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The Solid-state Structures of a Non-hydrated Yttrium Carboxylate and a Yttrium Carboxylate Hemihydrate Obtained by Reaction of Yttrium Alkoxides with Carboxylic Acids

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Summary. The yttrium carboxylates Y(methacrylate)$_3$ and Y(acetate)$_3 \cdot 0.5$ H_2O were prepared by reaction of $Y(OCH_2CH_2OMe)_3$ with methacrylic or acetic acid and characterized by X-ray structure analyses. Both carboxylates have chain structures with both bridging and chelating-bridging carboxylate ligands. In Y(acetate)$_3 \cdot 0.5$ H_2O, every second yttrium atom is nine-coordinate due to the additional coordination of a water molecule.

Keywords. Yttrium; X-ray structure determination; Carboxylate ligands; Chain structures; Methacrylates.

Introduction

Yttrium carboxylate are known to form aqua or ammine adducts easily, but only few derivatives were structurally characterized. The dihydrate $Y[OOC\text{-}3,5\text{-}C_6H_3(NH_2)_2]_3 \cdot 2H_2O$ is polymeric with two bridging and one chelating carboxylate ligands per yttrium atom, and with a large Y–Y distance (~500 pm). Eight-coordination is reached by coordination of two water molecules [1]. In contrast, the derivatives $Y(OOCR)_3 \cdot 2H_2O$ ($R = CH_3$ [2], C_5H_{11} [3]) are centrosymmetric dimers with nine-coordinate yttrium atoms, which are connected by two chelating-bridging (μ,η^2) carboxylates. The coordinating shell of each metal atom is complemented by four oxygen atoms from two chelating carboxylate ligands and two oxygen atoms from coordinated water molecules. The trihydrate $Y(OOC\text{-}3\text{-}C_6H_4NH_2)_3 \cdot 3H_2O$ is a monomeric compound with three chelating carboxylate

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ligands and three water molecules completing the nine-coordination of the yttrium atom [4].

In this paper, we report the first solid-state structure of a non-hydrated yttrium carboxylate, Y(methacrylate)$_3$, and a hemihydrate, Y(acetate)$_3 \cdot 0.5\ H_2O$. This allows developing a clear picture on how the structures of yttrium carboxylates develop when the degree of hydration is increased.

Results

When metal alkoxides are treated with carboxylic acids, carboxylate-substituted metal oxide clusters are frequently obtained [5]. The oxo groups originate from water which is generated *in situ* by ester formation between the employed acid and the alcohol liberated upon substitution of the alkoxide groups. The slow formation of water results in a controlled hydrolysis and condensation of carboxylate-substituted metal alkoxides. Several mono-, bi-, and trimetallic oxo clusters, mainly of the early transition metals, have been obtained by this route, among them the bimetallic yttrium/titanium clusters $Ti_4Y_2O_4(OMc)_{14}L_2$ ($OMc =$ methacrylate; $L = Me$OCH$_2$CH$_2$OH or *Mc*OH) and $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2O\text{-}Me)_2(McOH)_2$ [6].

In an attempt to prepare monometallic, carboxylate-substituted oxo yttrium clusters, we reacted a CH_2Cl_2 solution of $Y(OCH_2CH_2OMe)_3$ (15–18% solution in 2-methoxyethanol) with a 3-fold excess of methacrylic or acetic acid. However, we obtained the carboxylates $Y(OMc)_3$ (1) and $Y(OAc)_3 \cdot 0.5\ H_2O$ (**2**, $OAc =$ acetate) rather than oxo clusters. The same products were obtained with one or ten molar equivalents of the acids under the same conditions. The composition of **2** shows that although ester was formed in the reaction of the yttrium alkoxide, the produced water was not consumed by hydrolysis reactions.

