Lithium and potassium aminoalkoxides

Abstract: The structures of the Group 1 metal aminoalkoxides Li[OCH(CH₂CNMe₂)₂] (1) and K[OCH(CH₂CNMe₂)₂]-H OCH(CH₂CNMe₂)₂ (2) have been determined. 1 is a hexameric drum in which two Li₃O₃ rings are joined co-facially, whereas 2 is tetrameric and adopts a K₄O₄ ladder structure, novel for homoleptic potassium alkoxides.

Keywords: aminoalkoxide; lithium; potassium; X-ray.

Introduction

Group 1 metal alkoxides are key reagents in a variety of synthetic protocols, particularly in conjunction with metal alkyls where they act as superbases (Bradsm and Verkrujsse, 1987; Bradsm, 1990; Lochmann, 2000) and precursors to alkoxy derivatives of less electropositive metals (Bradley et al., 1978; Veith et al., 1998), themselves closely related species [Li(dmae)]₄ (Hdmae=HOCH₂CH₂NMe₂, dimethylaminoethanol), in which the hexagonal structural motif previously seen for LiOSiMe₂(naphthyl) (Bazhenova et al., 1987), LiOCMe₂Ph (Chisholm et al., 1991a), LiOCMe₂PET (Jones et al., 1992), LiO(CH₂)CNMe₂ (Willard and Carpenter, 1985) and lithium 1-methyl-(hydroxymethyl) pyrrolidine (Strohmann et al., 2004). It is, however, in contrast to the octameric structure of the closely related species [Li(dmae)]₄, where the hexagonal drum in 1 is capped along one side by a further [Li(dmae)]₄ unit (Andrews et al., 2002). The structure of Li(tdmap) [Htdmap=HOC(CH₂NMe₂)₂, 1,3-bis(dimethylamino)-2-(dimethylaminomethyl)-propan-2-ol] has also been reported and is a dimer; however, the structure is influenced by the inclusion of two equivalents of LiNMe₂ in the structure (Müller and Schätzle, 2004). Both 1 and Li(dmae) use only one pendant NMe₂ group for coordination to lithium, the second such ligand in 1 remaining free for further elaboration. We thus conclude that it is steric bulk of the ligand that distinguished the degree of oligomerisation in two structures. Around the Li₃O₃ ring, the Li-O bond lengths alternate between short and long [e.g., Li(1)-O(5) 1.905(5), Li(1)-O(4) 1.936(4) Å], implying some degree of covalent vs. coordinate nature, although the data are at the limit of the ±3σ rule; Li-O bonds within the Li₃O₃ rings that link hexagonal faces are generally longer [1.957(4)–1.986(4) Å]. The tetrahedral coordination about lithium

Results and discussion

Compounds 1 and 2 were prepared by deprotonation of Htdmap by LiBu₄ and KH, respectively. Both are air-sensitive solids (particularly 2) soluble in common organic solvents.

Our own interest in the chemistry of metal derivatives of functionalised alkoxides as precursors for the chemical vapor deposition of metal oxide thin films (Hollingsworth et al., 2006, 2008, 2010; Johnson et al., 2008a,b) has given us the opportunity to structurally characterise both lithium and potassium salts of the bis-aminoalkoxide HOCH(CH₂NMe₂)₂ [1,3-bis-(dimethylamino)-propan-2-ol; Hbdmap], the results of which are reported herein.
Figure 1  The asymmetric unit of 1 showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Metrical data around Li(1) and O(1) as representative: Li(1)-O(1) 1.975(4), Li(1)-O(4) 1.936(4), Li(1)-O(5) 1.887(4), Li(1)-N(7) 1.815(4), O(1)-Li(1) 1.389(3), N(1)-Li(1) 2.189(2) Å, Li(1)-O(1)-Li(5) 84.02(18), Li(4)-O(1)-C(1) 111.12(19), Li(4)-O(1)-Li(5) 80.11(17), Li(1)-N(7) 124.4(2), Li(1)-O(1)-C(1) 133.7(2), Li(1)-O(1)-Li(4) 80.11(17), O(1)-Li(1)-O(4) 1.936(4), Li(1)-O(5) 1.887(4), Li(1)-N(7) 2.171(5), O(1)-Li(4) 2.114(2) – 2.189(2) Å, which is typical of those found in Li(dmae) [2.114(2) – 2.189(2) Å (Andrews et al., 2002) with each bdmap ligand is completed by the N: → Li bond [e.g., Li(1)-N(7) 2.171(5), O(1)-Li(4) 2.114(2), K(2)-O(4) 2.114(2), K(2)-N(4) 2.114(2), K(2)-N(5) 2.114(2), K(2)-O(3) 2.114(2)] with each bdmap ligand coming on and off within the timescale of the experiment.

