New Precursors for Barium MOCVD. β-Ketoiminate Complexes Containing Appended Polyether "Lariats"
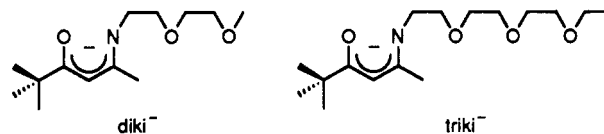
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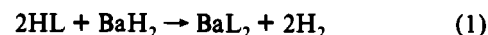
Minimizing molecular oligomerization, and hence lattice cohesive energies, by saturating the metal coordination sphere with sterically encumbered nonpolar or fluorinated ligands is an attractive strategy for the design of volatile MOCVD (metal-organic chemical vapor deposition) precursors. For the growth of barium-containing ferroelectric[1] or high-T_c superconducting films,[2-4] the small charge-to-radius ratio of Ba^{2+} presents a significant challenge in precursor ligand design.[5] Non-fluorinated precursors such as "Ba(dpm)$_2$" (dpm = dipivaloylmethanate) suffer from compositional uncertainties[6] as well as a less than optimum, variable, and unstable vapor pressure,[6a,7] while more volatile fluorinated precursors[2] such as Ba(hfa)$_2$·tetraglyme (hfa = hexafluoroacetylacetonate)[2a-c,4b,5c] require additional processing to remove fluoride from the resulting films.[2,4b] We report here the synthesis and structural characterization of two fluorine-free barium precursors based upon an encapsulating β-ketoiminate-polyether ligand[8] and their utility in barium transport for the MOCVD of BaPbO$_3$ (a metal-like perovskite[9]) films.

The β-ketoiminate ligands Hdiki and Htriki containing polydentate "lariat" appendages were prepared by condensation in benzene[10] of 2,2-dimethyl-3,5-hexanedione[11] with the corre-

diki⁻   triki⁻

sponding amino ethers. The Hdiki precursor was prepared by reaction of methyl iodide with 2-(2-aminoethoxy) ethoxide while that for Htriki was prepared via reaction of 2-ethoxyethyltosylate with 2-(2-aminoethoxy)ethoxide. Hdiki and Htriki were characterized by standard analytical and spectroscopic techniques.[12] Ba(diki)$_2$ and Ba(triki)$_2$ were obtained in yields of 44 and 42%, respectively, as colorless, crystalline solids by the reaction of the ligand protio derivatives with BaH$_2$ under inert atmosphere (eq 1), followed by repeated crystallization from hot heptane. They

$$2HL + BaH_2 \rightarrow BaL_2 + 2H_2 \qquad (1)$$

$$L = diki^-, triki^-$$

were characterized by NMR, mass spectrometry, elemental analysis,[13] X-ray diffraction (vide infra), and dynamic TGA (10 °C/min under N$_2$). The latter reveals significant volatility with $T_{50\%}$ = 278 °C (39% residue to 500 °C) and 255 °C (29% residue to 500 °C), for Ba(diki)$_2$ and Ba(triki)$_2$, respectively.[14] Both complexes can be sublimed with some decomposition at 80–120° at 10⁻⁵ Torr but are less volatile than the most volatile fluorinated β-diketonate precursors.[2a-d,5c] The major volatile decomposition product of Ba(diki)$_2$, which collects as droplets on the upper parts of the sublimation cold finger, was shown to be Hdiki by ¹H NMR. Ba(diki)$_2$ and Ba(triki)$_2$ are slightly air-sensitive, undergoing discoloration after 2–3 h of exposure to air.

The crystal structures of Ba(diki)$_2$[15] and Ba(triki)$_2$[16] (Figure 1, parts A and B, respectively) reveal distorted trigonal dodecahedral coordination geometries. In the case of Ba(triki)$_2$, the terminal lariat ethoxy groups remain uncoordinated. Metrical parameters for the two complexes are rather similar, with Ba–O(ketoiminate) distances 0.21–0.34 Å shorter than those involving the uncharged ether oxygen atoms. The Ba–O(ketoiminate)

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(12) Hdiki is isolated by distillation (110–112 °C (10⁻² Torr)) as a yellow oil in 74% yield. **Hdiki.** ¹H NMR (300 MHz, CDCl$_3$): δ 1.06 (s, 9H), 1.97 (s, 3H), 3.29 (s, 3H), 3.43 (m, 2H), 3.49 (m, 2H), 3.58 (m, 4H), 5.13 (s, 1H), 11.01 (br s, 1H). Htriki is isolated by distillation (146–150 °C (10⁻² Torr)) as a yellow oil in 71% yield. **Htriki.** ¹H NMR (300 MHz, CDCl$_3$): δ 1.07 (s, 9H) 1.15 (m, 3H), 1.92 (s, 3H), 3.39–3.60 (m, 14H), 5.08 (s, 1H), 10.93 (br s, 1H).

