Multidentate Aminoalkoxides. Synthesis and Complexation Behavior to Lithium and Sodium

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The tris(dimethylaminomethyl)-substituted alcohol $(R_2NCH_2)_3COH$ (R = Me: **1**) was synthesized by reaction of 1-chloro-2,3-epoxy-2-chloromethylpropane with a large excess of 40% aqueous $HNMe_2$ in 95% yield as colorless liquid (b.p. 87 °C/1 mbar). Similar syntheses led to the respective amino alcohols with R = Et, CH_2Ph. The dimethylamino alcohol **1** was characterized crystallographically as hydrochloride salt **2**. Reaction of **1** with elemental sodium in toluene gave the tetrameric alcoholate $[(Me_2NCH_2)_3CONa]_4$ (**3**) which has a heterocubane structure in the solid state. In addition to three oxygen atoms, each sodium atom is coordinated by two amino groups from two different adjacent ligands (Na-N 2.529(3)/2.628(3) Å). Reaction of **1** with $LiNMe_2$ afforded the lithium alcoholate which crystallized as dimeric mixed-anion aggregate $[(Me_2NCH_2)_3COLi{\cdot}LiNMe_2]_2$ (**4**). It has a four-rung ladder structure consisting of two four-membered $Li(NMe_2)LiO$ rings connected through a central LiOLiO ring. All ligand amino groups are lithium-coordinated (Li-N 2.117(6)/2.101(6)/2.218(6) Å) as is the amido nitrogen atom (Li-N 1.964(6)/2.027(6) Å). Reaction of **1** with Li*t*Bu in *n*-hexane also led to deprotonation at oxygen. In addition, in one ligand one methyl group is deprotonated, in a second one two methyl groups are lithiated leading to doubly and triply charged anions, respectively. The product crystallizes as the dimeric mixed-anion aggregate $[(^-H_2CN(Me)CH_2)(Me_2NCH_2)_2CO^-{\cdot}5\ Li^+{\cdot}\ (^-H_2CN(Me)CH_2)_2(Me_2NCH_2)CO^-]_2$ (**5**) having a core of 10 Li^+ cations, 4 alcoholate oxygen atoms, and 6 N(Me)-CH_2^- groups.

Key words: Aminoalcohols, Lithium Complexes, Sodium Complexes, Structure Determination

Introduction

Mixed-anion aggregates of the alkali metals have attracted considerable interest because these cations have a strong tendency to crystallize with just one counteranion. Also mixed-metal compounds of the alkali metals are rare. This is most probably due to the predominantly ionic nature of group 1 metal salts which is also true for lithium organyls. Crystallization of monovalent cations with more than one counteranion should be strongly favored by the formation of a solid solution (mixed crystals), which is increasingly more improbable with increasing complexity of the anion, however. This is also born out by the well known structural diversity of homologous alkali metal salts of more complex anions.

Despite considerable recent effort the number of crystallographically characterized mixed-anion aggregates of the alkali metals (and magnesium) is still small. In particular, we now have crystallographic information on mixed-anion aggregates containing two different carbon-centered anions [1, 2], carbon- and nitrogen-centered anions [2c, 3], carbon- and oxygen-centered anions [4 – 7], nitrogen- and oxygen-centered anions [8, 9], as well as two different oxygen-centered anions [10, 11]. Some of these aggregates are also mixed-metal complexes [3a, e, f, g, i, 9b, c], in one case even three metals (Li, Na, K) were found to act concomitantly as counterions [9d].

Apart from the inherent challenge to find more precise criteria which favor mixed-anion and mixed-metal aggregates of the alkali metals, further impetus for a more specific search for mixed-anion compounds came from the suggestion that mixed alkyl/alkoxide [4] or alkyl/phenoxide [6] aggregates of group 1 metals may serve as models for superbases [12]. Mixed aggregates of Li*n*Bu with chiral alcoholates were successfully employed for the enantioselective alkylation of aldehydes [5], and mixed alkyl/phenoxides of lithium have been used as initiators for the ring-opening polymer-

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ization of L-lactides [7]. Certain multidentate anions were found to be particularly effective in complexing more alkali metal cations than required for charge neutrality thereby leading to strongly Lewis-acidic mixed-anion and potentially also mixed-metal aggregates [8]. In the case of lithium some of these systems were aptly coined Li^+ sponges [8a].

Following the recent synthesis of the phosphinomethyl-substituted alcohols $(Me_2PCH_2)_2$ CHOH and $(Me_2PCH_2)_3COH$ we could show that after deprotonation they are efficient ligands to lithium and sodium including phosphine coordination to these metals [13]. The tertiary lithium alcoholate is easily capable to bind more than one lithium cation under formation of mixed-anion aggregates. Further deprotonation occurred at its methylene carbon atoms leading finally (after loss of Li_2O) to the tris(phosphino)-substituted trimethylene-methane dianion, which itself crystallized as mixed-anion aggregate [13]. This work prompted us to investigate also the synthesis and deprotonation with strong bases of the corresponding aminomethyl-substituted alcohol $(Me_2NCH_2)_3COH$ (**1**). The secondary alcohol $(Me_2NCH_2)_2CHOH$ [14] has already been the subject of similar studies [9e].