The potassium salt 2 crystallises with one molecule of alcohol per alcoholate and is tetrameric, i.e., [K(bdmap) (Hbdmap)] (Figure 2). In its $^1$H NMR spectrum of 1, which shows that the CH, CH2, and CH3 protons show no separation between the alcohol and the alcoholate, but a very broad signal integrating to one hydrogen at ca. 11.38 ppm is consistent with the HO group of the coordinated Hbdmap; the $^{13}$C NMR spectrum shows no separation for the distinct Hbdmap/bdmap signals. The structure is built around a K2O2 ladder, viz:

![Image of K2O2 ladder structure](image)

Figure 2  The asymmetric unit of 2 showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Selected metrical data: K(1)-O(1) 2.770(2), K(1)-O(2) 2.737(2), K(1)-O(3) 2.817(2), K(1)-O(4) 2.857(2), K(1)-O(5) 2.903(2), K(1)-N(5) 2.779(3), K(1)-N(7) 3.095(3), K(2)-O(1) 2.850(3), K(2)-O(2) 2.686(3), K(2)-O(3) 2.664(2), K(2)-O(4) 2.781(2), K(2)-N(1) 3.059(3), K(2)-N(4) 3.110(3), K(2)-N(5) 3.110(3), K(2)-N(6) 3.110(3). Symmetry operation: -x, -y, -z.
and $O,N$ chelation], whereas each of the second pair spans one edge of the ladder in a $\mu_3$-$O$ and $O,N,N$ chelating mode. Thus, of the eight Hbdmap/bdmap ligands, six retain one uncoordinated amine function and only two fully utilise their bonding capacity. The two types of ligand are linked by an O-H O hydrogen bond $[O(1)-H(1)...O(2), H(1)...O(2) 1.42(6), O(1)...O(2) 2.407(4) \AA, \angle O(1)-H(1)...O(2) 155(5)^\circ; O(3)-H(3)...O(4), H(3)...O(4) 1.34(6), O(3)...O(4) 2.407(3) \AA, \angle O(1)-H(1)...O(2) 157(5)^\circ]$. The generally strained nature of the bonding makes discerning trends in metrical data difficult, and only broad generalisations can be made. K-O bonds involving the $\mu_3$-$O$ $[2.770(2)-2.857(2) \AA]$ are generally shorter than those involving the $\mu_3$-$O$ $[2.864(2)-2.903(2) \AA]$, whereas the $N\rightarrow K$ are generally long $[2.947(3)-3.110(3) \AA]$, save for the chelating nitrogen associated with the $\mu_3$-$O(3)$ which is notably shorter $[K(1)-N(5) 2.779(3) \AA]$. For comparison, the $N\rightarrow K$ bonds in $Li,K$ (dmae)$_2$O are 2.848(5) and 2.850(4) $\AA$ (Andrews et al., 2002).

The known structural chemistry of homoleptic potassium alkoxides is limited (Bradley et al., 2001). Although all the reported structures contain $K_2$O$_2$ rings, the most common structural variation is the $K_2$O$_2$ cubane (Weiss et al., 1970; McGreary et al., 1991; Veith et al., 2010), e.g., $[KO(Bu t)]_4$ (Weiss et al., 1967); other variations, i.e., polymeric $[KOMe]_{\infty}$ (Weiss, 1963), dimeric $[KOSiPh_2(OSiPh_2)_2OSiPh_2OH]_2$ (Laermann et al., 1997) and hexameric drum $[KO(CH_2)CMe_6]$ (Willard and Carpenter, 1986), are extremely rare. Precedent for alcohol-solvated potassium alkoxides exists in the form of $[KOBu(BOBu)]_n$, which forms a polymeric structure built up of hydrogen-bonded $K_2$O$_2$ rings (Chisholm et al., 1991b). The structure of 2 is thus a new variation for this class of alkoxide.

In contrast to the $^1H$ NMR spectrum of 1, that of 2 shows the methylene protons $[CH_2]$ are non-equivalent by virtue of the locked arrangement of the ligand bridging two potassium centres. However, there are no separate signals for the free, non-coordinated arm of one bdmap ligand, suggesting some degree of structural non-rigidity in solution, nor does the spectrum differentiate the protonated and non-protonated alkoxides present.

In addition to these comments on the relationship of 1 and 2 to specific analogues, it is worth noting that both structures conform to the “ring-laddering/ring stacking” principles first enunciated in the seminal work of Snailh and Mulvev on lithium amides (Gregory et al., 1991; Mulvev, 1991) and, subsequently, on intermetallic Group 1 amides (Mulvev, 1998) and later developed to include lithium heterocarboxylates (Downard and Chivers, 2001); similar structural principles also apply to lithium enolates (Seebach, 1988). Thus, 1 can be described either as a ladder of three $[Li_2O_2]$ dimers which cyclise head-to-tail or as two six-membered $[Li_2O_2]$ trimers which associate face-to-face. Similarly, 2 is a ladder in which two $[K_2O_2]$ dimers join to form a linear array of three fused $K_2O_2$ rings.

