Heterotrimetallic Butoxides

DOI: 10.1002/anie.200705268

Heterotrimetallic Salts: Synthesis, Structures, and Superbase Reactivity of Crystalline *tert*-Butoxides $[Li_4Na_2K_2(OtBu)_8(\mu\text{-}L)]_n$**

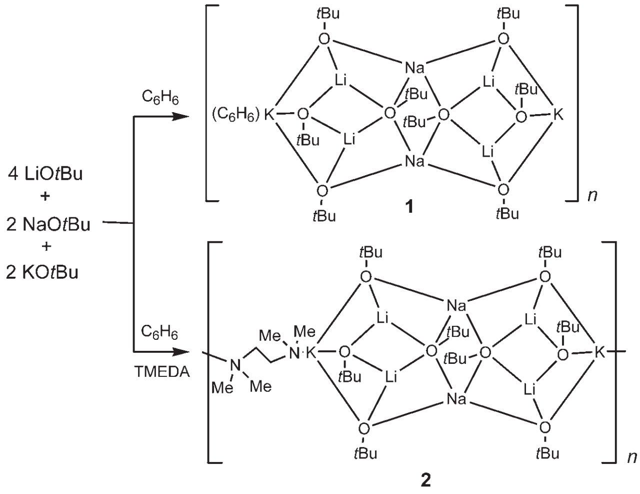
Xuehong Wei, Qingchen Dong, Hongbo Tong, Jianbin Chao, Diansheng Liu,* and Michael F. Lappert**

Mixed-metal alkoxides have received increasing attention in the past decade as precursors for superconductors or other materials required for production of metal oxide thin films by sol–gel or metal–organic chemical vapor deposition (MOCVD) techniques.[1] Mixtures of organolithium compounds and heavier alkali metal alkoxides such as NaO*t*Bu or KO*t*Bu have featured in organic synthesis as superbase reagents exhibiting symbiotic deprotonating capability as compared with the free lithium compounds;[2] for synergic mixed alkali metal/Mg and alkali metal/Zn reagents, see reference [2h].

The structures of the crystalline homoleptic alkali metal *tert*-butoxides are well documented: the lithium compound is either hexa-[3] or octameric,[4] the Na salt is both hexa- and nonameric in the same crystal,[3] and K,[5] Rb,[5] and Cs[6] congeners are tetramers. Hetero alkali metal alkoxides with well-defined structures are rare but include the isoleptic binary metal compounds $[Li_4M_4(OtBu)_8]$ (M = Na,[7] K,[8] Rb,[7] and Cs[7]). As for ternary alkali metal compounds, to the best of our knowledge, the sole example is the heteroleptic bis(amido)alkoxide $[\{LiNaK[(N(H)Ph]_2(OtBu)(tmeda)_2\}_2]$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine), described by Mulvey and coworkers.[9]

We now report the synthesis and structures of the crystalline tetralithium disodium dipotassium complexes $[Li_4Na_2K_2(OtBu)_8(\mu\text{-}L)]_n$, in which successive monomeric units are joined through their K ions by the bridging ligand L [L = $\eta^6{:}\eta^6\text{-}C_6H_6$ (**1**); *N,N′*-tmeda (**2**)].

The crystalline polymeric complex $[Li_4Na_2K_2(OtBu)_8(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]_n$ (**1**) was prepared in high yield by mixing LiO*t*Bu, NaO*t*Bu, and KO*t*Bu in the appropriate stoichiometric ratio in benzene (Scheme 1). Similarly, crystalline polymeric $[Li_4Na_2K_2(OtBu)_8(\mu\text{-}N,N'\text{-tmeda})]_n$ (**2**) was obtained by adding half an equivalent of tmeda to the above benzene solution prior to crystallization. Surprisingly, although these were the optimal conditions for isolating **1** and **2**, their formation did not depend on this choice of relative proportions of the Li, Na, and K *tert*-butoxides. Thus, using 1:1:1, 1:2:1, 1:1:2, or 1:2:2 equivalents of the three alkoxides also afforded crystalline **1** or **2**, albeit in lower yield.



Scheme 1. Synthesis of complexes **1** and **2**.

