SHORT COMMUNICATION

A YBa_2 Cluster Based on Simple Ligands (O*t*Bu)

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Reaction of a 1:2 mixture of $Y[N(SiMe_3)_2]_3$ and $Ba[N(SiMe_3)_2]_2$ with *t*BuOH (8 mol equivalents) in Et_2O at 25 °C yields $YBa_2(OtBu)_7(tBuOH)$, which has a triangular structure with two μ_3-O*t*Bu and three μ_2-O*t*Bu ligands, one terminal O*t*Bu on Y and on one Ba, and one terminal *t*BuOH on the second Ba. All metals are thus five-coordinate. The crystal structure is comprised of chains of triangles held together by hydrogen bonds from *t*BuOH of one YBa_2 unit to the terminal O*t*Bu on Ba of the next YBa_2 unit. This serves as support for the idea that, in certain cases, the heterometallic alkoxide product from alcoholysis of a mixture of two metal complexes can faithfully duplicate the global solution metal stoichiometry.

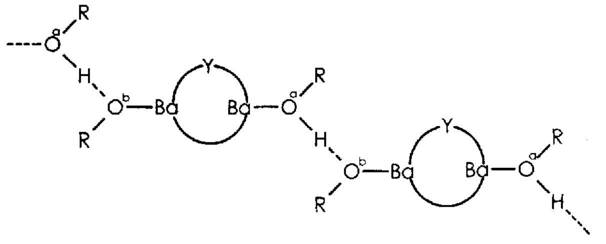
The synthesis of effective precursors to solid materials becomes more challenging as the stoichiometry of ternary (and higher) solids is considered. Thus, a precursor to $YBa_2Cu_3O_7$ requires a means to direct the 1:2:3 metal stoichiometry in a molecular species, as well as an efficient synthetic approach. The precursor aggregate or cluster will be governed by the preferred metal coordination numbers, as well as the multiple structural potential (e.g., terminal, μ_2-, μ_3-, etc.) of the chosen anionic and neutral ligands.

In the case of $YBa_2Cu_3O_7$, the Y:Ba stoichiometry is quite naturally approached with a triangular structural motif which is so commonly adopted by $M'M_2$ heterometallic alkoxides: $KZr_2(OiPr)_9$[1], $ClCuZr_2(OiPr)_9$[2], $Ba[Zr_2(OiPr)_9]_2$, and $[BaZr_2(OiPr)_{10}]_2$[3], $BaZr_4(OH)(OiPr)_{17}$[4], $KBa_2(OSiPh_3)_5(MeOC_2H_4OMe)_2$[5], $K_2Sb(OtBu)_5$(dioxane)[6], $NaCe_2(OtBu)_9$[7], $[ClCdZr_2(OiPr)_9]_2$[8], $KU_2(OtBu)_9$[9], and $NaTh_2(OtBu)_9$[10]. This triangular unit normally has the core ligation $M_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_3$[11] with various numbers of terminal ligands. There are two important concerns regarding a triangular YBa_2 precursor[12]: 1) the potential for the metals to disorder in the solid state[13]; 2) the need to retain some functionality for later synthetic incorporation of copper. We report on some progress along this theme[14].

Reaction of YX_3, BaX_2, and *t*BuOH at 25 °C in ether according to eq. (1) yields a mixed metal product with the solid-state structure (X-ray diffraction) shown in Figure 1. It has precisely the $YBa_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_3$ substructure, with three terminal ligands. The metal ions show no sign of disorder, in spite of all being five-coordinate, in part because the Y–O (terminal) distance [2.06(2) Å] is much shorter than the Ba–O (terminal) distances [2.66(2) and 2.67(2) Å]. Even more decisive in preventing metal disorder is the fact that the barium centers carry the one *t*BuOH (i.e., alcohol) ligand. This ligand is bent [122(1)° for O29 and 123(2)° for O34] and involved in intermolecular hydrogen bonding to the terminal alkoxide on barium of a neighboring molecule (Scheme 1). The crystal lattice is thus comprised of hydrogen bonded chains (Figure 2). The intermolecular hydrogen bonds are short[15] [O/O distance = 2.50(2) Å], which is consistent with the distances from Ba to O^a and to O^b being identical.

$$YX_3 + 2\,BaX_2 + 8\,tBuOH \rightarrow YBa_2(OtBu)_7(tBuOH) + 7\,HX \qquad (1)$$
$$X = N(SiMe_3)_2$$

