Inorg. Chem. **2005**, *44*, 9192–9196

Inorganic Chemistry

Article

New Synthetic Approach to Yttrium Hydroxoacetates, Structural Characterization, and Use as a Precursor for Coated Conductors

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Received April 6, 2005

A novel synthetic approach is given for the preparation of a metal–organic lanthanide sol–gel precursor solution and its application for the production of coated conductors. Besides all other problems concerning the technical process itself, the key to a successful deposition of oxide layers is the choice of the precursor solution and the understanding of the mechanism of deposition. Moreover, the isolation and characterization of the species involved in the reaction is very important. Regarding the complex process occurring during the formation of the surface layer, it is obvious that the best choice should have a compound already containing the final composition of the layer. Two compounds of composition $[Y(OAc)_3(H_2O)_2]_2$ (**1**) and $[Y(OAc)_3]_2(H_2O)$ (**2**) were isolated from their precursor solution and characterized by X-ray structural analysis. A short outlook will give an insight into the possible bonding mechanisms of the surface layer. These experiments were made with the mixed metal–oxide system yttrium-stabilized zirconium oxide, which is widely used as a substrate for superconducting oxides. A study of the structure of hydrated yttrium acetates, by single-crystal X-ray diffraction, infrared spectra, and elemental analysis demonstrates that there are two separate structures for hydrated yttrium acetates, which play a role as an intermediate in the building of ceramic oxide layers for coated conductors.

Introduction

Lanthanide oxides and yttrium oxides are of great interest for a wide range of high-technology materials such as superconductors, yttrium iron garnets in microwave filters, etc.[1] Chemical routes to these materials using a well-defined molecular precursor should allow better control of their properties and larger flexibility of the products (ceramics, coatings, etc.) in comparison with the solid-state synthesis.[2] The structural chemistry of acetate hydrates of three-valent lanthanides $M(OAc)_3(H_2O)_x$ (with $x = 1$, 1.5, 3, and 4) is well-known.[3] They are easily accessible in crystalline form from their aqueous acetic acid solutions. Their crystal structures are built from acetate-linked building blocks as dimers ($x = 3$ and 4), chains ($x = 1$), or dimers and chains ($x = 1.5$). In general, the latter compounds contain water between the chains and dimers. The hydrated and anhydrous lanthanide acetates have several coordination modes because of their lanthanide ion may achieve coordination numbers between 6 and 10 and their acetate ion may be either a mono-, bi-, or polydentate ligand.[4,5] It is well-known that the ionic radius decreases in the series of lanthanide ions and therefore the coordination changes for both the lanthanide ion and the acetate ligand, resulting in a decrease of the coordination sphere.[6] The reaction of $Y(MeCOCHCOMe)_3 \cdot 1.5H_2O$ in an acetic acid solution with the addition of 2-propanol at room temperature resulted in reproducible yields of $[Y(OAc)_3(H_2O)_2]_2$ (**1**) and $[Y(OAc)_3]_2(H_2O)$ (**2**),

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10.1021/ic0505192 CCC: $30.25

respectively characterized by single-crystal X-ray diffraction and elemental analysis.

Experimental Section

General Procedures. All synthetic manipulations were conducted in a dry, anaerobic environment provided by a Schlenk-line or an argon-filled glovebox. Solvents for the synthesis were of reagent grade or better and were dried according to standard methods. The starting material $Y(MeCOCHCOMe)_3 \cdot 1.5H_2O$ (Strem) was used as received.

