Designed Synthesis and Molecular Structure of the First Heterotermetallic Alkoxide

Michael Veith,* Sanjay Mathur, and Volker Huch

Institut für Anorganische Chemie
Universität des Saarlandes
Postfach 151150, D-66041 Saarbrücken, Germany

Received September 25, 1995

The potential application of heterometallic alkoxy derivatives as versatile precursors for oxide-based ceramics, used for obtaining high-tech inorganic materials, has brought about an unprecedented search in the synthetic strategies being designed for the rational construction of mixed-metal alkoxides.[1] Although mixtures of alkoxides and heterobimetallic alkoxides have been used extensively as attractive precursors to multicomponent oxide materials,[2] no attempt has been made to employ a heterotermetallic alkoxide in ceramics processing technology, mainly due to (i) the limited choice of alkoxometalate units (classical alkoxometalates are limited to $M(OR)_3^-$ (M = Ge, Sn, Pb), $M(OR)_4^-$ (M = Al, Ga), $M(OR)_5^-$ (M = Sn, Pb), $M(OR)_6^-$ (M = Nb, Ta), and $M_2(OPr^i)_9^-$ (M = Zr, Hf) (R = an alkyl group) and (ii) the lack of convincing evidence for the existence of heterotermetallic species in solution as well as in the solid state. Mehrotra et al. have pioneered the synthesis of heterometallic alkoxides;[1c,d] however, in the absence of single-crystal X-ray studies the heterotermetallic alkoxides prepared so far via salt elimination (metathesis) or Lewis acid−base reactions have often been questioned for their heterotermetallic nature. In our contribution to overcome this barrier, we report the synthesis and characterization of the first heterotermetallic isopropoxide, $[\{Cd(OPr^i)_3\}Ba\{Zr_2(OPr^i)_9\}]_2$ in solution and in the solid state. Our interest in cadmium arises from the distinct advantage of ^{113}Cd NMR spectroscopy[3] as a sensitive probe for studying the change in cadmium coordination sphere.

The reaction (eq 1) of $KZr_2(OPr^i)_9$ (obtained from an equimolar reaction of $Zr_2(OPr^i)_8(Pr^iOH)_2$ with $KOPr^i$ in refluxing benzene) with CdI_2 in a 1:1 molar ratio in toluene at 70 °C for ~4 h, followed by the filtration of KI and removal of solvent, affords the iodobimetallic isopropoxide $ICd\{Zr_2(OPr^i)_9\}$ (**1**) as a white solid in 95% yield. **1** crystallizes as large transparent crystals from a mixture of toluene−hexane at −30 °C in ~55% yield. Another 15% of the product could be obtained by concentrating the mother liquor. **1** is thermally stable and sublimes almost quantitatively at 140 °C/10^{-2} Torr. The molecule is stereochemically rigid at 20 °C, and ^{1}H and ^{13}C NMR spectra[4] in C_6D_6 are indicative of a C_{2v} molecular symmetry,[5,6] which could be further corroborated by ^{13}C CP MAS NMR studies (Figure 1a). Cryoscopic molecular weight measurements in benzene indicate **1** to be a monomer. In the solid state[7] (Figure 1c), too, **1** exists as a monomer in which the central atom, cadmium, bears a terminal iodide ligand and a face-sharing bioctahedral $[Zr_2(OPr^i)_9]^-$ unit via two triply (μ_3-) and two doubly (μ_2-) bridging isopropoxy groups. The steric bulk of iodide ligand prevents **1** from dimerization, and thus it differs from the dimeric complex described by Mehrotra et al.[8]

