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## Inorganic Chemistry

## Synthesis of Homoleptic Barium Alkoxides and Aryloxides and Their Reactions with Al(CH<sub>3</sub>)<sub>3</sub>: a Convenient Route to Heterometallic Species

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Reactions of metallic Ba with benzofuranol (dbbfoH) or diethylene glycol give homoleptic and homonuclear complexes Ba(dbbfo)<sub>2</sub>-(dbbfoH)<sub>2</sub>·3dbbfoH and Ba{O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>}{O(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>}<sub>2</sub> (60–89%). Both compounds and formerly described Ba{O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>-Me}<sub>2</sub> react with Al(CH<sub>3</sub>)<sub>3</sub> to yield trinuclear heterobimetallic low-coordinated barium compounds with structure and geometry depending on the reaction stoichiometry and crystallization procedure.

Heavier alkaline-earth metal complexes remain in the zone of growing interest because of their potential as precursors for materials of numerous applications. These metal alkoxides and aryl oxides especially with low nuclearity, high thermal stability, and volatility are highly desirable for the preparation of superconducting thin films by metal organic chemical vapor deposition.<sup>1</sup> Lately, they also find increasing utility as catalysts, e.g., for dehydrogenative coupling of hydrosilanes with terminal alkynes<sup>2</sup> or polymerization of lactones.<sup>3</sup> In turn, heterometallic alkoxides<sup>4</sup> are precursors to numerous ceramic materials.

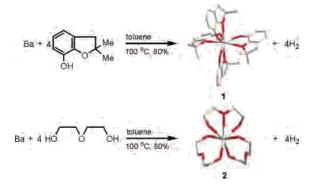
Numerous barium alkoxides and aryloxides have been synthesized to date.<sup>5</sup> Unfortunately, they are usually oxo species forming large aggregates. The first structurally characterized homoleptic tetrabarium alkoxide was reported in 1994 by Caulton et al.<sup>6a</sup> In 2002, Chi and co-workers presented a structure of Ba with a four-coordinated polyether-

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Scheme 1. Syntheses of 1 and 2



substituted fluoro alcohol.<sup>6b</sup> To our knowledge, no other structures of homoleptic barium alkoxides have been reported since then. The population of structurally characterized heterometallic Ba compounds with alkoxo ligands is much bigger. Among the most investigated are Ba/Cu<sup>7,8b</sup> and Ba/Y<sup>8</sup> because of their physical properties and applicability, although today, organometallic Ba-containing compounds have become more and more interesting in this context.<sup>9</sup>

In this communication, we report the syntheses and partial characterization of a series of homoleptic mononuclear as well as heterobimetallic Ba compounds.

As shown in Scheme 1, an excess of O,O'-coordinating 2,3-dihydro-2,2-dimethyl-7-benzofuranol (dbbfoH), already utilized in our research,<sup>10</sup> was combined with metal Ba under

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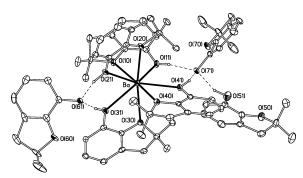


Figure 1. ORTEP view of 1.

anaerobic conditions. Workup gave stable but air-sensitive  $Ba(dbbfo)_2(dbbfoH)_2 \cdot 3dbbfoH$  (1 · 3dbbfoH) as a white powder in 60% yield.

Colorless crystals of 1.3dbbfoH were grown from a biphasic C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>/hexanes system, and the crystal structure was determined as described in the Supporting Information.<sup>11</sup> In the complex molecule, presented in Figure 1, the Ba atom is surrounded by four bidentate ligands.

Close analysis of the O–H and O···H distances shows that all ligands from the metal coordination sphere "keep" hydroxy hydrogens. That makes **1**·3dbbfoH formally ionic with two dbbfo<sup>–</sup> ligands and one neutral benzofuranol outside the coordination sphere of the metallic cation. Hence, the complex formula in the solid state should formally be written as [Ba(dbbfoH)<sub>4</sub>][dbbfo]<sub>2</sub>·dbbfoH. Similar compounds with organic<sup>12</sup> and metal containing anions outside the coordination sphere were reported.<sup>7a,13</sup>

Outer-sphere and inner-sphere ligands are interacting by numerous hydrogen bonds. As shown by <sup>1</sup>H NMR, they persist in solution what makes all ligands equivalent and gives one set of proton signals. The dynamism of hydrogen bonds is confirmed by a very broad singlet located at 10.79 ppm.

The existence of hydrogen bonds usually discriminates the volatility of the compound. In an effort to obtain a polymorph with no ligand/solvate in the unit cell, we set out reactions with different Ba/dbbfoH stoichiometries. Unfortunately, the same product has always been obtained.

We then turned our attention to a related ligand. Reactions of Ba with an excess of O,O',O''-coordinating diethylene glycol gave neutral monomeric Ba{ $O(CH_2CH_2O)_2$ }{ $O(CH_2-CH_2OH)_2$ } (2), as evidenced by the X-ray crystal structure depicted in Figure 2.<sup>14</sup> It clearly shows a nine-coordinated Ba atom bound to one bisalkoxo and two neutral diethylene glycols with no solvates in the unit cell.