Each of the crystalline compounds **1** and **2** was characterized by 1) satisfactory microanalysis, 2) NMR spectra in C_6D_6 at 298 K, which showed a single O*t*Bu environment (^{1}H and (slightly broad) ^{13}C NMR spectra), but at 183 K in $C_6D_5CD_3$ there were several closely spaced ^{13}C NMR signals at $\delta = 31\text{–}36.5$ and $\delta = 67.4\text{–}67.9$ ppm), $\delta(^7Li)$ at 1.34 ppm (**1**) or 1.42 ppm (**2**), and a broad Na signal [$\delta = 16.6$ ppm, $\Delta\nu_{1/2} = 2.85$ kHz (**1**), $\delta = 6.20$ ppm, $\Delta\nu_{1/2} = 1.40$ kHz (**2**)], and 3) X-ray structure determination. The molecular weight, determined by cryoscopy on dilute solutions in benzene, of both **1** and **2** corresponded to the tetranuclear species. Each of **1** and **2** in C_5D_5N readily deprotonated the methyl group of toluene at ambient temperature to form KCH_2Ph ($\delta = 3.04$ ppm in C_5D_5N[2g]), whereas the individual alkali metal *tert*-butoxides were unreactive even at 90 °C; furthermore, binary mixtures (Li/Na, Li/K, or Na/K *tert*-butoxides) in C_5D_5N failed to react with toluene at ambient temperature. By contrast, [(tmeda)Na(μ-Bu)(μ-tmp)Mg(TMP)] (tmp = 2,2,6,6-tetramethylpiperidide) selectively *meta*-deprotonated toluene.[10]

The molecular structure of a monomeric unit (together with one of its KL bridges) for each of the crystalline complexes **1** and **2** is shown in Figure 1 and 2, respectively;

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[*] Prof. Dr. X.-H. Wei, Q.-C. Dong, H.-B. Tong, J.-B. Chao,
Prof. Dr. D.-S. Liu
School of Chemistry and Chemical Engineering
Shanxi University
92 Wucheng Road, Taiyuan, 030006 (P. R. China)
Fax: (+86) 351-7011-688
E-mail: xhwei@sxu.edu.cn
dsliu@sxu.edu.cn
Prof. Dr. M. F. Lappert
Department of Chemistry
University of Sussex
Brighton, BN1 9QJ (UK)
Fax: (+44) 1273-677196
E-mail: m.f.lappert@sussex.ac.uk

[**] We thank the NSFC (No. 20572065, No. 20472046) and SXNSF (20021010) for funding. L = $\eta^6{:}\eta^6\text{-}C_6H_6$, *N,N′*-tmeda.

corresponding Figure 3 a and b illustrate their polymeric structures, built from the monomers by η^6:η^6-C_6H_6 (**1**) or *N*,*N*′-tmeda (**2**) as bridges between K ions of adjacent units.

The monomeric unit of **1** has a twofold rotation axis along the Na⋯Na″ vector, which relates, for example, K and K′, an inversion center *M* (the midpoint of the Na⋯Na″ vector), and a mirror plane perpendicular to the rotation axis relating, for example, O1 and O‴. The rhomboidal NaO3Na″O3′ core, which is symmetrically fused through NaO3 (or O3′Na″) to a distorted cube (e.g., comprising as vertices KO1LiO2-Li‴O1‴*M*O3). In addition to the core, the following arrays of atoms are also coplanar: LiLi′Li″Li‴, KNaK′Na″, LiLi‴NaNa″Li′Li″, LiLi‴O1O1‴, O1O1′O1″O1‴, and O1NaO1′O1″Na″O1‴ with K and K′ 0.81 Å above and below that six-membered plane. Each of the rings LiO2Li‴O3, LiO1NaO3, LiO1KO2, and Li‴O1‴KO2 is puckered, with the atoms O2, Li, Li or K 0.35, 0.47, 0.42, or 0.99 Å out of the plane LiO3Li‴, O1NaO3, O1KO2, or Li‴O1‴O2, respectively; similar remarks apply to the puckered rings Li′O2′Li″O3′, Li′O1″Na″O3′, Li′O1K′O2′, and Li″O1‴K′O2 and the atoms O2′, Li′, Li′, or K′, respectively. Six of the O*t*Bu groups triply bridge metal atoms, but two centered on O3 and O3′ are quadruply bridging. The lithium atoms are three-coordinate, while the sodium and potassium atoms are four-coordinate (e.g., Na is near to O1, O1′, O3, and O3′; and K is near to O1, O1‴, O2, and the centroid *M* of the bridging benzene ring (3.590–3.692 Å) and also has close contacts to C7′ (3.312(3) Å) and C4‴ (3.394(3) Å) atoms of *tert*-butyl groups). The alkali metal *tert*-butoxides closest to **1** are those forming the isomorphous series $[Li_4M_4(OtBu)_8]$.[7,8] The Li—O*t*Bu and K—O*t*Bu distances in **1** are significantly longer than in $[Li_4M_4(OtBu)_8]$. Thus, the average Li—O*t*Bu(μ_3), Li—O*t*Bu(μ_4), and K—O*t*Bu(μ_3) bond lengths in the latter are 1.854, 1.885, and 2.643 Å, respectively, which compare with corresponding values for **1** of 1.872, 1.988, and 2.735 Å, respectively. In $[K(OtBu)]_4$[5c] and $[Na(\mu_3\text{-}OtBu)]_4[Na(\mu_3\text{-}OtBu)]_9$,[5d] the average K—O and Na—O bond lengths are 2.623 and 2.25 Å,[5d] respectively, which compare with M—O*t*Bu(μ_3) distances of 2.784 Å (M = K) and 2.297 Å (M = Na) for **1**.