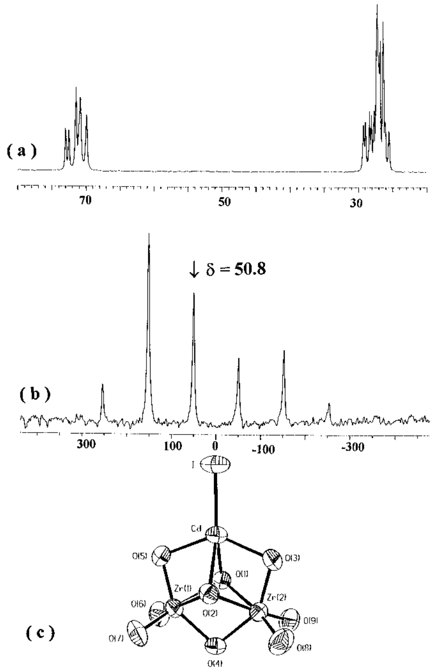

Figure 1. Solid state CP MAS ^{13}C (a) and ^{113}Cd NMR (b) spectra of **1** (ppm). The arrow indicates the isotropic shift, all other lines being the spinning side bands. (c) ORTEP drawing of the metal oxygen core of **1**. All oxygen atoms bear isopropyl groups, which have been omitted for clarity. Selected bond distances (Å): Cd−I 2.637 (4), Cd−O(3) 2.324(5), Cd−O(5) 2.369(5), Cd−O(1) 2.335(4), Cd−O(2) 2.327(4), Zr−O 1.908(4)−2.299(4). Selected bond angles (deg): O(3)−Cd−I 112.83(13), O(5)−Cd−I 110.48(14), O(2)−Cd−O(5) 71.8(2), O(3)−Cd−O(2) 72.1(2), O(2)−Cd−O(1) 65.91(14), Zr(1)−O(2)−Cd 92.3(2), Zr(2)−O(2)−Cd 90.88(14).

$$CdI_2 + KZr_2(OPr^i)_9 \rightarrow \underset{\mathbf{1}}{ICd\{Zr_2(OPr^i)_9\}} + KI \qquad (1)$$

The observed ^{113}Cd NMR chemical shifts[9] for **1** in solution (δ 67.09) and the solid state (δ 50.82, Figure 1b) (when account is taken for the wide dispersion range (>900 ppm) and sensitivity of cadmium chemical shifts to small changes in local cadmium environment[3]) indicate that the cadmium coordination to the $Zr_2(OPr^i)_9$ fragment seems to be retained in both states.

In order to demonstrate the utility of halo bimetallic alkoxy derivatives as convenient precursors for interesting heterometallic alkoxides, **1** was reacted (eq 2) with $KBa(OPr^i)_3$[10] in toluene by stirring of the reaction mixture at room temperature for ~8 h. After the filtration of KI, the solution was stripped

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[4] ^{1}H NMR (200.13 MHz, 20 °C, C_6D_6): methine peaks at δ 4.72 (septet, J = 6 Hz), 4.55 (septet, J = 6 Hz), 4.34 (septet, J = 6 Hz); four methyl peaks as distinct doublets (intensity 2:2:1:4) at δ 1.53 (μ-OPr^i), 1.47 (μ-OPr^i, Zr−OPr^i−Zr), 1.31 (μ-OPr^i, Zr−OPr^i−Zr), and 1.24 (μ-OPr^i). ^{13}C {^{1}H} NMR (50.3 MHz, 20 °C, C_6D_6): δ 71.54, 70.17, 69.88, 69.83, 69.80 (*C*H) and 26.82, 26.71, 26.48, 26.44, 26.05 (*C*H$_3$).

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[7] Crystal data for **1**: $C_{27}H_{63}CdIO_9Zr_2$, M_r = 953.51, triclinic, $P\bar{1}$, a = 9.815(10) Å, b = 11.450(9) Å, c = 20.69(2) Å, α = 95.41(8)°, β = 99.84(9)°, γ = 111.22(7)°, V = 2104(4) Å^3, Z = 2, T = 293(2) K, D_c = 1.505 Mg m^{-3}, 7412 independent reflections, 6642 ($I > 2\sigma(I)$) reflections observed, R_w = 0.0470, largest difference peak and hole: 1.234 and −1.908 e Å^{-3}.

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[9] ^{113}Cd chemical shifts in solution and the solid state for **1** and **2** are referenced externally to a 0.1 M solution of $Cd(NO_3)_2$ in D_2O and solid $Cd(NO_3)_2{\cdot}4H_2O$, respectively.