Experimental Section

All experiments were carried out with rigorous exclusion of air and moisture under purified dry argon in standard Schlenk techniques. Solvents were dried under argon over sodium or sodium-potassium alloy and were freshly distilled prior to use. Reagents: 1-chloro-2,3-epoxy-2-chloromethylpropane: from 3-chloro-2-chloromethyl-1-propene (95%, Acros) and 3-chloroperbenzoic acid (Acros) at 0 °C in chloroform by standard procedures; 40% dimethylamine/H_2O (Fluka); 2.5 M Li*n*Bu/hexane (Aldrich); 1.7 M Li*t*Bu/hexane (Merck); sodium (Riedel-deHaen); $LiNMe_2$: from 65 ml of 2.5 M Li*n*Bu/hexane (160 mmol) and 11.2 g (250 mmol) of gaseous $HNMe_2$ (Fluka) condensed upon the Li*n*Bu, subsequent addition of 60 ml of hexane and isolation of the solid by centrifugation. Yield: 7.8 g (153 mmol; 95%). Instruments: NMR spectra: Bruker WM-250 (^{1}H), JEOL JMN-GX-400 (^{1}H, ^{13}C (101 MHz), ^{7}Li (155 MHz)); Bruker AMX-600 (^{1}H, ^{13}C (152 MHz)). Standards: ^{1}H/^{13}C NMR: internal toluene, external tetramethylsilane, TMS, or internal methanol-d_4; ^{7}Li NMR: external 1 M LiBr in THF-d_8. Chemical shifts are in ppm with negative signs referring to high field. ^{1}H and ^{13}C chemical shifts are reported relative to TMS while those of ^{7}Li are reported relative to the standard mentioned above. IR spectra : Perkin-Elmer 1760 X FT-IR. EI-MS: Varian MAT 112S (70 eV); FAB-MS: Finnigan MAT312/AMD 5000 (700 eV, 70 °C). The elemental analyses were performed by the microanalytical laboratory of the University of Konstanz on a Heraeus CHN-O-Rapid instrument. Melting points were determined in sealed capillaries in a Büchi 530 apparatus and are uncorrected.

*Synthesis of $(Me_2NCH_2)_3COH$ (**1**)*

A 500 ml two-necked flask fitted with a dropping funnel and a thermometer was charged with 120 ml of a 40% aqueous solution of dimethylamine (0.95 mol). 1-chloro-2,3-epoxy-2-chloromethylpropane (10.1 g, 72 mmol) was slowly added dropwise under stirring whereupon the temperature of the cloudy solution rose from 14 to 40 °C. The dropping funnel was replaced by a reflux condenser and the solution was refluxed for 6 h at 90 °C which was accompanied by gas evolution (mostly $HNMe_2$). After standing overnight, the solution was cooled in an ice bath and 30 g of NaOH was slowly added in small portions which resulted in further gas evolution and phase separation. After addition of chloroform the phases were separated and the aqueous phase was washed with several small portions of chloroform until a total of 250 ml of chloroform was used. The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated *in vacuo* (1 mbar) leaving 20.3 g of an orange liquid. Distillation at 1 mbar yielded at 87 °C 13.9 g (68 mmol, 95%) of colorless **1** which slowly crystallized at −34 °C over a period of several weeks in small crystals suspended in remaining liquid of **1**. – IR (NaCl): $\delta = 3448$ (m, br.) (O-H), 2942 (s), 2817 (s), 2769 (s), 1558 (m), 1456 (s), 1405 (m), 1264 (m), 1099 (m), 1037 (s), 858 (m), 600 (w) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 3.83$ (s (br.), 1H, OH), 2.13 (s, 6H, CH_2), 2.10 (s, 18H, CH_3). – ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 73.45$ (s, CO), 64.58 (s, CH_2), 47.57 (s, CH_3). – FAB-MS: *m/z* (%) = 204 (18) [M^+]. – $C_{10}H_{25}N_3O$ (203.33): calcd. C 59.1, H 12.4, N 20.7; found C 58.7, H 12.2, N 20.8.

Synthesis of $(Et_2NCH_2)_3COH$

The synthesis followed closely that of **1** but a 100 ml two-necked flask was used. To 40 ml (28.1 g, 380 mmol) of diethylamine 5.0 g (35 mmol) of 1-chloro-2,3-epoxy-2-chloromethylpropane was slowly added dropwise under stirring whereupon the solution turned cloudy. After refluxing at 55 °C for 7 h and standing overnight, workup was done by adding 50 ml of water and 50 ml of *n*-hexane as well as ∼ 10 g of NaOH. The organic phase was separated and the aqueous one washed with additional *n*-hexane. After drying with $MgSO_4$ the combined organic phases were distilled. At 81 °C/0.2 mbar 2.2 g (7.7 mmol, 22%) of yellowish $(Et_2NCH_2)_3COH$ distilled which crystallized as thin needles after some time. – IR (NaCl): $\delta = 3447$ (w) (O-H), 2967 (s), 2804 (s), 1457 (m), 1386 (m), 1294 (m), 1202 (m), 1061 (m), 781 (m), 526 (w) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$,

Table 1. Crystal structure data for compounds **2** – **5**.