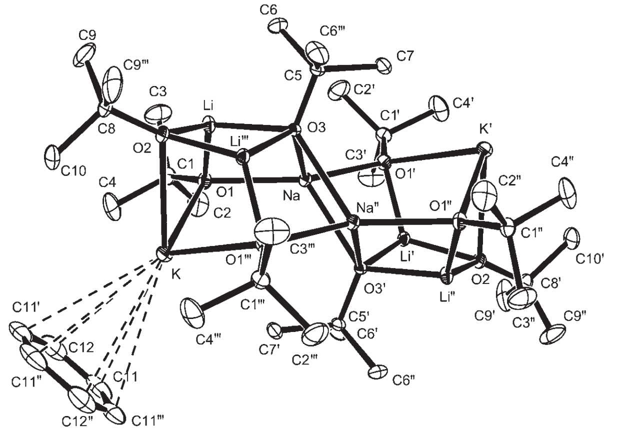

Figure 1. a) Structure of a monomeric unit of **1** (with one of its K⋯C_6H_6 bridges). Selected bond lengths [Å] and angles [°]: Li—O1 1.866(3), Li—O2 1.879(3), Li—O3 1.988(3), Na—O1 2.2971(14), Na—O3 2.4222(14), K—O1 2.7837(16), K—O2 2.686(2), K⋯C4′ 3.394(3), K′—C7 3.312(3); O1-Li-O2 120.76(16), O1-Li-O3 106.73(11), O2-Li-O3 99.49(13), Li-O2-Li‴ 82.13(16), Li-O3-Li‴ 76.74(15), O3-Na-O3′ 101.99(6), Na-O3-Na″ 78.01(16), O1K-O2 73.03(3), O1‴-K-O1 102.30(6). Symmetry transformations used to generate equivalent atoms: ′ $x,-y,z$; ″ $-x+1,y,-z+2$; ‴ $-x+1,-y,-z+2$.

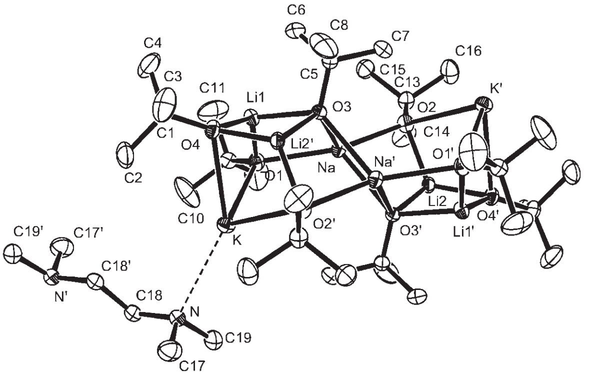

Figure 2. Structure of a monomeric unit of **2** (with one of its K⋯tmeda bridges). Selected bond lengths [Å] and angles [°]: Li1—O1 1.877(5), Li1—O3 1.994(5), Li1—O4 1.876(5), Li2—O2 1.882(5), Li2—O4′ 1.883(5), Li2—O3′ 2.008(5), Na—O1 2.326(3), Na—O2 2.324(3), Na—O3 2.424(3), Na—O3′ 2.427(2), K—O1 2.781(3), K—O2′ 2.814(3), K—O4 2.732(2), K—N 3.017(3), K—C7′ 3.400(4), K—C16′ 3.367(5); O4-Li1-O1 123.0(3), O4-Li1-O3 99.8(2), O1-Li1-O3 106.9(2), Li1-O3-Li2′ 76.1(2), Li1-O4-Li2′ 82.0(2), Li1-O1-Na 86.14(17), Li1-O(3)-Na 81.03(16), Li1-O3-Na′ 128.07(17), Li1-O1-K 78.90(17), Li1-O4-K 80.25(17), Li2-O2-Na 86.02(17), Li2-O2-K′ 80.14(17), Li2′-O3-Na 128.42(18), Li2′-O3-Na′ 80.63(16), Li2′-O4-K 82.37(18), O2-Li2-O4′ 120.8(3), O2-Li2-O3′ 105.9(2), O4′-Li2-O3″ 99.1(2), O2-Na-O1 148.93(9), Na-O3-Na′ 78.33(8), O2-Na-O3 117.95(10), O1-Na-O3 81.78(10), O2-Na-O3′ 81.62(9), O1-Na-O3′ 119.74(9), O3-Na-O3′ 101.67(8), Na-O2-K′ 110.96(9), O4-K-O1 73.48(8), O4-K-O2′ 72.35(7), O1-K-O2′ 100.72(8). Symmetry transformations used to generate equivalent atoms: ′ $-x+1,-y+2,-z+1$; ″ $-x+1,-y+1,-z$.