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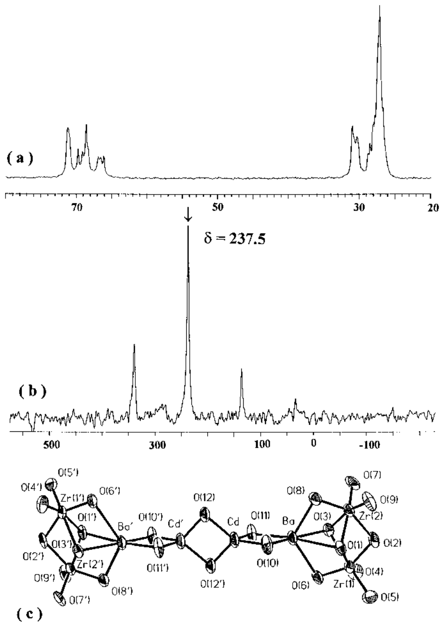

Figure 2. Solid state CP MAS ^{13}C (a) and ^{113}Cd NMR (b) spectra of **2** (ppm). (c) ORTEP representation of the central metal oxygen framework of **2**. All oxygen atoms bear isopropyl groups, which have been omitted for clarity. Selected bond distances (Å): Ba−O(10) 2.383(11), Ba−O(11) 2.660(11), Ba−O(8) 2.606(10), Ba−O(6) 2.793(11), Cd−O(10) 2.327(12), Cd−O(11) 2.067(11), Cd−O(12) 2.179(11), Zr−O 1.908(10)−2.334(10). Selected bond angles (deg): Ba−O(10)−Cd 87.9(4), Cd−O(11)−Ba 86.6(4), Cd′−O(12)−Cd 93.6(5), O(12)−Cd−O(10) 123.7(5), O(12)′−Cd−O(11) 119.5(5), O(10)−Cd−O(11) 101.1 (4), O(12)′−Cd−O(12) 86.4(5).

to dryness in vacuo to obtain a white solid (97%). The product was recrystallized from a mixture of toluene−pentane at −8 °C to obtain colorless square-shaped plates of $[\{Cd(OPr^i)_3\}Ba\{Zr_2(OPr^i)_9\}]_2$ (**2**). Although the high solubility of the complex and its sensitivity toward the temperature of crystallization reduces the yield of recrystallized material, **2** could be obtained in 50% yield. The molecular complexity of **2** ($\eta = 1.6$) in benzene showed a concentration dependence, and in more concentrated solutions it approaches the value corresponding to dimeric species. However, the ^{113}Cd NMR chemical shifts for **2** in solution gave only one resonance (δ 235.41) comparable to the chemical shift observed in the solid state (δ 237.54, Figure 2b) ascribable to a four-coordinate cadmium atom. In contrast to the deceptively simple spectroscopic pattern generally observed for fluxional alkoxide molecules,[1c] the ^1H and ^{13}C NMR spectra[11] of **2** at room temperature are informative of the structural pattern existing in solution. Owing to the presence of 12 isopropoxide environments, as seen in the asymmetric unit of **2** (Figure 2c), 12 resonances are expected in the ^{13}C CP MAS NMR (Figure 2a) spectrum, but only eight overlapping signals of different intensities were observed, probably due to the small differences in their chemical shifts.[12]

$$\underset{\textbf{1}}{ICd\{Zr_2(OPr^i)_9\}} + KBa(OPr^i)_3 \rightarrow$$

$$\tfrac{1}{2}\underset{\textbf{2}}{[\{Cd(OPr^i)_3\}Ba\{Zr_2(OPr^i)_9\}]_2} + KI \quad (2)$$

The heterotermetallic nature[13] of **2** was established by single-crystal X-ray studies which show **2** to be a dimer in the solid state possessing a crystallographic center of symmetry (Figure 2c). The molecule may be visualized as two $(\mu_2\text{-}OPr^i)_2CdBaZr_2(\mu_2\text{-}OPr^i)_2(\mu_2\text{-}OPr^i)_3(\mu\text{-}OPr^i)_4^+$ fragments linked together by two isopropoxy groups bridging the cadmium centers. The Cd−O(12′) bond distance of 1.979 Å is considerably shorter than the Cd−O(12) distance (2.179 Å) and is consistent with an asymmetric bridging in **2**. In an alternative description,[14−16] the barium atom first interacts with a face-shared dioctahedral $Zr_2(OPr^i)_9$ moiety via two terminal and two bridging isopropoxy groups to give triangular $BaZr_2(\mu_3\text{-}OPr^i)_2(\mu_2\text{-}OPr^i)_3(\mu\text{-}OPr^i)_4^+$ units, which are finally linked together by a $\{Cd_2(\mu_2\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4\}^{2-}$ unit. All barium and zirconium atoms have a coordination number of 6 but are substantially away from an ideal octahedral geometry. It is interesting to note that bimetallic alkoxides with structure similar to that of the central $[Ba(\mu_2\text{-}OPr^i)_2Cd(\mu_2\text{-}OPr^i)]_2$ unit of **2** have been reported recently.[17]