(13) **Ba(diki)$_2$.** ¹H NMR (300 MHz, C$_6$D$_6$): δ 1.43 (s, 9H), 1.82 (s, 3H), 3.03 (s, 3H), 3.07 (m, 2H), 3.29 (m, 2H), 3.39 (m, 2H), 3.66 (m, 2H), 5.10 (s, 1H). Anal. Calcd for C$_{26}$H$_{48}$N$_2$O$_6$Ba: C, 50.21; H, 7.78; N, 4.50; Ba, 22.08. Found: C, 49.30; H, 7.72; N, 4.26; Ba, 22.26. MS (EI, 70 e V, *m/e⁺*): 622 (M), 607 (M – CH$_3$), 546 (M – OC$_2$H$_4$OCH$_3$), 470 (M – 2OC$_2$H$_4$ – OCH$_3$ – 2CH$_3$), 380 (M – L), 304 (M – L – OC$_2$H$_4$OCH$_3$), 186 (L – C$_4$H$_9$). **Ba(triki)$_2$.** ¹H NMR (300 MHz, C$_6$D$_6$): δ 1.12 (m, 3H), 1.44 (s, 9H), 1.83 (s, 3H), 3.36–3.59 (m, 14H), 5.08 (s, 1H). Anal. Calcd for C$_{32}$H$_{60}$N$_2$O$_8$Ba: C, 52.07; H, 8.19; N, 3.80; Ba, 18.60. Found: C, 51.55; H, 8.38; N, 3.47; Ba, 18.27. MS: (EI, 70 eV, *m/e⁺*): 738 (M), 723 (M – CH$_3$), 681 (M – C$_4$H$_9$), 604 (M – C$_2$H$_4$OC$_2$H$_4$OC$_2$H$_5$), 438 (M – L), 244 (L – C$_4$H$_9$).

(14) Reported TGA results for "Ba(dpm)$_2$". (a) 25% residue to 500 °C: Yuhya, S.; Kikuchi, K.; Yoshida, M.; Sugawara, K.; Shiohara, Y. *Mol. Cryst. Liq. Cryst.* **1990**, *184*, 231. (b) 41% residue to 500 °C: Kim, S. H.; Cho, C. H.; No, K. S.; Chun, J. S. *J. Mater. Res.* **1991**, *6*, 704. (c) 20% residue to 500 °C.[6a]
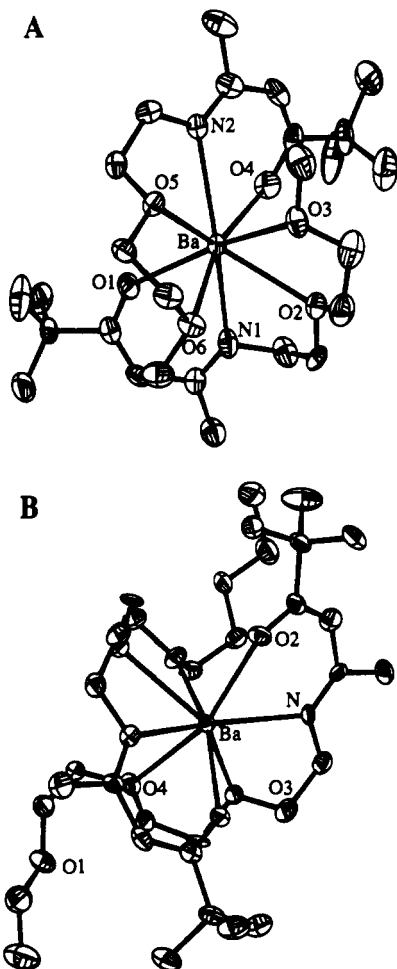
A

B

Figure 1. (A) ORTEP drawing of Ba(diki)$_2$ showing 50% probability ellipsoids. Important interatomic distances (Å) and angles (deg) are as follows: Ba–O1 = 2.575 (6), Ba–O2 = 2.822 (6), Ba–O3 = 2.887 (6), Ba–O4 = 2.540 (6), Ba–O5 = 2.830 (5), Ba–O6 = 2.910 (6), Ba–N1 = 2.824 (7), Ba–N2 = 2.832 (6); O1–Ba–O4 = 113.7 (2), O2–Ba–O5 = 123.9 (2), O3–Ba–O6 = 71.9 (2), N1–Ba–N2 = 153.8 (2). (B) ORTEP drawing of Ba(triki)$_2$ showing 50% probability ellipsoids. Important interatomic distances (Å) and angles (deg) are as follows: Ba–O1 = 5.323 (5), Ba–O2 = 2.580 (5), Ba–O3 = 2.841 (5), Ba–O4 = 2.799 (5), Ba–N = 2.857 (5); O2–Ba–O2 = 116.6 (3), O3–Ba–O3 = 130.5 (2), O4–Ba–O4 = 73.5 (2), N–Ba–N = 156.3 (2). Note: Ba lies on a 2-fold axis.