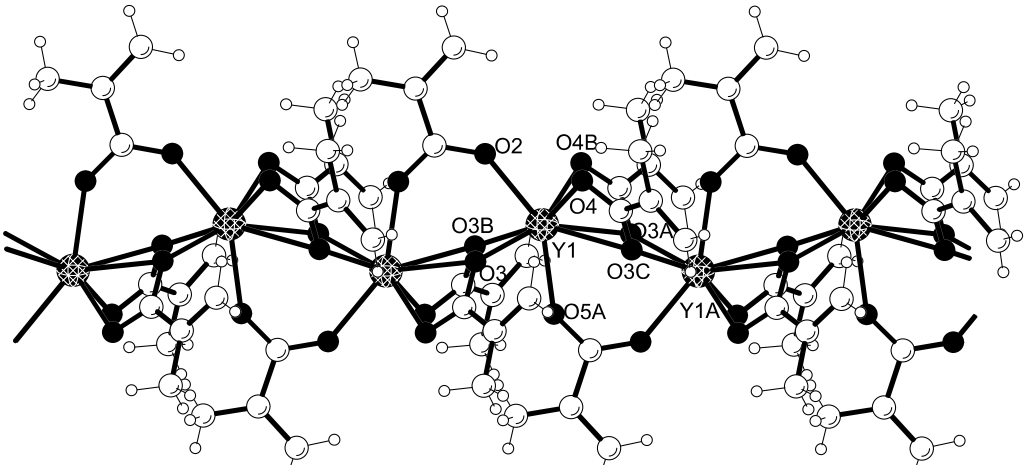

Fig. 1. The chain structure of Y(O*Mc*) (**1**); Y(1)-O(2) 226.0(4), Y(1)-O(3) 231.4(4), Y(1)-O(3A) 267.0(6), Y(1)-O(4) 231.6(4), Y(1)-O(5A) 225.8(4), Y(1)···Y(1A) 401.41(5) pm (the atoms labeled with the letter A are symmetry related to the unlabeled atoms by −x, −y, z−1/2)

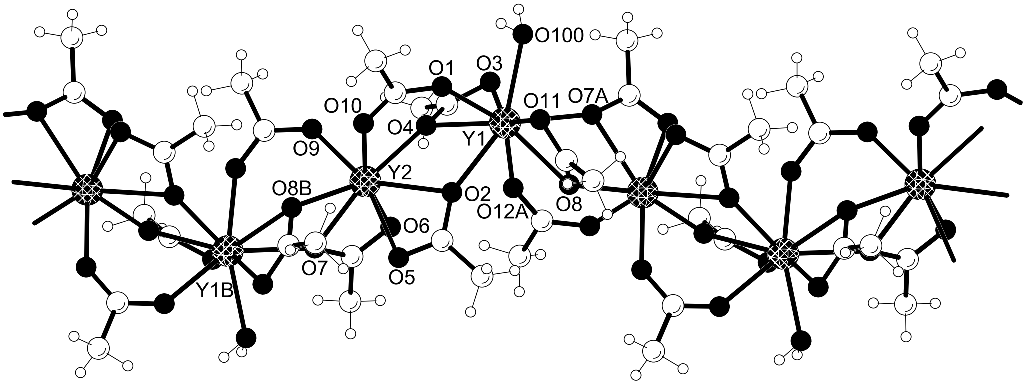

Fig. 2. The chain structure of $Y(OAc)_3 \cdot 0.5\ H_2O$ (**2**); Y(1)-O(1) 233.8(4), Y(1)-O(2) 237.9(4), Y(1)-O(3) 246.7(4), Y(1)-O(4) 243.8(4), Y(1)-O(7A) 237.4(4), Y(1)-O(8) 255.0(5), Y(1)-O(11) 242.6(4), Y(1)-O(12A) 232.1(4), Y(1)-O(100) 235.5(4), Y(2)-O(2) 254.6(5), Y(2)-O(4) 229.2(4), Y(2)-O(5) 237.6(5), Y(2)-O(6) 238.8(4), Y(2)-O(7) 246.5(4), Y(2)-O(8B) 234.7(4), Y(2)-O(9) 224.7(4), Y(2)-O(10) 225.5(4), Y(1)···Y(2) 394.97(8), Y(2)···Y(1B) 399.32(8) pm (the atoms labeled with the letter A are symmetry related to the unlabeled atoms by $x+1/2$, $-y+1/2$, $z+1/2$, those labeled with the letter B by $x-1/2$, $-y+1/2$, $z-1/2$)

The carboxylates **1** and **2** precipitated from solution and dissolved neither in the parent alcohol nor in toluene, dichloromethane, or chloroform. On the other hand, this allowed us to determine for the first time the solid-state structure of a hydrate-free yttrium(III) carboxylate.