- (11) Crystallographic data for 1: C<sub>70</sub>H<sub>82</sub>BaO<sub>14</sub>, FW = 665.35, monoclinic, P2<sub>1</sub>/c, a = 20.147(3) Å, b = 14.825(3) Å, c = 21.798(3) Å, β = 99.13(2)°, V = 6428.1(18) Å<sup>3</sup>, Z = 4, ρ<sub>calc</sub> = 1.327 g/cm<sup>3</sup>, μ = 0.682 mm<sup>-1</sup>, R<sub>1</sub> = 0.0440, wR<sub>2</sub> = 0.0736, GOF = 1.006.
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(14) Crystallographic data for **2**:  $C_{12}H_{28}BaO_9$ , FW = 453.68.35, triclinic, *P*1, *a* = 9.568(2) Å, *b* = 9.764(2) Å, *c* = 11.541(2) Å,  $\alpha$  = 69.95-(1)°,  $\beta$  = 77.33(1)°,  $\gamma$  = 60.93(1)°, *V* = 883.4(3) Å<sup>3</sup>, *Z* = 2,  $\rho_{calc}$  = 1.706 g/cm<sup>3</sup>,  $\mu$  = 2.286 mm<sup>-1</sup>, R<sub>1</sub> = 0.0275, wR<sub>2</sub> = 0.0639, GOF = 1.039.

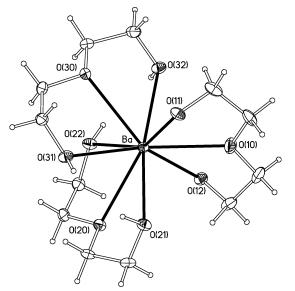
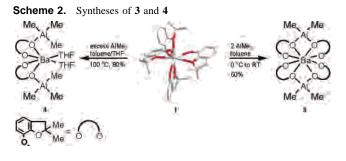


Figure 2. ORTEP view of 2.



To determine a possible volatility of the 1.3dbbfoH and 2, thermogravimetric analysis was performed. Unfortunately, for both compounds no clean process was observed. In the case of 1.3dbbfoH, thermal decomposition starts at approximately 160 °C. On the basis of the weight loss, it is most probably associated first with an extrusion of three alcohols from outside the coordination sphere followed by "evaporation" of inner-sphere alkoxo ligands. In 2, the process seems to initiate with the loss of two neutral glycols. In both cases, the solid residues were not investigated.

As mentioned before, heterometallic alkoxides are of interest as precursors for oxide-ceramic materials. There are a few basic ways of preparation.<sup>4e,f</sup> The presence of neutral alcohols in the Ba coordination sphere in  $1\cdot$ 3dbbfoH and 2 made these compounds excellent targets for transformation (via O metalation) into heterometallic species.

As shown in Scheme 2, complex 1.3dbbfoH was treated at 0 °C with 2 equiv of Al(CH<sub>3</sub>)<sub>3</sub>. Workup gave neutral heterobimetallic Ba{( $\mu$ -dbbfo)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (**3**) as colorless crystals in 60% isolated yield.<sup>15</sup> The reaction of Al(CH<sub>3</sub>)<sub>3</sub> with hydroxy hydrogens resulted in a linkage of benzofuranoxo ligands by a Al(CH<sub>3</sub>)<sub>2</sub> moiety to form a pair of four-coordinating ligands. Instead, the reaction of **1** with an excess of Al(CH<sub>3</sub>)<sub>3</sub> followed by recrystallization from a C<sub>6</sub>H<sub>5</sub>-

<sup>(15)</sup> Crystallographic data for **3**: C<sub>44</sub>H<sub>56</sub>Al<sub>2</sub>BaO<sub>8</sub>, FW = 904.19, monoclinic, C2/c, a = 12.500(2) Å, b = 17.710(2) Å, c = 20.468(2) Å,  $\beta = 103.25(1)^{\circ}$ , V = 4410.5(10) Å<sup>3</sup>, Z = 4,  $\rho_{calc} = 1.362$  g/cm<sup>3</sup>,  $\mu = 0.989$  mm<sup>-1</sup>, R<sub>1</sub> = 0.0381, wR<sub>2</sub> = 0.0747, GOF = 1.115.

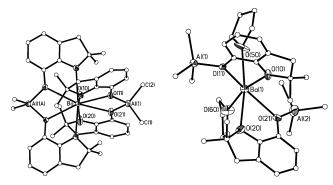


Figure 3. ORTEP views of 3 and 4.

CH<sub>3</sub>/tetrahydrofuran (THF) mixture resulted in six-coordinated Ba complex Ba{ $(\mu$ -dbbfo)Al(CH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>(THF)<sub>2</sub> (**4**).<sup>16</sup> Here Al(CH<sub>3</sub>)<sub>3</sub> simply coordinates to oxygen atoms. Figure 3 shows molecules of **3** and **4**.

A similar result was obtained in the reaction of previously reported Ba{O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Me}<sub>2</sub><sup>5c</sup> with Al(CH<sub>3</sub>)<sub>3</sub>. Also in this case the reaction led to six-coordinated heterotrimetallic adduct Ba{ $\mu$ -(Me)O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>} (**5**).

In conclusion, we have presented an easy and high-yield synthetic strategy to access homoleptic barium alkoxides. In these complexes, in order to satisfy the coordination requirements of the large Ba atom, usually neutral alcohol molecules are coordinated. We have demonstrated that they can easily be modified with metal organometallics into heterometallic alkoxides, potentially useful in material science. In future research, reagents other than  $Al(CH_3)_3$ organometallic reagents will be tried in similar reactions.

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**Supporting Information Available:** Text and tables giving experimental and crystallographic details. Crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(16)</sup> Crystallographic data for 4:  $C_{34}H_{56}Al_2BaO_6 \cdot 0.5C_7H_8$ , FW = 798.16, monoclinic,  $P2_1$ , a = 10.698(3) Å, b = 38.025(6) Å, c = 10.968(3)Å,  $\beta = 97.99(3)^\circ$ , V = 4418.4(19) Å<sup>3</sup>, Z = 2,  $\rho_{calc} = 1.200$  g/cm<sup>3</sup>,  $\mu = 0.975$  mm<sup>-1</sup>,  $R_1 = 0.0678$ , w $R_2 = 0.1323$ , GOF = 0.931.