	2	**3**	**4**	**5**
Formula	$C_{10}H_{28}Cl_3N_3O$	$C_{40}H_{96}N_{12}Na_4O_4$	$C_{24}H_{60}Li_4N_8O_2$	$C_{40}H_{90}Li_{10}N_{12}O_4$
M_r	312.70	901.25	520.56	872.64
Crystal size [mm]	$0.2\times0.4\times0.4$	$0.3\times0.35\times0.4$	$0.2\times0.4\times0.5$	$0.2\times0.3\times0.4$
T [K]	293	183	183	183
Crystal system	orthorhombic	tetragonal	monoclinic	orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P4_2/n$ (No. 86)	$P2/n$ (No. 13)	$P2_12_12$ (No. 18)
a [Å]	9.651(5)	15.672(4)	13.491(2)	13.849(1)
b [Å]	10.935(4)	15.672(4)	8.864(2)	15.254(1)
c [Å]	15.449(4)	11.255(5)	14.026(3)	12.923(1)
β [deg.]	90.	90.	92.13(1)	90.
V, Å^3	1630(1)	2764(2)	1676.2(5)	2730.0(4)
Z	4	2	2	2
$D_{calcd.}$ [gcm^{-3}]	1.274	1.083	1.031	1.062
μ(Mo-K$_\alpha$) [cm^{-1}]	5.54	0.98	0.65	0.66
F(000) [e]	672	992	576	952
hkl Range	$+11,+12,+18$[a]	$+18,-18,+13$	$\pm16,-10,-16$	$+16,-18,-15$[a]
Scan	ω	ω	ω	$\theta/2\theta$
$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.595	0.595	0.595	0.595
Refl. measured	3322	2634	3090	2901
Refl. unique	2872	2445	2961	2848
R_{int}	0.101	0.048	0.049	0.150
Param. refined	155	136	172	300
R(F)/wR(F^2) (all refl.)[b]	0.186/0.207	0.135/0.152	0.189/0.160	0.083/0.126
x(Flack)	0.5(2)	–	–	0(2)
GoF (F^2)[b]	0.99	1.03	0.98	1.04
$\Delta\rho_{fin}$ (max/min) [eÅ^{-3}]	0.44/-0.44	0.18/-0.22	0.21/-0.19	0.23/-0.21

[a] Plus Friedel opposites. [b] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_c|$; $wR(F^2)=\{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\ \Sigma[w(F_o{}^2)^2]\}^{1/2}$; $GoF(F^2)=S=\{\Sigma[w(F_o{}^2-F_c{}^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflexions and p is the total number of parameters refined; $w=1/[\sigma^2(F_o{}^2)+(X\cdot P)^2+Y\cdot P)$, $P=[\max(F_o{}^2,0)+2F_c{}^2]/3$. **2**: X = 0.099; **3**: X = 0.626, Y = 0.9726; **4**: X = 0.066, Y = 0.0805; **5**: X = 0.0585, Y = 1.0514.

25 °C): δ = 4.54 (s, 1H, OH), 2.62 (q, ^3J(HH) = 4.8 Hz, 12H, CH_2Me), 2.46 (s, 6H, CH_2CO), 0.95 (t, ^3J(HH) = 4.8 Hz, 18H, CH_3). – ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 73.53 (s, CO), 60.58 (s, *C*H$_2$CO), 48.66 (s, *C*H$_2$Me), 12.27 (s, CH_3). – FAB-MS: *m/z* (%) = 288 (69) [M$^+$]. – $C_{16}H_{37}N_3O$ (287.49): calcd. C 66.9, H 13.0, N 14.6; found C 66.4, H 13.9, N 13.9.

Synthesis of [(PhCH$_2$)$_2$NCH$_2$]$_3$COH

The synthesis followed closely that of **1** but a 50 ml two-necked flask was used. To 25 ml (∼ 95%, 25.6 g, 120 mmol) of dibenzylamine 5.0 g (35 mmol) of 1-chloro-2,3-epoxy-2-chloromethylpropane was slowly added dropwise under stirring which resulted in the immediate precipitation of a solid. Stirring was continued for 6 h at 100 °C. After standing overnight, the solid was filtered off and washed with 50 ml of *n*-hexane. The mother liquor and the *n*-hexane used for washing were combined. Evaporation of the solvents *in vacuo* and subsequent removal of excess (PhCH$_2$)$_2$NH by distillation at 0.2 mbar and 118 °C left a solid which was recrystallized several times from methanol. Yield: 0.8 g (1.2 mmol, 7%). M.p. 105 °C. – IR (KBr): ν = 3514 (m) (O-H), 3025 (s), 2803 (s), 1952 (w), 1870 (w), 1808 (w), 1601 (m), 1494 (s), 1452 (s), 1371 (s), 1256 (s), 1122 (s), 1084 (s), 1072 (m), 1050 (m), 1026 (s), 968 (s), 942 (m), 745 (s), 699 (s), 500 (m), 470 (m) cm^{-1}. – ^{1}H NMR (600 MHz, C_6D_6, 25 °C): δ = 7.29 (d, ^3J(HH) = 4.9 Hz, 2H, *o*-H), 7.17 (t, ^3J(HH) = 5.0 Hz, 2H, *m*-H), 7.10 (t, ^3J(HH) = 4.9 Hz, 1H, *p*-H), 3.97 (s, 1H, OH), 3.62 (s, 12H, CH_2Ph), 2.55 (s, 6H, CH_2CO). – ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 140.04 (s, *ipso*-C), 129.53 (s, *o*-C), 128.48 (s, *m*-C), 127.14 (s, *p*-C), 75.48 (s, CO), 60.27 (s, *C*H$_2$CO, *C*H$_2$Ph). – FAB-MS: *m/z* (%) = 660 (25) [M$^+$]. – $C_{46}H_{49}N_3O$ (659.92): calcd. C 83.7, H 7.5, N 6.4; found C 83.6, H 7.8, N 6.00.