### Experimental

#### General procedures

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Hexanes and toluene solvents were dried using a commercially available solvent purification system (Innovative Technology Inc. MA, USA) and degassed under argon prior to use. Deuterated benzene ($CD_2$) NMR solvent was purchased from Fluorochem Hadfield, UK and dried by refluxing over potassium before isolating via vacuum distillation. All dry solvents were stored under argon in Young’s ampoules over 4 A molecular sieves. 1,3-Bis(dimethylamino)-2-propanol (Hbdmap) was dried and purified by distillation prior to use. Solution $^1H$ and $^{13}C(H)$ NMR spectra were recorded with a Bruker Avance 300 spectrometer, whereas $^7Li$ NMR spectra were recorded using a Bruker Avance 500 spectrometer Bruker Coventry, UK. All spectra were obtained at ambient temperature ($25^\circ C$). $^1H$ and $^{13}C$ NMR chemical shifts are given in parts per million and referenced internally to residual non-deuterated solvent resonances. The following abbreviations are used: s (singlet), d (doublet), qi (quintet), dd (doublet of doublets), tt (triplet of triplets) and br (broad).

#### Synthesis of Li$[O(CH(NMe_2)])_2](1)$: A stirred solution of HOCH$(CH(NMe_2))_2$ (Hbdmap) (0.65 ml, 4 mmol) in 20 ml of hexanes was slowly treated at -78°C with a 2.5-m solution of BuLi in hexanes (1.6 ml, 4 mmol). The solution was allowed to warm to ambient temperature and refluxed for 24 h, before the volume was reduced in vacuo. Crystallisation from the reaction solution at -28°C afforded the product as colourless crystals. Yield: 0.340 g, 56%, m.p 216 – 219°C. Analysis, found (calc. for $C_{14}H_{35}KN_4O_2$: $C$ 50.7 (50.9), $H$ 10.5 (10.7), $N$ 16.8 (17.0)%. $^1H$ NMR (300 MHz, $C_6D_6$): 11.38 (br s, 1H, OH), 4.04 (tt, 2H, $C_2$CHO, 6.7), 2.41 (d, 4H, $CH_2$, $CH_2CHO$, $J_{CHCH}=7.6$), 2.33 (s, 2H, NCH$_2$). $^{13}C$ NMR (75.5 MHz, $C_6D_6$): 71.3 (s, $C_2$CHO), 46.5 (s, NMe$_2$).

#### Synthesis of K$[O(CH(NMe_2)])_2]HOCH(CH(NMe_2))_2(2)$: HOCH$(CH(NMe_2))_2$ (Hbdmap) (3.26 ml, 20 mmol) was added dropwise to a stirred toluene (20 ml) solution of KH (0.401 g, 10 mmol) and the mixture refluxed for 24 h. The toluene was then removed under reduced pressure to yield a golden oil. Crystallisation from the crude oil at ambient temperature afforded the product as yellow, highly air-sensitive crystals. Yield: 2.618 g, 79%, m.p 38—40°C. Analysis, found (calc. for $C_{16}H_{40}KKN_2O_2$: $C$ 50.7 (50.9), $H$ 10.5 (10.7), $N$ 16.8 (17.0)%. $^1H$ NMR (300 MHz, $C_6D_6$): 11.38 (br s, 1H, OH), 6.04 (t, 2H, $CHO$, $J_{CHCH}=7.6$), 2.86 (dd, 4H, $C_2$CHO), $J_{CHCH}=11.9$, $J_{CHCH}=4.7$), 2.35 (dd, 4H, $C_2$CHO, $J_{CHCH}=11.9, J_{CHCH}=4.7$). $^{13}C$ NMR (75.5 MHz, $C_6D_6$): 68.4 (NCH$_2$), 65.8 (OCH), 66.6 (NMe$_2$).

#### Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data
were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-Kα radiation (λ = 0.71073 Å). Structure solution followed by full-matrix least squares refinement was performed using the WinGX-1.70 (University of Glasgow, Scotland) suite of programmes (Farrugia, 1999). Corrections for absorption (multi-scan) were made in the case of 1. For 2, a pseudo-merohedral twin law to account for 30% twinning (180.0° rotation about -1, 1, 0. direct lattice direction) was included in the refinement model for this structure. Although the R factors remain somewhat higher than desirable, the structure has converged well and is completely unambiguous. Data were truncated to a max Bragg angle of 25° because of intensity drop-off at higher resolution. For 2, the asymmetric unit consists of half a tetranuclear complex which is located around a centre of inversion at the mid-point of the central K₂O₂ ring. Two out of the four ligands are disordered over two sites in the ratio 65:35. The OH hydrogen atoms have been located in the difference Fourier map and were freely refined.

Supporting information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 897223 and 897224 for 2 and 1, respectively. Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Table 1 Crystal data and structure refinement for compounds 1 and 2.

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References