Scheme 1



$YBa_2(OtBu)_7(tBuOH)$ is extremely poorly soluble in C_6D_6, where it shows only one ^{1}H-NMR *t*Bu resonance at 25 °C. We attribute this low solubility to the hydrogen bonding. When the molecule is recrystallized in the presence of THF (5% THF in pentane), the crystals have the composition $YBa_2(OtBu)_7(tBuOH)(THF)_2$, both by ^{1}H-NMR integration (2 THF: 8 *t*Bu) and by thermogravimetric analytical assay (all THF is lost by 90 °C). This THF adduct is more soluble in benzene than is the compound in Figure 1, but the ^{1}H-NMR spectrum in $[D_8]$toluene shows a single *t*Bu signal (δ = 1.45) for the methyl protons. The THF signals of coordinated and *added* free THF (three equivalents per YBa_2 unit) are coalesced down to −95 °C, which indicates rapid THF ligand exchange. By cooling to −30 °C in

Figure 1. ORTEP view of $YBa_2(OtBu)_7(tBuOH)$, showing selected atom labeling. Note the bent angles at O29 and O34

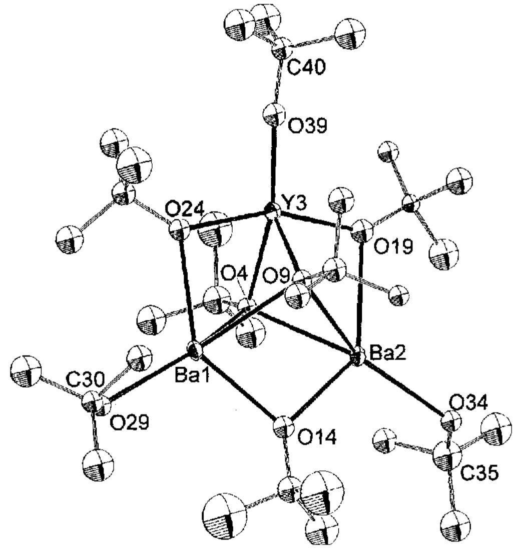
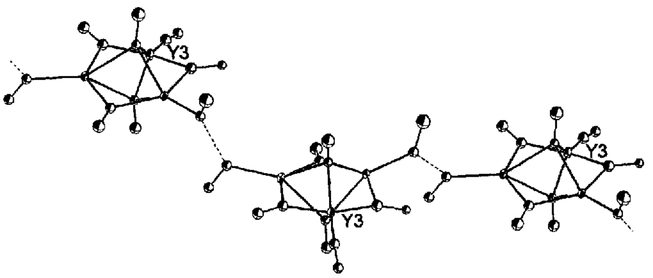


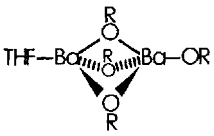
Figure 2. Representation of the hydrogen bonding (dotted line) which creates an infinite chain of $YBa_2(OtBu)_7(tBuOH)$ monomers in the solid state



$[D_8]$toluene, the methyl signals decoalesce into a ~6:1 pattern, but further decoalescence was not achieved. It is probable that this rapid fluxionality of the O*t*Bu groups is due to rapid proton transfer (from the *t*BuOH ligand), which encourages O*t*Bu migration and/or dissociation. The one resolved (−30 °C) *t*BuO resonance is then logically attributed to the terminal ligand on yttrium.

The molecular structure of $YBa_2(OtBu)_7(tBuOH)$ is distorted from its idealized C_2 symmetry, as the two μ_3-O*t*Bu groups do not bind symmetrically to the barium atoms. While Ba2 forms one long bond with O9 [2.852(17) Å] and one short bond with O4 [2.700(17) Å], Ba1 forms bonds of similar lengths with both O9 and O4 [2.787(16) and 2.765(16) Å, respectively]. The shortest Ba−O distances in the molecule are those of the *bridging* alkoxide oxygen O14 with bond lengths of 2.558(18) and 2.567(17) Å to Ba1 and Ba2, respectively. It is of interest to note that this is 0.10 Å *shorter* than the Ba−O bonds to the alkoxide engaged in hydrogen bonding. The length of Ba1−O29 and Ba2−O34 must be due to the alcohol having much reduced donor power relative to *t*BuO. Furthermore, the bond lengths of the μ_3-alkoxides to Y are also unsymmetric [2.204(17) and 2.371(17) Å to O9 and O4, respectively]. In general, the bond lengths are comparable to those in related molecules[16−18].

The molecule $YBa_2(OtBu)_7(tBuOH)$ can be conceptually dissected into $Y(OtBu)_3$ and $tBuOBa(\mu_2\text{-}OtBu)_3Ba(HOtBu)$ (**I**), which emphasizes the relationship of the latter to $(RO)(THF)_mBa(\mu_2\text{-}OR)_3Ba(THF)_n$, where $n = 2$, $m = 1$ when R = CPh_3 and $n = 1$, $m = 0$ when R = $SitBu_3$[16]. This comparison is particularly significant in that $Ba(OtBu)_2$ is insoluble in benzene (i.e., probably polymeric) until *t*BuOH is added, which leads to production of the tetramer $[Ba(OtBu)_2(tBuOH)_2]_4$[17]. $Y(OtBu)_3$ thus severely alters the degree of aggregation of $Ba(OtBu)_2$/*t*BuOH.



