the unit cell are occupied by toluene molecules. Each void (665 Å^3, 313 electrons) should contain 6 toluene molecules. Only 4 toluene molecules were inserted and refined, however, because of their large U_{ij}'s.

In the crystal structure of **2** one β-ketoesterate-OiPr and in that of **4** two β-ketoesterate-OiPr groups are disordered. In addition, in **4** the proton to the μ_5-O is disordered with 50% occupancy, i.e. the μ_5-O half of the structure and the μ_5-OH half cannot be distinguished crystallographically. In contrast to the previously reported nonanuclear lanthanoid clusters, which crystallized in space group Pn–$3n$ as well, the large solvent accessible voids in the crystal structure of **4** were partially occupied by chloroform molecules.

Acknowledgments

Appendix A

CCDC 804674, 804675, 804676 and 804677 contain the supplementary crystallographic data for compounds **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] O. Poncelet, W.J. Sartain, L.G. Hubert-Pfalzgraf, K. Folting, K.G. Caulton, Inorg. Chem. 28 (1989) 263.
[2] L.G. Hubert-Pfalzgraf, S. Morlens, S. Daniele, A. Thozet, Inorg. Chem. Commun. 7 (2004) 751.
[3] D.C. Bradley, H. Chudzynska, M.B. Hursthouse, M. Motevalli, Polyhedron 10 (1991) 1049.
[4] S. Daniele, L.G. Hubert-Pfalzgraf, P.B. Hitchcock, M.F. Lappert, Inorg. Chem. Commun. 3 (2000) 218.
[5] O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran, R. Astier, J. Chem. Soc., Chem. Commun. (1989) 1846.
[6] U. Schubert, J. Mater. Chem. 15 (2005) 3701.
[7] U. Schubert, Acc. Chem. Res. 40 (2007) 730.
[8] R. Lichtenberger, U. Schubert, J. Mater. Chem. 20 (2010) 9287.
[9] L.G. Hubert-Pfalzgraf, L. Cauro-Gamet, A. Brethon, S. Daniele, P. Richard, Inorg. Chem. Commun. 10 (2007) 143.
[10] A. Gleizes, S. Sans-Lenain, D. Medus, N. Hovnanian, P. Miele, J.D. Foulon, Inorg. Chimica Acta 209 (1993) 47.
[11] O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran, Polyhedron 9 (1990) 1305.
[12] P.B. Hitchcock, Q.-G. Huang, M.F. Lappert, X.-H. Wei, J. Mater. Chem. 14 (2004) 3266.
[13] O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran, Inorg. Chem. 29 (1990) 2883.
[14] L.G. Hubert-Pfalzgraf, N. Miele-Pajot, R. Papiernik, J. Vaissermann, J. Chem. Soc., Dalton Trans. (1999) 4127.
[15] G. Xu, Z.-M. Wang, Z. He, Z. Lue, C.-S. Liao, C.-H. Yan, Inorg. Chem. 41 (2002) 6802.
[16] E.H. Barash, P.S. Coan, E.B. Lobkovsky, W.E. Streib, K.G. Caulton, Inorg. Chem. 32 (1993) 497.

[17] G. Kickelbick, U. Schubert, Chem. Ber. 130 (1997) 473.
[18] G. Trimmel, S. Gross, G. Kickelbick, U. Schubert, Appl. Organomet. Chem. 15 (2001) 401.
[19] M. Jupa, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. (2004) 1835.
[20] R. Lichtenberger, M. Puchberger, S.O. Baumann, U. Schubert, J. Sol-Gel Sci. Technol. 50 (2009) 130.

[21] D.C. Bradley, R.C. Mehrotra, I.P. Rothwell, A. Singh, Alkoxo and Aryloxo Derivatives of Metals, Academic Press, San Diego, 2001 (Chapter 5.2.2).
[22] R. Lichtenberger, S.O. Baumann, M. Bendova, M. Puchberger, U. Schubert, Monatsh. Chem. 141 (2010) 717.
[23] e.g. U. Schubert, Chem. Mater. 13 (2001) 3487.