*Synthesis of [(Me$_2$HNCH$_2$)$_3$COH]$^{3+}$ 3 Cl$^-$ (**2**)*

A 25 ml round-bottom flask was charged with 1.0 g (4.9 mmol) of **1** and 10 ml of a HCl solution in 1,4-dioxane (about 77 mmol) was added from a dropping funnel. The white precipitate was stirred overnight, filtered off, washed with 1,4-dioxane, and dried *in vacuo*. The raw product (1.1 g) was recrystallized from 15 ml of methanol. Yield: 0.8 g (2.6 mmol, 52%). M.p.: no melting was observed until 220 °C. – ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 3.67 (s, 6H, CH_2), 3.10 (s, 18H, CH_3). – ^{13}C {^{1}H} NMR (101 MHz, D_2O/methanol-d_4, 25 °C): δ = 71.10 (s, CO), 62.91 (s, CH_2), 47.56 (s, CH_3). – $C_{10}H_{28}Cl_3N_3O$ (312.71): calcd. C 38.4, H 9.0, N 13.4; found C 38.4, H 9.1, N 13.4.

Table 2. Selected interatomic distances (Å) and angles (°) for **2** with estimated standard deviations in units of the last significant figure in parentheses.

Distances			
C1-O1	1.425(9)	N1-C12	1.49(1)
C1-C11	1.51(1)	N1-C13	1.51(1)
C1-C21	1.54(1)	N2-C22	1.50(1)
C1-C31	1.53(1)	N2-C23	1.48(1)
N1-C11	1.53(1)	N3-C32	1.50(1)
N2-C21	1.49(1)	N3-C33	1.51(1)
N3-C31	1.51(1)		
Angles			
O1-C1-C11	111.8(7)	C12-N1-C13	109.6(8)
O1-C1-C21	106.1(1)	C21-N2-C22	110.9(7)
O1-C1-C31	110.7(6)	C21-N2-C23	112.8(7)
C1-C11-N1	113.3(7)	C22-N2-C23	110.0(7)
C1-C21-N2	114.3(7)	C31-N3-C32	110.5(7)
C1-C31-N3	113.9(7)	C31-N3-C33	111.8(6)
C11-N1-C12	111.6(7)	C32-N3-C33	109.7(7)
C11-N1-C13	112.3(7)		

*Synthesis of [(Me$_2$NCH$_2$)$_3$CONa]$_4$ (**3**)*

In a 30 ml Schlenk tube 1.0 g (4.9 mmol) of **1** was dissolved in toluene. After addition of 160 mg (7 mmol) of elemental sodium the mixture was stirred for 5 h at 100 °C. At the surface of the molten sodium nugget evolution of gas was clearly visible. The excess sodium was filtered off and the remaining solution was left standing at room temperature. After several days colorless crystals of **3** formed which were isolated and dried *in vacuo*. Yield: 0.3 g (1.3 mmol, 27%). – IR (PE): ν = 1368 (m), 1264 (m), 1099 (m), 1037 (s), 858 (m) cm^{-1}. – ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): α = 2.29 (s, 6H, CH$_2$), 2.27 (s, 18H, CH$_3$). – ^{13}C {^{1}H} NMR (101 MHz, THF-d$_8$, 25 °C): δ = 75.29 (s, CO), 65.64 (s, CH$_2$), 48.19 (s, CH$_3$).

*Synthesis of [(Me$_2$NCH$_2$)$_3$COLi·LiNMe$_2$]$_2$ (**4**)*

In a 70 ml Schlenk tube 0.96 g (18.9 mmol) of LiNMe$_2$ was suspended in 36 ml of THF and cooled to −40 °C. 1.1 g (5.5 mmol) of **1** was added with a syringe resulting in a brown suspension. The reaction mixture was stirred at room temperature overnight. After centrifugation (5 min at 2000 rpm) the supranatant red solution was removed with a syringe and the solvent was partly evaporated *in vacuo*. After several days at −34 °C colorless crystals formed which were dried *in vacuo*. Yield: 0.2 g (0.8 mmol, 14%). – IR (PE): ν = 2461 (m), 1386 (m), 1249 (m), 1205 (m), 1136 (s), 1022 (m), 933 (s), 560 (m) cm^{-1}. – ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ = 2.48 (s, 6H, LiNMe$_2$), 2.30 (s, 6H, CH$_2$), 2.23 (s, 18H, CH$_3$). – ^{13}C {^{1}H} NMR (101 MHz, THF-d$_8$, 25 °C): δ = 72.60, 71.29 (s, CO/CH$_2$), 49.43, 49.27 (s, NCH$_3$/[N(CH$_3$)$_2$]$^-$). – ^{7}Li {^{1}H} NMR (155 MHz, THF-d$_8$, 25 °C): δ = 6.51 (s).

Table 3. Selected interatomic distances (Å) and angles (°) for **3**. For symmetry code see Fig. 2.

Distances			
Na-O	2.311(2)	N1-C11	1.470(4)
Na-O^2	2.258(2)	N2-C21	1.473(4)
Na-O^3	2.309(2)	N3-C31	1.478(4)
Na-N2	2.530(3)	N1-C12	1.433(6)
Na-N3^3	2.627(3)	N1-C13	1.408(7)
C1-O	1.379(4)	N2-C22	1.458(6)
C1-C11	1.552(4)	N2-C23	1.455(5)
C1-C21	1.545(5)	N3-C32	1.454(4)
C1-C31	1.543(5)	N3-C33	1.459(4)
Angles			
Na-O-Na^2	83.09(7)	O^3-Na-N3^3	71.84(8)
Na-O-Na^3	84.23(8)	N2-Na-N3^3	102.89(9)
Na^2-O-Na^3	88.91(8)	O-C1-C11	107.0(2)
O^2-Na-O^3	89.79(8)	O-C1-C21	111.6(3)
O^2-Na-O	97.05(8)	O-C1-C31	111.0(2)
O^3-Na-O	95.63(8)	C1-C11-N1	119.1(3)
O-Na-N2	73.55(8)	C1-C21-N2	117.5(3)
O-Na-N3^3	140.38(8)	C1-C31-N3	115.1(3)
O^2-Na-N2	111.97(9)	C21-N2-Na	103.9(2)
O^2-Na-N3^3	119.67(9)	C31-N3-Na^2	104.6(2)
O^3-Na-N2	156.4(1)		