I

There has been considerable concern expressed[19] over whether simply forming a mixture of AX_m and BX_n in a mol ratio p:q, then executing a hydrolysis or alcoholysis (HY), could succeed in generating a product, $A_pB_qY_{pm+qn}$ which possesses the global solution stoichiometry. Possible sources of failure include production of multiple products with stoichiometry deviating from p:q. In this context, it is interesting that the present work gives cause for optimism in at least one case. On the other hand, pre-aggregation is not counterproductive. Reaction of the proton-bearing cubane aggregate of barium with YX_3 (eq. 2) in pentane at 25 °C produces the same YBa_2 cluster (Figure 1). However, the use of other Ba:Y stoichiometries gives unattractive mixtures of this YBa_2 compound with numerous other (unidentified) products.

$$[Ba(OtBu)_2(tBuOH)_2]_4 + 2\,YX_3 \rightarrow 2\,YBa_2(OtBu)_7(tBuOH) + HX \qquad X = N(SiMe_3)_2 \qquad (2)$$

$YBa_2(OtBu)_7(tBuOH)$ is the first yttrium barium alkoxide containing only one ligand type (O*t*Bu and its conjugate acid). The availability of an yttrium-barium compound with only one type of ligand should permit mechanistic study of the relative hydrolytic sensitivity of different *sites* within this molecule. Such knowledge is essential to progress in sol-gel science for heterometallic precursors. Finally, it is significant that $YBa_2(OtBu)_7(tBuOH)$ retains an acidic proton functionality (i.e., the alcohol) that might be manipulated for introduction of copper[20].

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Experimental

Reactions were performed under purified nitrogen with standard Schlenk techniques. All solvents were distilled from Na/benzophenone and stored under nitrogen.

$YBa_2(OtBu)_7(HOtBu)(THF)_2$: In a glove box, a Schlenk flask was charged with 6.3 g (10.5 mmol) of $Ba[N(SiMe_3)_2]_2(THF)_2$ and 3.0 g (5.3 mmol) of $Y[N(SiMe_3)_2]_3$. The solids were dissolved in 50 ml of pentane. After slow addition of 8.0 ml of a 5.4 M solution

of *tert*-butyl alcohol (43.2 mmol) in heptane, the reaction solution mixture was left stirring for 12 h. After removal of small amounts of solid by filtration, the solution was concentrated (to about 30 ml) in vacuo and put into a freezer (−20 °C). After 3 d, 5.3 g (92%) of $YBa_2(OtBu)_7(HOtBu)(THF)_2$ was obtained. The compound is soluble in Et_2O, but it is not volatile due to loss of THF at 90 °C. – ^1H NMR (C_6D_6): δ = 1.45 (*t*Bu), 1.38, 3.52 (THF). – $C_{40}H_{89}Ba_2O_{10}Y$: calcd. C 43.92, H 8.21; found C 43.30, H 8.09.

Crystal Structure Determination[21]: $C_{32}H_{73}Ba_2O_8Y$ (formula mass 949.51); the diffractometer used for data collection was designed and constructed locally. A Picker four-cycle goniostat equipped with a Furnas Monochromator (HOG crystal) and Spellman generator is interfaced to an IBM PC computer with Slo-Syn stepping motors to drive angles. Crystal size 0.05 × 0.10 × 0.10 mm, temperature −172 °C; monoclinic, $P2_1/c$, a = 15.017(4), b = 14.654(4), c = 19.716(5) Å, β = 93.69(1)°, V = 4329.69 Å^3, Z = 4, $d_{calcd.}$ = 1.457 g · cm^{-3}; 2Θ range 6–45; no correction was made for absorption; 8643 total reflections, 5699 independent reflections ($R_{int.}$ = 0.136); 2508 observed reflections [$F > 2.33F(F)$]; 189 total variables. The structure determination was performed by a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the metal atoms were obtained from an initial E map. The positions of the remaining non-hydrogen atoms were obtained from subsequent iterations of a least-squares refinement followed by Fourier calculation. Hydrogens were included in fixed calculated positions. The anisotropic thermal parameters for several of the lighter non-hydrogen atoms did not refine properly, undoubtedly due to the weak data; $R(F)$ = 0.072 (2.33F data); max./min. residual electron density 1.1/−1.2 eÅ^3.

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