Preparation of $[Y(OAc)_3(H_2O)_2]_2$ (1). A total of 0.41 g (1 mmol) $Y(MeCOCHCOMe)_3 \cdot 1.5H_2O$ was dissolved in 5 mL of acetic-acid (100%) and 2-propanol (70:30, v/v) and stirred at room temperature for 5 min. After filtration over Celite, the resulting solution was kept at a constant temperature of 20 °C for 36 h, leading to crystallization of 0.42 g of $[Y(OAc)_3(H_2O)_2]_2$ (**1**) as a light-yellow solid, which decomposes between 240 and 242 °C. Because **1** was not soluble in coordinating and noncoordinating solvents, NMR data are not available. IR (KBr): ν 3400 (sst), 2437 (st), 1698 (st), 1558 (sst), 1417 (sst), 1355 (st), 1025 (m), 945 (m), 738 (st), 683 (st), 607 (st), 469 (m) cm^{-1}. MS (EI, m/z (%)): 617 [M − OAc] (18), 588 [M − OAc − CO] (100), 85. Anal. Calcd for $C_6H_{13}O_8Y$: C, 23.86; H, 4.34; Y, 29.4. Found: C, 24.14; H, 4.28; Y, 28.5.

Preparation of $[Y(OAc)_3]_2(H_2O)$ (2). The filtrate from the synthesis of **1** was kept at a constant temperature of 20 °C for a period of 3 weeks for crystallization. We obtained 0.11 g of $[Y(OAc)_3]_2(H_2O)$ (**2**) as yellowish crystals, which decompose between 280 and 285 °C. IR (KBr): ν 3441 (sst), 2955 (st), 1550 (sst), 1410 (st), 1353 (st), 1023 (m), 947 (m), 757 (m), 648 (m), 432 (st) cm^{-1}. MS (EI, m/z (%)): 617 [M − OAc] (18), 588 [M − OAc − CO] (100). Anal. Calcd for $C_{12}H_{20}O_{13}Y_2$ (**2**): C, 26.20; H, 3.66; Y, 32.0. Found: C, 25.61; H, 3.52; Y, 31.3.

X-ray Diffraction Studies. X-ray diffraction experiments were performed on single crystals grown as mentioned above. Crystals were removed from the supernatant and transferred onto a microscope slide coated with paraffin oil. Selected crystals were affixed to a glass fiber in wax and oil and frozen in a cooled nitrogen stream. Data collection was performed using Mo Kα ($\lambda = 0.710\ 73$ Å) radiation by a STOE AED 2 four-circle goniometer. The data were processed and refined by using the full-matrix least-squares method on F^2 by solving the structures with the programs SHELXS-97 and SHELXL-97.[7,8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystal data and structure refinements of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

Growth of Epitaxial Layers on Single-Crystal Substrates. The solution from which the single crystals of **1** and **2** were grown was originally developed as a stable liquid precursor for the growth of yttrium-stabilized zirconia (YSZ) on different substrates made from mixtures between Y- and Z-containing precursor solutions. Spin coating at 5000 rpm was employed to deposit the precursor film on YSZ(001) single crystals. Heat treatment was done in Ar/H_2 (5%) or air at 780−1300 °C for 2−4 h. A ramp rate of 1−10 K/min was used. The deposited films were measured by Rutherford backscattering, energy-dispersive X-ray (EDX) analysis, and atomic force microscopy (AFM).[9]

Table 1. Crystallographic Data and Structure Refinement for Compounds **1** and **2**

	$\mathbf{1}\cdot 4H_2O$	**2**
formula	$C_{12}H_{34}O_{20}Y_2$	$C_{12}H_{20}O_{13}Y_2$
fw	676.21	550.10
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	*Cc*
temp, K	200(2)	293(2)
λ, Å	0.71073	0.71073
a, Å	8.812(2)	15.857(3)
b, Å	9.177(2)	16.469(3)
c, Å	10.346(1)	8.357(2)
α, deg	91.86(3)	90
β, deg	113.97(3)	115.24(3)
γ, deg	117.91(3)	90
V, $Å^3$	649.4(2)	1962.4(7)
Z	1	4
ρ_{calcd}, g/cm^3	1.729	1.862
μ, mm^{-1}	4.528	5.946
cryst size, mm^3	0.60 × 0.60 × 0.50	0.40 × 0.30 × 0.40
no. of reflns collcd	7564	6707
no. of indep reflns (R_{int})	3617 (0.1139)	3436 (0.0967)
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0542, 0.1384	0.0832, 0.2119
R1,[a] wR2[b] (all data)	0.0646, 0.1454	0.0852, 0.2156

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] from X-ray Analysis of $\mathbf{1}\cdot 4H_2O$