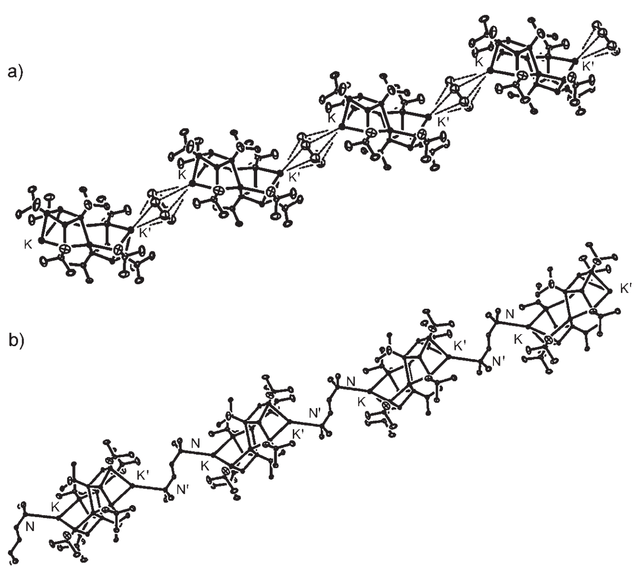

Figure 3. Extended structures of **1** (a) and **2** (b) showing the bridging benzene and tmeda molecules, respectively.

The crystalline polymeric complex **2** is built up of centrosymmetric $[Li_4Na_2K_2(OtBu)_8]$ units having essentially similar geometric parameters to those in **1**, linked through their potassium atoms via *N*,*N*′-tmeda bridges (K–N 3.017(3) Å). Bridging tmeda between K atoms seems to be unprecedented (CCDC search). The monomeric unit of **2** belongs to the triclinic crystal system, space group $P\bar{1}$, and hence, unlike **1**, has no further symmetry elements. Each potassium atom also has close contacts not only to three of the intramolecular oxygen atoms, but also to C7′ (3.400(4) Å) and C16′ (3.367(5) Å), and K and K′ are 0.75 Å above and below the O1NaO2O1′Na′O2′ plane.

In summary, we have reported herein the first heterotrimetallic homoleptic salts, namely, mixed (Li, Na, K) alkali metal *tert*-butoxides. These are crystalline polymers in which successive centrosymmetric monomeric polyhedral units of formula $[Li_4Na_2K_2(\mu_3\text{-O}t\text{Bu})_6(\mu_4\text{-O}t\text{Bu})_2]$ are joined through their terminal potassium ions by η^6:η^6-C_6H_6 (**1**) or *N*,*N*′-tmeda (**2**) bridges. They were obtained in high yield by mixing the three individual MO*t*Bu compounds in appropriate (2:1:1) stoichiometry in benzene for **1** (and for **2**, by final addition of tmeda), but their exclusive formation was independent of this chosen ratio of alkali metal alkoxides. Each of **1** and **2** in benzene solution is tetranuclear and behaves as a superbase showing symbiotic deprotonating ability when exposed to toluene at ambient temperature, as compared not only with individual Li, Na, or K *tert*-butoxides but also with binary mixtures of any two of these metal alkoxides. We hope to examine related systems, using as third component Rb, Cs, or Mg *tert*-butoxide and to compare the relative deprotonating strengths of these superbases.

Experimental Section

All manipulations were carried out under vacuum or argon by using Schlenk techniques.