Synthesis of [($^-$*H$_2$CN(Me)CH$_2$)(Me$_2$NCH$_2$)$_2$CO$^-$·5 Li$^+$ · (*$^-$*H$_2$C N(Me)CH$_2$)$_2$(Me$_2$NCH$_2$)CO$^-$]$_2$ (**5**)*

In a 30 ml Schlenk tube 1.0 g (4.9 mmol) of **1** was dissolved in 5 ml of *n*-hexane and cooled to −25 °C. Slowly adding 10.1 ml of a 1.7 M solution of Li*t*Bu in hexane (17.2 mmol) with a syringe resulted in boiling of the solvent. A yellowish precipitate started to form after addition of one equivalent (∼ 3.5 ml) of Li*t*Bu. After warming to room temperature the reaction mixture was stirred overnight. After centrifugation (5 min at 2000 rpm) the supranatant yellowish solution was removed with a syringe. After several days at −34 °C colorless crystals formed which were dried *in vacuo*. Yield: 0.2 g (0.9 mmol, 19%). – IR (PE): ν = 1368 (m), 1298 (m), 1244 (m), 1088 (s), 1016 (s), 930 (m), 908 (m), 787 (m), 632 (m), 446 (m) cm^{-1}. – ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): δ = 2.29 (s, 12H, CH$_2$), 2.27 (s, 33H, CH$_3$/CH$_2^-$). – ^{13}C {^{1}H} NMR (101 MHz, THF-d$_8$, 25 °C): δ = 75.33 (s, CO), 65.66 (s, CH$_2$), 48.20 (s, CH$_3$). – ^{7}Li {^{1}H} NMR (155 MHz, THF-d$_8$, 25 °C): δ = 4.52 (very broad singlet).

Structure analyses

Single crystals of **2**, **3**, **4**, and **5** suitable for X-ray diffraction were obtained as described above. Those of **3**, **4**, and **5** were mounted under nitrogen on glass fibers in an inert oil drop at 183(2) K [15]. A single crystal of **2** was mounted at room temperature in a capillary. The crystals were examined directly on a four-circle diffractometer (Enraf-Nonius CAD4) with graphite-monochromated Mo-

Table 4. Selected interatomic distances (Å) and angles (°) for **4**. Symmetry code: see Fig. 3.

Distances			
Li1-O1	1.969(6)	C1-C21	1.559(4)
Li2-O1	1.943(5)	C1-C31	1.549(5)
Li2^1-O1	1.938(5)	N1-C11	1.467(4)
Li1-N2	2.117(6)	N2-C21	1.480(4)
Li1-N3	2.101(6)	N3-C31	1.475(4)
Li2-N1	2.218(6)	N1-C12	1.463(4)
Li1-N4^1	1.964(6)	N1-C13	1.460(5)
Li2-N4	2.027(6)	N2-C22	1.459(5)
N4-C41	1.451(4)	N2-C23	1.462(5)
N4-C42	1.443(4)	N3-C32	1.466(4)
1C1-O1	1.379(3)	N3-C33	1.456(5)
C1-C11	1.555(4)		
Angles			
O1-Li1-N4^1	101.5(3)	C1-O1-Li2^1	163.9(2)
O1-Li1-N2	85.0(2)	O1-Li2-N4	136.8(3)
O1-Li1-N3	89.1(2)	O1^1-Li2-N4	100.3(3)
N2-Li1-N3	96.4(2)	O1-Li2-O1^1	97.7(2)
N2-Li1-N4^1	127.5(3)	N1-Li2-O1	82.5(2)
N3-Li1-N4^1	135.3(3)	N1-Li2-N4	111.7(2)
Li1-O1-Li2	148.1(3)	N1-Li2-O1^1	132.4(3)
Li1-O1-Li2^1	78.3(2)	C11-N1-Li2	91.7(2)
C1-O1-Li1	94.6(2)	C21-N2-Li1	98.0(2)
C1-O1-Li2	109.9(2)	C31-N3-Li1	98.2(2)

Table 5. Selected interatomic distances (Å) and angles (°) for **5**. Symmetry code: see Fig. 4.