Y(1)−O(1)	2.312(3)	O(11)−C(11)	1.262(5)
Y(1)−O(2)	2.320(3)	C(11)−O(12)	1.247(5)
Y(1)−O(11)#1	2.335(3)	C(11)−C(12)	1.484(5)
Y(1)−O(31)	2.373(3)	O(21)−C(21)	1.259(5)
Y(1)−O(21)	2.405(3)	C(21)−O(22)	1.262(5)
Y(1)−O(12)	2.419(3)	C(21)−C(22)	1.492(6)
Y(1)−O(22)	2.439(3)	O(31)−C(31)	1.263(5)
Y(1)−O(32)	2.444(3)	C(31)−O(32)	1.254(5)
Y(1)−O(11)	2.541(3)	C(31)−C(32)	1.499(6)
O(1)−Y(1)−O(2)	75.97(11)	O(31)−Y(1)−O(21)	78.16(10)
O(1)−Y(1)−O(31)	97.53(12)	O(1)−Y(1)−O(21)	148.37(11)
O(2)−Y(1)−O(31)	130.76(11)		

Table 3. Selected Bond Lengths [Å] and Angles [deg] from X-ray Structural Analysis of **2**

Y(1)−O(31)	2.326(8)	Y(2)−O(32)#2	2.233(8)
Y(1)−O(61)	2.347(8)	Y(2)−O(62)	2.269(8)
Y(1)−O(1)	2.348(7)	Y(2)−O(22)#2	2.302(8)
Y(1)−O(41)	2.375(8)	Y(2)−O(51)	2.331(8)
Y(1)−O(71)	2.376(8)	Y(2)−O(42)#2	2.364(9)
Y(1)−O(52)	2.405(8)	Y(2)−O(72)	2.417(9)
Y(1)−O(22)	2.462(8)	Y(2)−O(71)	2.480(8)
Y(1)−O(21)	2.492(8)	Y(2)−O(41)#2	2.537(8)
Y(1)−O(51)	2.539(9)		
O(32)−Y(2)#1	223.3(8)	O(22)−Y(2)#1	230.2(8)
O(41)−Y(2)#1	253.7(8)		
O(42)−Y(2)#1	236.4(9)		

Results and Discussion

The commercially available $Y(MeCOCHCOMe)_3$ has to be dissolved in a suitable solvent for spin coating. However, all solvents so far used result in solutions that are not stable for a day.[2,10] A requirement for spin coating is a solution that is stable for a long period of time. It is possible to circumvent this problem by dissolving $Y(MeCOCHCOMe)_3$ in acetic acid and 2-propanol.[11] The concentration of the yttrium salt could be up to 0.25 mol. When the first

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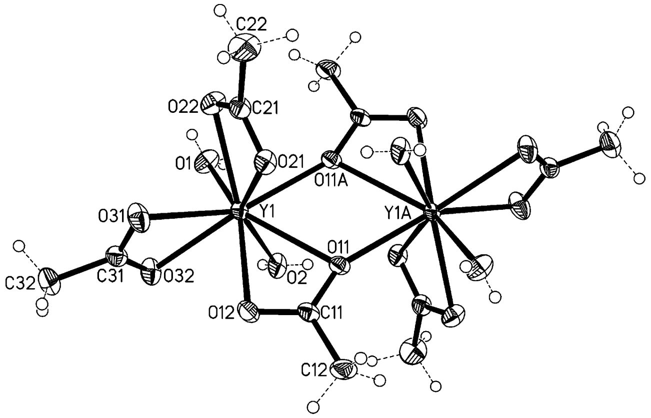

Figure 1. ORTEP view of **1**·4H_2O showing the numbering of atoms. The hydrogen atoms are omitted for a clearer view.