Although both **1** and **2** have polymeric chain structures (Figs. 1 and 2) with a similar coordination of the yttrium atoms, the geometry of the chains is different. In both structures, one carboxylate ligand is bridging and two are chelating-bridging (μ,η^2). Each yttrium atom is thus coordinated by eight oxygen atoms of the carboxylate ligands: two of the chelating units, two of the additional μ-O, and two from the bridging ligands.

All yttrium atoms in **1** are equivalent by space group symmetry. The four μ-O bridges [Y(1)-O(3)] of the μ,η^2-methacrylate ligands are very asymmetric, with two short [231.4(4) pm] and two long Y-O distances [267.0(6) pm], the latter being part of the chelating unit. The carboxylate ligands are thus intermediate between bridging and chelating-bridging, and the coordination number of Y is better described as $[6+2]$. The shortest Y-O distances are those of the bridging carboxylates [Y(1)-O(2) 226.0(4) and Y(1)-O(5) 225.8(4) pm], which are opposite to each other [O(2)-Y(1)-O(5) 148.9(2)°]. The geometrical arrangement of the ligands around the metal atom results in a Y–Y–Y angle of 146.14(2)°, *i.e.* the polymeric structure of **1** is a zigzag chain.

The repeating unit in **2** is a dimer of the composition $Y_2(OAc)_6(H_2O)$ in which the two yttrium atoms Y(1) and Y(2) have a different coordination environment. First, Y(1) is eight-coordinated, while the coordination number of Y(2) is increased to nine by coordination of a water molecule. Second, the arrangement of the ligands is different. For example, the angle O(1)-Y(1)-O(12) is 138.9(1)° which is similar to the corresponding angle in **1**, whereas the angle O(9)-Y(2)-O(10) is 88.6(2)°. This means that the bridging carboxylates are "*trans*" at Y(1) and "*cis*" at Y(2). As a result of the different yttrium coordination, the chain structure of **2** is different to that of **1** (Fig. 2). In **2**, three coordination polyhedra form a linear segment [Y(1)-Y(2)-Y(1A) 175.41(2)°], and the chain is then bent at Y(1) [Y(2)-Y(1)-Y(2A) 129.05(1)°].

The asymmetry of the μ-O bridges in **2** is less pronounced as in **1**, the shorter Y-O distances being in the range 229.2–237.6 pm, and the longer in the range 243.8–255.0 pm. Water coordination to Y(1) results in a slight asymmetry of the bridging acetate ligands, with shorter Y(2)-O distances [compare Y(1)-O(1) 233.8 pm and Y(1)-O(12) 232.1 pm with Y(2)-O(9) 224.7 pm and Y(2)-O(10) 225.5 pm]. The same is true for the average Y-$O_{chelating}$ distances [Y(1)-O 247.0, Y(2)-O 244.4 pm].

Each hydrogen atom of the coordinated water molecule [O(100)] undergoes a hydrogen bridge to a non-bridging oxygen atom of a μ,η^2-coordinated acetate ligand of neighboring chains [O(100)$\cdots$O(3) 273.8(5), O(100)$\cdots$O(11) 275.7(5) pm].

Discussion

Y(O*Mc*)$_3$ (**1**) is the first structurally characterized non-solvated yttrium carboxylate; the structure of this compound may therefore serve as a starting point for the discussion on how the structures change with an increasing degree of hydration. Compound **1** forms a chain structure, where one methacrylate ligand in **1** is clearly bridging, while the other two are in between bridging and chelating-bridging. The coordination number of the yttrium atoms in **1** is therefore best described as [6 + 2]. The structure of the hemihydrate Y(O*Ac*)$_3 \cdot 0.5\ H_2O$ (**2**) is relatively similar (with two clearly chelating-bridging ligands), apart from a somewhat different conformation of the chain. The water molecule is accommodated by increasing the coordination number of every second yttrium atom from eight to nine.