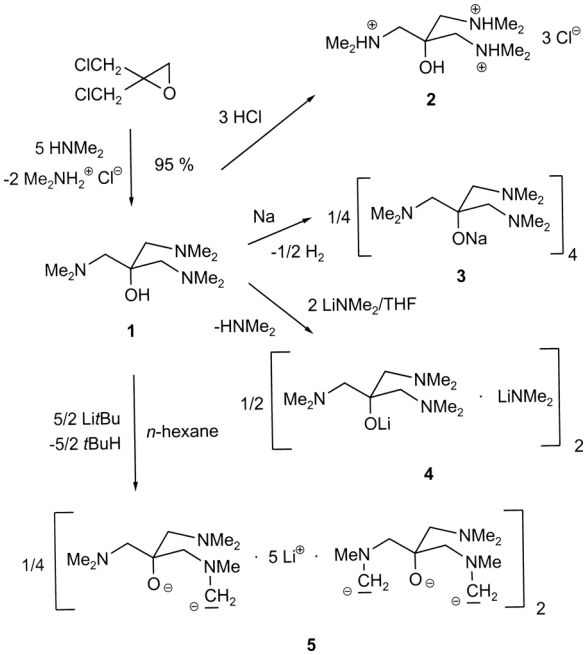
Distances			
Li1-N1	2.250(6)	Li5-O2	1.970(6)
Li1-O1	1.936(6)	Li5-N5	2.068(6)
Li2-O1	1.896(7)	Li5-C22^1	2.190(7)
Li2-N2	1.964(7)	Li5-C63^1	2.270(7)
Li2-C22	2.159(8)	Li6-O2	1.979(5)
Li2-C43	2.150(8)	Li6-C63	2.182(5)
Li3-O2	1.910(7)	N2-C21	1.470(5)
Li3-N4	2.043(7)	N2-C23	1.464(5)
Li3-C43	2.163(8)	N2-C22	1.499(5)
Li3-O1^1	1.892(7)	N4-C41	1.472(5)
1Li4-O2	2.154(6)	N4-C42	1.455(5)
Li4-N6	2.037(7)	N4-C43	1.505(5)
3Li4-C63	2.262(7)	N6-C61	1.472(4)
Li4-C22	2.329(7)	N6-C62	1.467(5)
Li4-C43	2.375(7)	N6-C63	1.500(4)
Angles			
C1-O1-Li1	116.7(3)	C21-N2-C22	112.0(3)
C1-O1-Li2	99.9(3)	C23-N2-C22	113.8(3)
C1-O1-Li3^1	117.6(3)	C41-N4-C42	110.2(3)
C2-O2-Li3	110.0(3)	C41-N4-C43	109.3(3)
C2-O2-Li4	88.7(2)	C42-N4-C43	111.9(3)
C2-O2-Li5	108.5(3)	C61-N6-C62	108.6(3)
C2-O2-Li6	119.0(6)	C61-N6-C63	111.2(3)
C21-N2-C23	111.3(3)	C62-N6-C63	111.8(3)

K_α radiation ($\lambda = 0.71069$ Å). The crystal systems indicated by preliminary search and indexing procedures were checked for higher metrical symmetry by reduced-cell calculations (DELOS [16], LePage [17]). Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle reflexions from various parts of reciprocal space carefully centered on the diffractometer. Lp and linear decay but no absorption corrections were applied. For **3**, and **4** all H atoms were calculated at idealized geometrical positions. They were included as fixed-atom contributions in final refinement cycles (**3**: $U_{iso} = 0.08$ Å^2; **4**: $U_{iso} = 0.05$ Å^2). For **2** the H atoms at N and O, for **5** those at the deprotonated methyl groups were located in difference maps, all others were calculated at idealized geometrical positions. In both structures all H atoms were included as fixed-atom contributions in final refinement cycles ($U_{iso} = 0.05$ Å^2). Refinements were done on F^2 of all reflexions with anisotropic displacement parameters for the non-H atoms. Programs used: SHELXS-/SHELXL-97 (structure solution and refinement) [18], PLATON (molecular geometry) [19], ORTEP-III (molecular drawings) [20]. Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table 1. Tables 2 – 5 contain selected distances and angles.

Results and Discussion

*Synthesis of $(Me_2NCH_2)_3COH$ (**1**), $(Et_2NCH_2)_3COH$, and $[(PhCH_2)_2NCH_2]_3COH$*

In contrast to the synthesis of $(Me_2PCH_2)_3COH$ by reaction of 1-chloro-2,3-epoxy-2-chloromethylpropane with $LiPMe_2$ [13], the corresponding reaction



Scheme 1.

with $LiNMe_2$ did not yield **1** but gave intractable mixtures of compounds instead. For a clean and efficient (95% yield) synthesis of **1** it is sufficient to react the epoxide with a 40% aqueous solution of $HNMe_2$ in a 13-fold excess (Scheme 1) which was already employed for the synthesis of $(Me_2NCH_2)_2CHOH$ [14]. It should be mentioned that condensation of $HNMe_2$ onto the epoxide failed to give **1** in a clear-cut reaction. The tertiary aminomethyl alcohol **1** is a colorless liquid at room temperature with a b.p. of 87 °C/1 mbar. It is easily characterized by its ^1H, ^{13}C NMR, and IR spectra (see Experimental Section). Similar reactions afforded the analogues tertiary amino alcohols $(Et_2NCH_2)_3COH$ and $[(PhCH_2)_2NCH_2]_3COH$. In these syntheses the epoxide was added slowly to a large excess of diethylamine and dibenzylamine, respectively, without solvent.

*Synthesis and structure of $[(Me_2HNCH_2)_3COH]^{3+}$ 3 Cl^- (**2**)*

The crystal structure of the hydrochloride salt of **1** was determined which was prepared with a saturated solution of HCl in 1,4-dioxane (compound **2**, Scheme 1). Its NMR characterization was straightforward (see Experimental Section). A X-ray structure determination was undertaken in order to provide structural parameters for comparison with the alkali metal complexes of **1** (Table 2). As Fig. 1 shows, the triple cation adopts an extended conformation in the solid state. Its molecular symmetry approaches $3(C_3)$ when the OH hydrogen atom is neglected but this high symmetry is not mirrored in the crystal as there is no crystallographically imposed higher symmetry ($P2_12_12_1$, $Z = 4$). The OH hydrogen atom was located in difference maps which points to no appreciable disorder in the solid. The reduction in molecular symmetry imposed by an ordered OH hydrogen atom and a subsequently less symmetric hydrogen bond network makes the low crystal symmetry immediately plausible.