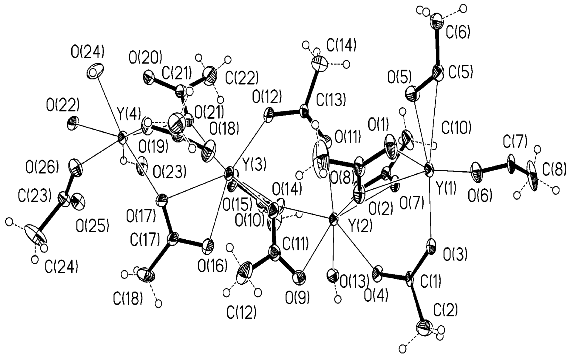

Figure 2. ORTEP view of of **2** showing the numbering of atoms. The hydrogen atoms are omitted for a clearer view.

precipitates are filtered off after approximately 36 h, a solution, stable for at least 2 weeks, is obtained. Obviously, the addition of 2-propanol leads to a kinetic stabilization of the solution. Alcohols with high molecular weight are not suitable for this purpose because of their low volatility and deposition within the Y_2O_3 layers. Moreover, during the heating process, this results in crack formation and porous surfaces. We isolated from this solution two compounds **1** and **2** that give an indication of the composition of the layer after spin coating. Obviously, the MeCOCHCOMe ligand has been displaced by acetate and water molecules. However, caution should be exercised when comparing structures in solution to the solid-state structures. The two isolated yttrium compounds (**1** and **2**) that differ only by the amount of water show significant differences in their structures. During the crystallization of **1**, the amount of water within the solution decreases. This is demonstrated by the composition of compound **2**, which contains less water in comparison to **1**.

The structures are shown in Figures 1 and 2, and selected structural parameters are listed in Tables 2 and 3. In Figure 3 is given the packing diagram of **2** in the single crystal as a result of intra- and intermolecular hydrogen bonding. **1**·4H_2O crystallizes in space group $P\bar{1}$, with one formula per unit cell. A four-membered ring, containing two yttrium atoms in 9-fold coordination symmetry and two bridging acetate groups, is the basis of this molecule. The coordination sphere of each yttrium atom is completed by two oxygen atoms undergoing a chelate formation. This bonding mode is the reason for the differences in the Y−O bond lengths, which range from 2.312 to 2.541 Å. As clearly seen from Figure 1, the coordination sphere is completed by two acetate groups and two water molecules. Four additional water molecules are present in the crystal lattice.