Some of the structural features are retained in the dihydrates $Y(OOCR)_3 \cdot 2H_2O$ ($R = 3,5\text{-}C_6H_3(NH_2)_2$ [1], CH_3 [2], C_5H_{11} [3]). To vacate coordination sites at the metal atoms for the coordination of the water molecules, part of the chelating-bridging groups is converted in chelating ligands and the number of bridging entities is reduced. The main difference between polymeric $Y[OOC\text{-}3,5\text{-}C_6H_3(NH_2)_2]_3 \cdot 2H_2O$ and dimeric $Y(OOCR)_3 \cdot 2H_2O$ ($R = CH_3$, C_5H_{11}) is that one chelating ligand in the latter compounds is converted to a bridging ligand in the former compound, resulting in a chain structure. There is some flexibility with regard to the coordination number: the possibility of nine-coordination in $Y(OOCR)_3 \cdot 2H_2O$ ($R = CH_3$, C_5H_{11}) allows one carboxylate ligand to retain the chelating-bridging coordination. The trihydrate $Y(OOC\text{-}3\text{-}C_6H_4NH_2)_3 \cdot 3H_2O$ is the end-point of the structural evolution from a chain structure to a monomeric compound, in which all the carboxylate ligands are chelating.

Experimental

All experiments were performed in an inert-gas atmosphere (Ar). All solvents were dried by standard methods before use.

Y(OMc)₃ (**1**)

An amount of 1.22 g (14.2 mmol) methacrylic acid was added dropwise at room temperature to a solution of 1.46 g $Y(OCH_2CH_2OMe)_3$ (11% in methoxyethanol solution, 4.65 mmol) in 10 cm^3 CH_2Cl_2 under stirring in a *Schlenk* tube. After 7 d at room temperature colorless crystals were formed, which were separated and dried *in vacuo*. Yield 0.65 g (53%); IR: $\bar{\nu} = 2965$(w), 1525(s), 1457(s), 1420(s), 1244(s), 944(m), 837(m), 607(m) cm^{-1}.

Y(OAc)₃ (**2**)

An amount of 0.86 g (14.3 mmol) acetic acid was added dropwise at room temperature to a solution of 1.61 g $Y(OCH_2CH_2OMe)_3$ (11% in methoxyethanol solution, 5.2 mmol) in 10 cm^3 CH_2Cl_2 under stirring in a *Schlenk* tube. After 4 d at room temperature colorless crystals were formed, which were separated and dried *in vacuo*. Yield 0.86 g (56%); IR: $\bar{\nu} = 2928$(w), 1612(s), 1580(s), 1537(s), 1415(s), 1341(s), 1020(m), 949(m), 673(m) cm^{-1}.

*X-Ray Structure Analyses of **1** and **2***

Data collection (Table 1): The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a nitrogen stream. Mo-K_α radiation ($\lambda = 71.069$ pm, graphite monochromator) was used for all measurements. The data collection (**1**: 173 K, **2**: 173 K) covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The crystal-to-detector distance was 5 cm. The data were corrected for polarization and *Lorentz* effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections.

The structure was solved by direct methods (SHELXS97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all

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

	$Y(OMc)_3$ (**1**)	$Y(OAc)_3 \cdot 0.5\ H_2O$ (**2**)
Empirical formula	$C_{12}H_{15}O_6Y$	$C_{12}H_{18}O_{12}Y_2 \cdot H_2O$
Formula weight	344.15	550.1
Crystal system	orthorhombic	monoclinic
Space group	*Cmc*2₁	*Cc*
Unit cell dimensions		
a/pm	1453.61(2)	1584.4 (1)
b/pm	1280.33(1)	1646.4(1)
c/pm	768.02(9)	832.42(6)
β/°		115.831(1)
Volume/pm^3	$1429.4(3) \cdot 10^6$	$1954.4(2) \cdot 10^6$
Z	4	4
Calcd. density/g/cm^3	1.599	1.870
Absorption coefficient μ/mm^{-1}	4.098	5.971
Crystal size/mm^3	0.20 × 0.20 × 0.20	0.20 × 0.18 × 0.15
2θ range/°	2.12–25.00	2.47–25.00
Reflections coll./unique	3748/1161	8727/3336
Data/restraints/parameters	1161/1/97	3336/2/246
GOF on F^2	1.055	1.064
R [I > 2σ(I)]	0.0289	0.0330
wR2	0.0727	0.0788
Largest diff. peak and hole/e · $Å^{-3}$	0.718/−0.416	0.420/−0.259

non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge C82 1EZ, UK [fax int. code +(1223) 336-033, e-mail: teched@ccdc.cam.ac.uk] quoting the depository numbers CCDC 281601 (**1**) and 281602 (**2**).

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