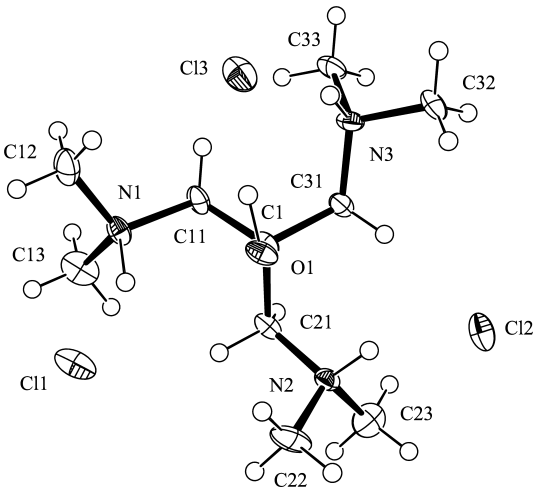


Fig. 1. Molecular structure of **2** in the crystal and crystallographic numbering scheme used (ORTEP-III. Displacement ellipsoids at the 50% probability level). For clarity, the H atoms were drawn as spheres with arbitrary radius.

*Synthesis and structure of $[(Me_2NCH_2)_3CONa]_4$ (**3**)*

Reaction of **1** with elemental sodium in hot toluene cleanly gave the sodium alcoholate **3**. Its ^1H and ^{13}C NMR characterization is in accord with the molecular formula but gives no indication as to association and structural details. This information is provided nicely for the solid state by the structure determination (Table 3, Fig. 2). Compound **3** is tetrameric in the solid with a central Na_4O_4 heterocubane core [21]. Each tetramer has crystallographic $\overline{4}(S_4)$ symmetry ($P4_2/n$, $Z = 2$). In the heterocubane cage there are three different Na-O bonds (Na-O 2.311(2), Na-O^2 2.258(2), Na-O^3 2.309(2) Å). In addition to three oxygen atoms, each sodium atom is coordinated by two amino groups from two different adjacent ligands (Na-N2 2.529(3), Na-$N3^3$ 2.628(3) Å). In that way each

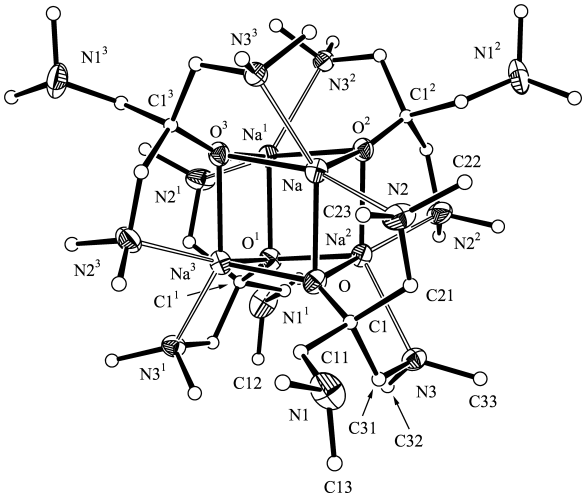


Fig. 2. Molecular structure of **3** in the crystal and crystallographic numbering scheme used (ORTEP-III. Displacement ellipsoids at the 30% probability level). For clarity, the C atoms were drawn as spheres with arbitrary radius, and the H atoms were omitted. Symmetry code as superscript: 1: $0.5-x$, $0.5-y$, z; 2: y, $0.5-x$, $0.5-z$; 3: $0.5-y$, x, $0.5-z$.

ligand has two of its aminomethyl arms coordinated to different sodium atoms, which are, however, both bonded to the oxygen atom of the same ligand (see Fig. 2: N2 coordinated to Na and N3 to Na^2, respectively). The third ligand aminomethyl arm remains uncoordinated. The pentacoordination of each sodium atom is grossly distorted both from a trigonal bipyramid as well as from a square pyramid, as can be seen from the bond angles involved (Table 3). The distortion is clearly caused by the grossly different Na-O and Na-N bond lengths and the formation of NaOCCN five-membered chelate rings upon coordination of the amino groups to sodium. Crystallographically characterized discrete Na_4O_4 heterocubane units are still rare although the number has been steadily growing over the last years [22]. One Na_4O_4 heterocubane structure of the 2,6-bis[(dimethylamino)methyl]-4-methylphenolate ligand, whose two dimethylamino arms form chelate rings by Na-N coordination similar to the situation in **3**, has Na-O and Na-N bond lengths which are directly comparable to those in **3** [22p]. Due to the formation of six-membered chelate rings the coordination geometry at sodium is much more regular in this example, however [22p].