distances are ~0.1 Å shorter than the corresponding Ba–O(diketonate) distances in nine-coordinate Ba(β-diketonate)$_2$·tetraglyme complexes (β-diketonate = hfa, dpm, and tri-fluoroacetylacetonate),[5d] possibly reflecting, among other factors, higher oxygen donor basicity and lower coordination numbers in the present complexes. Ba–O(ether) distances are comparable in the two classes of complexes. No Ba–N(ketoiminate) metrical data are available for comparison; however, the present distances are ~0.2 Å longer than Ba–N(SiMe$_3$)$_2$(terminal) distances in four-coordinate amide complexes.[17]

MOCVD experiments with Ba(diki)$_2$ were carried out in the hot wall, low-pressure reactor described previously,[2a] using an Ar carrier gas, Pb(dpm)$_2$[18] as a lead source, and water-saturated O$_2$ as an oxidizing agent ((001) MgO substrate temperature = 450 °C; 5 min 890 °C post-anneal in air). X-ray diffraction scans of the resulting films (Figure 2) show them to consist of
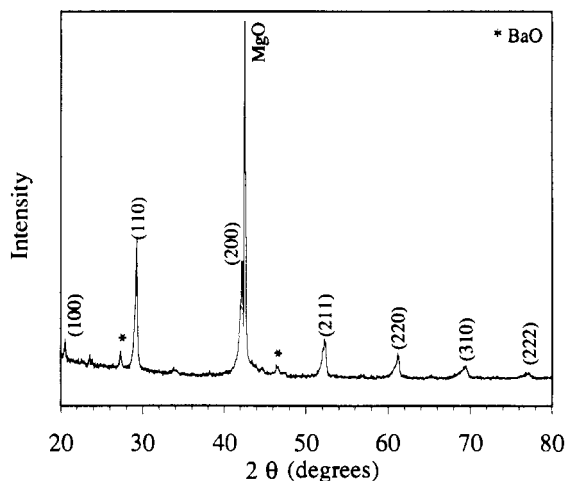

Figure 2. θ–2θ X-ray diffraction scan of an MOCVD-derived BaPbO$_3$ film grown on a (001)-oriented single-crystal MgO substrate.

crystalline BaPbO$_3$[19] with traces of contaminating BaO[19] (also consistent with SEM/EDX data).

In summary, these results show that it is possible to design encapsulating, fluorine-free ketoiminate ligation spheres which yield monomeric Ba^{2+} complexes of sufficient volatility for MOCVD. Further studies are focussing on the scope of ligand classes accessible and encapsulation of other metals.

Supplementary Material Available: Crystal structure analysis reports, including tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles, and crystallographic data and ORTEP plots for Ba(diki)$_2$ and Ba(triki)$_2$ (19 pages). Ordering information is given on any current masthead page.

(15) Monoclinic, space group $C2/c$ (No. 15) at –120 ± 1 °C with a = 32.764 (6) Å, b = 12.110 (2) Å, c = 15.690 (5) Å, β = 102.12 (2)°, and V = 6087(4) Å^3. For Z = 8 and fw = 622.01, D_c = 1.357 g/cm^3. A total of 5627 independent absorption-corrected reflections having 2θ(Mo Kα) < 49.9° were collected with graphite-monochromated Mo Kα radiation. The structure was solved using direct methods (SHELXS-86). Hydrogen atoms were refined with a group isotropic thermal parameter while all other atoms were refined with anisotropic thermal parameters. One hydrogen atom (H20A) was assigned a fixed geometry due to minor disorder. The final cycle of full-matrix least-squares refinement was based on 2776 observed reflections (I > 3.00σ(I)) and 458 variable parameters and converged with R = 0.044 and R_w = 0.040.

(16) Orthorhombic, space group *Pccn* (No. 56) at –120 ± 1 °C with a = 24.939 (4) Å, b = 10.546 (2) Å, c = 14.349 (4) Å, and V = 3774(2) Å^3. For Z = 4 and fw = 738.16, D_c = 1.299 g/cm^3. A total of 4157 independent absorption-corrected reflections having 2θ(Mo Kα) < 51.9° were collected with graphite monochromated Mo Kα radiation. The structure was solved using direct methods (SHELXS-86). Hydrogen atoms were refined with a group isotropic thermal parameter while all other atoms were refined with anisotropic thermal parameters. The final cycle of full-matrix least-squares refinement was based on 1689 observed reflections (I > 3.00σ(I)) and 286 variable parameters and converged with R = 0.036 and R_w = 0.035. This molecule lies on a 2-fold axis.

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(19) Joint Committee on Powder Diffraction Standards (JCPDS), Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA; No. 12-664 (BaPbO$_3$); No. 1-746 (BaO).