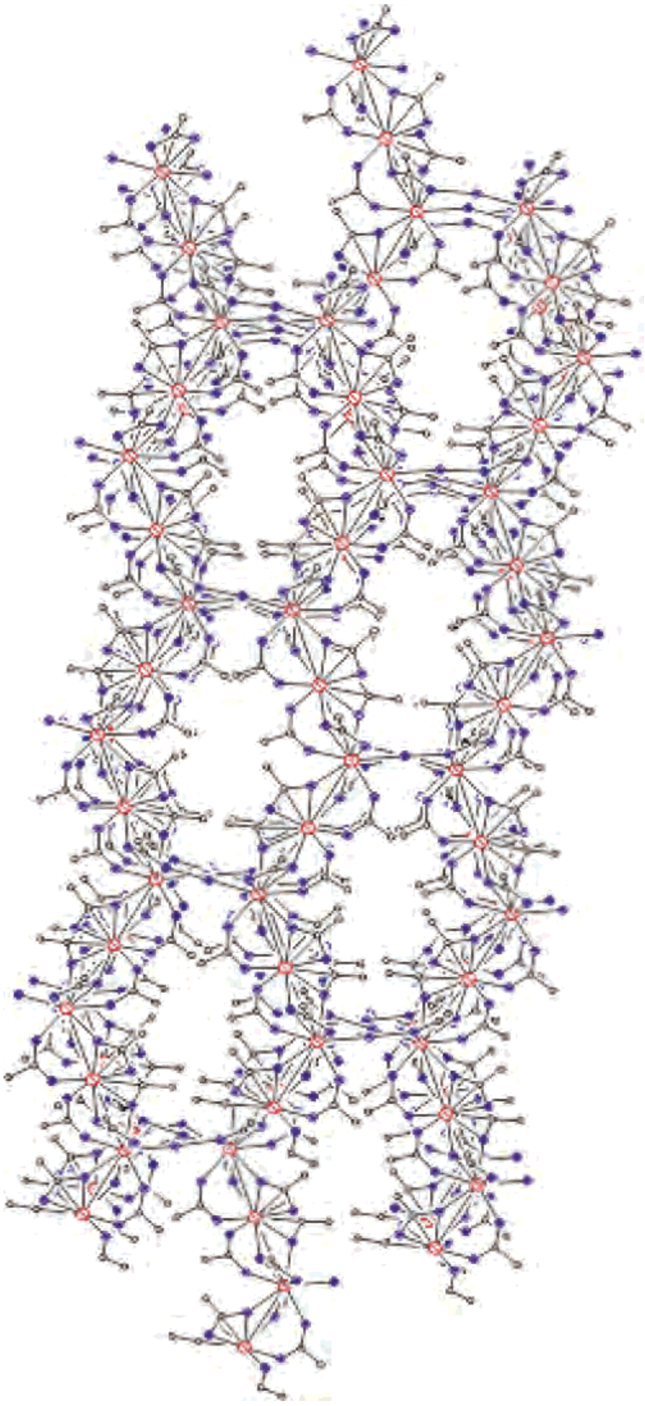

Figure 3. Packing of **2** showing the intra- and intermolecular hydrogen bonding. Red: yttrium atoms. Blue: oxygen atoms. Black: carbon atoms.

A completely different situation is seen for compound **2**. This molecule crystallizes in space group *Cc* with four separate formulas per unit cell. In contrast to **1**, the central unit consists of polymeric chains, where each of them

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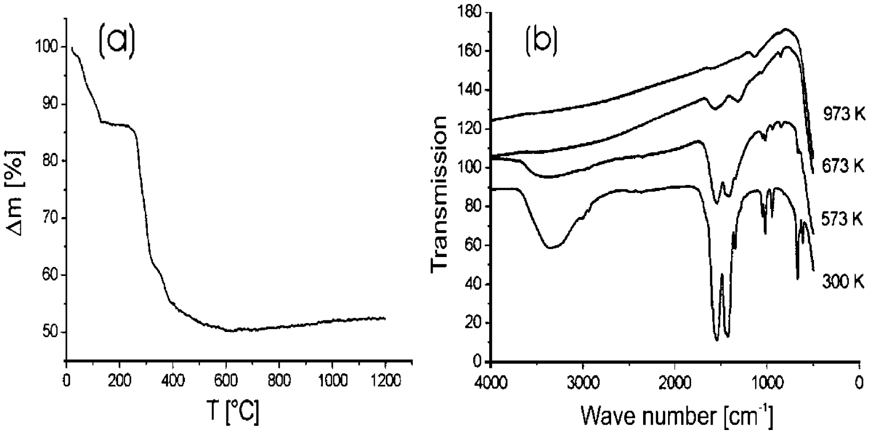
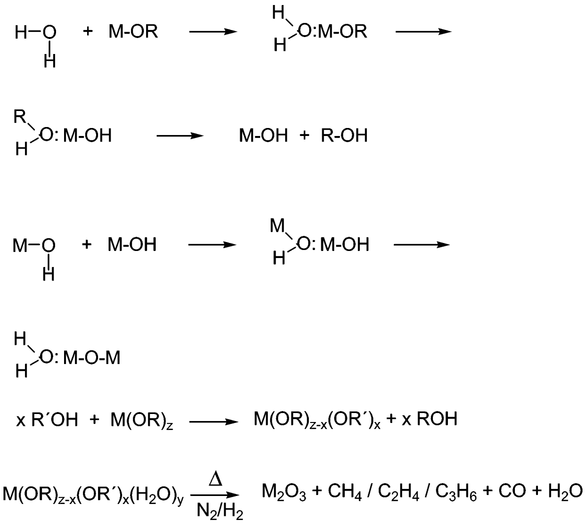


Figure 4. (a) Weight loss of the precursor during heating in flowing N_2. (b) IR spectra of samples annealed at different temperatures.

contains subunits comprised of two yttrium atoms. One water molecule is coordinated to two yttrium atoms, with Y−O bond lengths in the range from 2.233 to 2.539 Å. As is already known from water-free lanthanide acetates, $M(OAc)_3$, the cations are connected through different acetate bridging modes.[12] The coordination sphere of every other yttrium atom in **2** is completed by one additional water molecule, resulting in 9- and 8-fold symmetry at the yttrium centers.