1: NaO*t*Bu (1.06 g, 11.05 mmol) and KO*t*Bu (1.24 g, 11.05 mmol) were successively added to a stirred solution of LiO*t*Bu (1.77 g, 22.11 mmol) in benzene (25 mL) at 5 °C. The resulting solution was allowed to warm to room temperature, stirred for 12 h, then concentrated to about 15 mL and set aside for a few days at room temperature to give colorless crystals of **1** (3.29 g, 73 % yield), m.p. 176–178 °C; C,H analysis calcd (%) for $C_{32}H_{72}K_2Li_4Na_2O_8$: C 52.2, H 9.85; found: C 52.8, H 9.96 (coordinated benzene was removed prior to analysis); ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 1.42$ ppm; ^{13}C NMR (75.5 MHz, C_6D_6, 298 K): $\delta = 36.32$ ($C(CH_3)_3$), 66.81 ppm ($C(CH_3)_3$); ^{7}Li NMR (116.6 MHz, C_6D_6, 298 K): $\delta = 1.34$ ppm; ^{23}Na NMR (79.4 MHz, C_6D_6, 298 K): $\delta = 16.6$ ppm ($\Delta\nu_{1/2} = 2.85$ kHz).

2: Using a similar procedure as for **1**, except that the appropriate portion of tmeda was added before crystallization, yielded **2** (82 %), m.p. 146–147 °C; C,H,N analysis calcd (%) for $C_{32}H_{88}K_2Li_4Na_2N_2O_8$: C 53.5, H 10.40, N 3.28; found: C 52.8, H 10.03, N 3.06; ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 1.20$ (s, 72 H; $C(CH_3)_3$), 2.21 (s, 12 H; $\{N(CH_3)_2\}_2$), 2.46 ppm (s, 4 H, $(CH_2)_2$); ^{13}C NMR (75.5 MHz, C_6D_6, 298 K): $\delta = 36.49$ ($C(CH_3)_3$), 45.92 (tmeda), 67.06 ($C(CH_3)_3$), 67.86 ppm (tmeda); ^{7}Li NMR (116.6 MHz, C_6D_6, 298 K): $\delta = 1.42$ ppm; ^{23}Na NMR (79.4 MHz, C_6D_6, 298 K): $\delta = 6.20$ ppm ($\Delta\nu_{1/2}$=1.40 kHz).

Received: November 16, 2007
Revised: February 16, 2008

Keywords: heterometallic complexes · lithium · O ligands · potassium · sodium

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[11] Crystal structure data for **1**: $C_{38}H_{78}K_2Li_4Na_4O_8$, $M_r = 814.94$, colorless cubic crystal, approximately $0.30 \times 0.20 \times 0.20$ mm^3. graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 213$ K; monoclinic, space group *C2m*; $a = 16.255(9)$, $b = 12.862(7)$, $c = 13.657(7)$ Å; $\beta = 112.600(6)°$; $V = 2636(2)$ Å^3; $Z = 2$, $\mu = 0.234$ mm^{-1}, $\rho_{calcd} = 1.027$ Mg m^{-3}, $2\theta_{max} = 50.02°$, 5281 reflections collected, of which 2425 unique reflections were used ($R_{int} = 0.0304$). $R1 = 0.0839$ [for 1852 reflections with $I > 2\sigma(I)$], $wR_2 = 0.2456$ and $S = 1.058$ for 129 parameters. Largest diffraction peak/hole 1.231/−0.538 e Å^{-3}. **2**: $C_{38}H_{88}K_2Li_4N_2Na_4O_8$, $M_r = 853.04$, colorless block crystal, approximately $0.40 \times 0.30 \times 0.30$ mm^3. graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 213$ K; triclinic, space group $P\bar{1}$; $a = 10.478(5)$, $b = 10.612(5)$, $c = 14.175(6)$ Å; $\alpha = 105.68(5)$, $\beta = 99.93(5)$, $\gamma = 108.40(5)°$; $V = 1381.4(10)$ Å^3; $Z = 1$, $\mu = 0.227$ mm^{-1}, $\rho_{calcd} = 1.025$ Mg m^{-3}, $2\theta_{max} = 50.02°$, 5775 reflections collected, of which 4790 unique reflections were used ($R_{int} = 0.0140$). $R1 = 0.0687$ [for 3924 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1869$ and $S = 1.073$ for 261 parameters. Largest diffraction peak/hole 0.541/−0.305 e Å^{-3}. Data for **1** and **2** were collected on a Bruker SMART APEX diffractometer. The structures were solved and refined to convergence on F^2 by using published programs and techniques (G. M. Sheldrick, SHELXS and SHELXL-97, University of Göttingen, Germany, **1997**). All hydrogen atoms were added geometrically and refined by using a riding model. CCDC-666579 (**1**) and -666580 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.