A distinctive feature, unprecedented in metal alkoxide chemistry, is the exchange of central metal atoms between the two precursors for the formation of this novel heterotermetallic framework. Remarkably, no catastrophic distortion occurs for this structural change, and this rearrangement is possibly favored by the greater oxophilicity of Ba(II) and its propensity for higher coordination numbers.[14−18] Finally, it is conceivable that the successful use of the $Ba(OPr^i)_3^-$ moiety as a novel alkoxometalate unit for building the first well-characterized heterotermetallic isopropoxide is an interesting example of incorporating barium in a molecular alkoxide assembly, and the extension of this strategy to other metal combinations may provide access to the designing of "single-source" precursors.

Acknowledgment. We thank the DFG and Fonds der Chemischen Industrie for financial support. S.M. is thankful to the Alexander von Humboldt-Stiftung, Bonn, for the award of a research fellowship and to Dr. Michael Zimmer for recording the solid state NMR spectra.

Supporting Information Available: Tables of atomic coordinates with isotropic thermal parameters and of anisotropic displacement coefficients for compounds **1** and **2** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[10] This reaction is the first example of the use of the $Ba(OPr^i)_3^-$ unit as a novel alkoxometalate ligand. Synthesis: To a suspension of $Ba(OPr^i)_2$ (1.04 g, 4.07 mmol) in toluene (10 mL) was added a solution of $KOPr^i$ (freshly prepared by reaction of potassium (0.16 g, 4.09 mmol) with isopropyl alcohol (5 mL)) in 20 mL of toluene, and the obtained clear solution was heated to reflux for ~4 h. Removal of volatiles in vacuo followed by drying at 70 °C for 2 h gave a white solid (1.40 g, 97%) poorly soluble in benzene−toluene. Anal. Calcd for $BaC_9H_{21}KO_3$: C, 30.53; H, 5.94; Ba, 38.82; OPr^i, 50.12. Found: C, 30.20; H, 5.87; Ba, 38.90; OPr^i, 49.82. Spectral data: ^1H NMR (δ, C_6D_6) 1.33 (d, 18H), 4.26 (m, 3H); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) 29.97 (CH_3), 63.79(CH).

[11] ^1H NMR (200.13 MHz, 20 °C, C_6D_6): methine peaks are observed as three overlapping septets in the region δ 4.42−4.73; the methyl region exhibits six well-defined resonances (δ 1.34, 1.37, 1.43, 1.46, 1.51, 1.62), which integrate approximately 2:2:1:2:3:2. $^{13}C\{^1H\}$ NMR (50.3 MHz, 20 °C, C_6D_6): δ 70.79, 69.39, 68.37, 68.24, 66.17 (*C*H) and 30.35, 27.25, 26.83, 26.70, 26.46, 26.17 (*C*H_3).

[12] The presence of 12 signals corresponding to the different isopropoxide environments has been confirmed by a line deconvolution of the ^{13}C CP MAS NMR spectrum.

[13] Crystal data for **2**: $C_{72}H_{168}Ba_2Cd_2O_{24}Zr_4$, $M_r = 2282.42$, monoclinic, $P2_1/c$, $a = 23.20(2)$ Å, $b = 12.937(11)$ Å, $c = 19.33(2)$ Å, $\alpha = 90°$, $\beta = 97.30(8)°$, $\gamma = 90°$, $V = 5755(9)$ Å^3, $Z = 2$, $T = 193(2)$ K, $D_c = 1.317$ Mg m^{-3}, 5056 independent reflections, 4048 ($I > 2\sigma(I)$) reflections observed, $R_w = 0.0772$, largest difference peak and hole: 2.200 and −0.654 e Å^{-3}.

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