After spin coating, the samples showed a slightly inhomogeneous thickness distribution. At the corners of the substrate and along the edges, areas of increased thickness are observed. After pyrolysis, the final thickness of the film in the center of the sample was approximately 50 nm, as measured by Rutherford backscattering. EDX measurements showed that within experimental error the composition of the layer was the same as that in the precursor solution. To define heat-treatment parameters, the decomposition behavior of the precursor was investigated by thermogravimetry and IR spectroscopy (Figure 4). The thermal decompositions of **1** and **2** should be very similar because of the small difference in the water content. According to the weight loss and the mass spectra, the decompositions of **1** and **2** proceed according to Scheme 1. At lower temperatures (until 100 °C), a weight loss of 10% was observed. This might be due to absorbed solvent (2-propanol, acetic acid, free water, and acetyl acetone). Higher temperatures (up to 200 °C) complete the elimination of volatile molecules from the layer. Between 150 and 230 °C, no loss in weight was observed. This is in agreement with the observation by IR spectroscopy. At room temperature, the O−H vibrations between 3050 and 2800 cm^{-1}, the C=O vibrations between 1500 and 1600 cm^{-1}, and the C−O stretching modes (1030−1080 cm^{-1}) indicate the presence of acetic acid, acetyl acetone, and 2-propanol, respectively. Above 230 °C, up to 400 °C a weight loss of 30% took place. Consequently, above 300 °C, the vibrations for the OH groups of water and 2-propanol had disappeared. The vibrations indicate only the presence of CO and CH groups, which could be acetate in the layer. Finally, a weight loss of 5% took place between 400 and 600 °C. The last acetate groups decomposed under methane formation. Above 600 °C, there are no vibrations from organic ligands observable in the final layer. The essential advantage of our preparative approach was, in fact, that depending on the time two different lanthanide compounds can be obtained. The amount of water of crystallization in **1** and **2** depends on the time of crystallization. Compounds **1** and **2** are the first model systems that give an indication of the formation of the layers after spin coating. The identical ligands in **1** and **2** obviously allow a single route of decomposition, which is thermodynamically controlled through the formation of the stable products Y_2O_3, H_2O, and CO_2. The deposition process under an inert gas atmosphere results, therefore, in a stepwise decomposition, yielding finally Y_2O_3 (beginning at 590 °C), which is the substrate deposited on the surface of the ZrO_2 support.

Scheme 1. Proposed Decomposition Pathway for the Formation of Metal Oxide



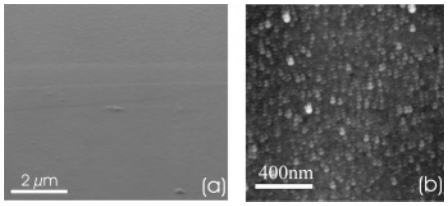


Figure 5. (a) Reflection electron microscopy image and (b) AFM image of the YSZ surface layer made above 1100 °C from **1** and **2** in a mixture with zirconium pentadionate deposited on a YSZ(001) single crystal. The roughness is under 2.4 nm.

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In summary, we have shown the preparation of an organoyttrium sol−gel precursor and its utility in the production of coated conductors over the ZrO_2 support. The method reported here produces a high-quality surface layer of YSZ, and also after heat treatment, the layers were smooth and continuous (Figure 5), with some inhomogeneities in the size of some 100 nm, seen by AFM investigations. These two new intermediates have been structurally characterized, which offers the possibility of exploring the bonding situation of the surface layers of YSZ.

Acknowledgment. We thank the European Community for the support by the Framework V Growth Program under Contract No. G5RD-CT2001-00550 SOLSULEIT.

Supporting Information Available: X-ray crystal structure solutions of **1**·$4H_2O$ and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0505192