*Synthesis and structure of [(Me$_2$NCH$_2$)$_3$COLi·LiNMe$_2$]$_2$ (**4**)*

Deprotonation experiments of **1** with $LiNMe_2$ led to the isolation of the dimeric mixed-anion aggregate $[(Me_2NCH_2)_3COLi{\cdot}LiNMe_2]_2$ (**4**) containing the deprotonated ligand **1** and $[NMe_2]^-$ anions in a ratio of 1:1. Charge neutrality is achieved by two lithium counterions. This information is born out by the crystal structure determination (see below) as our NMR measurements have been inconclusive so far with regard to the number and the assignment of resonances especially in the ^{13}C NMR spectra (see Experimental Section). The secondary alcohol $(Me_2NCH_2)_2CHOH$ [14] has been deprotonated with $LiNiPr_2$ and was also found to form a dimeric 1:1 mixed-anion aggregate $[(Me_2NCH_2)_2CHOLi{\cdot}LiNiPr_2]_2$ [9e]. ^{6}Li NMR investigations of pure ^{6}Li-labeled species indicated extensive dissociation in solution while the other NMR spectra likewise were difficult to interpret [9e]. We believe that rapid dynamic equilibria in solution between the anions, Li^+, and oligomeric species cause these complicated spectra. Clearly, a thorough variable-temperature and variable-concentration NMR investigation is desirable for these systems, which has not been undertaken yet, however [23].

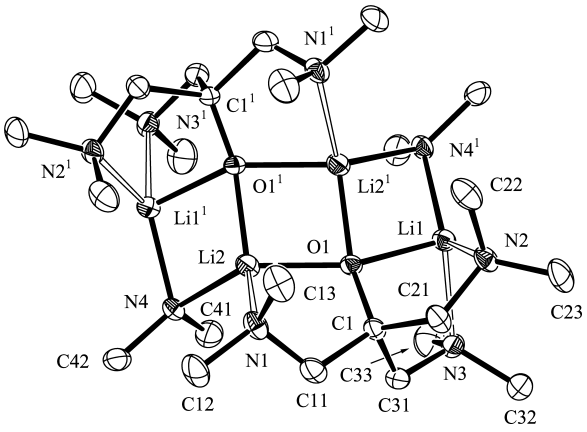


Fig. 3. Molecular structure of **4** in the crystal and crystallographic numbering scheme used (ORTEP-III. Displacement ellipsoids at the 30% probability level). The H atoms were omitted for clarity. Symmetry code as superscript: 1: $0.5-x$, y, $1.5-z$.

Much more straightforward is the information obtained from the crystal structure determination (Table 4, Fig. 3). As already stated above, **4** crystallizes as the mixed-anion dimer $[(Me_2NCH_2)_3COLi{\cdot}LiNMe_2]_2$. Each dimer has crystallographically imposed $2\,(C_2)$ symmetry as follows from the space group $P2/n$ and the unit cell contents of two dimers. Two deprotonated ligands **1**, two dimethyl amide anions, and four Li^+ counterions assemble in an extended four-rung ladder structure consisting of two four-membered $Li(NMe_2)LiO$ rings connected through a central LiOLiO ring. The ladder is strongly curved (in Fig. 3 away from the viewer). All ligand amine groups are coordinated to lithium atoms, two of them to one lithium atom, the third one to a second (Li1-N2 2.117(6), Li1-N3 2.101(6), Li2-N1 2.218(6) Å). Also each amido nitrogen atom is coordinated to two lithium atoms (Li1-N4^1 1.964(6), Li2-N4 2.027(6) Å). The lithium atoms in the middle of the ladder (Li2, Li2^1) have a grossly distorted four-fold coordination, the coordination geometry of the peripheral lithium atoms approximates fairly well to a trigonal pyramid (see Fig. 3 and angles in Table 4). Essentially the same structure has been found for $[(Me_2NCH_2)_2CHOLi{\cdot}LiNiPr_2]_2$ [9e]. The similarities even extend to crystallographic $2\,(C_2)$ symmetry of the dimers and the ladder curvature. Differences obviously arise from the fact that only two aminomethyl donor

groups are available for lithium coordination instead of three in **4**. In $[(Me_2NCH_2)_2CHOLi{\cdot}LiN\mathit{i}Pr_2]_2$ both amine donors of one ligand are coordinated to different lithium atoms making the peripheral lithium atoms only three-coordinate [9e]. Their coordinative unsaturateness in comparison to **4** is compensated by the bulkier *i*Pr groups of the peripheral amide anions, however. It should be mentioned that ladder structures (ring laddering) is often observed in organonitrogen lithium chemistry and particularly so with organoamides [24]. It seems that the presence of $LiNR_2$ in a mixed-anion aggregate with lithiated **1** (or $(Me_2NCH_2)_2CHOLi$) is sufficient to induce this almost ubiquitous structural motif.

Synthesis and structure of $[(^-H_2CN(Me)CH_2)(Me_2NCH_2)_2CO^-{\cdot}5\,Li^+{\cdot}(^-H_2CN(Me)CH_2)_2(Me_2NCH_2)CO^-]_2$ (**5**)

Reaction of a three-fold excess of Li*t*Bu with **1** in *n*-hexane resulted in OH deprotonation and, in addition, in lithiation of methyl groups. The resulting dimeric mixed-anion aggregate $[(^-H_2CN(Me)CH_2)(Me_2NCH_2)_2CO^- \cdot 5\,Li^+ \cdot (^-H_2CN(Me)CH_2)_2(Me_2NCH_2)CO^-]_2$ (**5**) could only be detected and characterized by single-crystal structure determination. It contains two doubly charged ligands **1** deprotonated at oxygen and one methyl group while two other ligands are triply charged each, resulting from lithiation at oxygen and two methyl groups. The anionic charge of altogether four alcoholate oxygen atoms and six $N(Me)\text{-}CH_2^-$ groups is compensated for by ten Li^+ cations. In solution rapid exchange occurs as the ^1H and ^{13}C NMR spectra show only two and three signals, respectively (see Experimental Section). In particular, they do not allow a distinction between neutral and deprotonated alkyl groups. The ^7Li NMR spectrum at room temperature consists solely of one broad structured singlet.

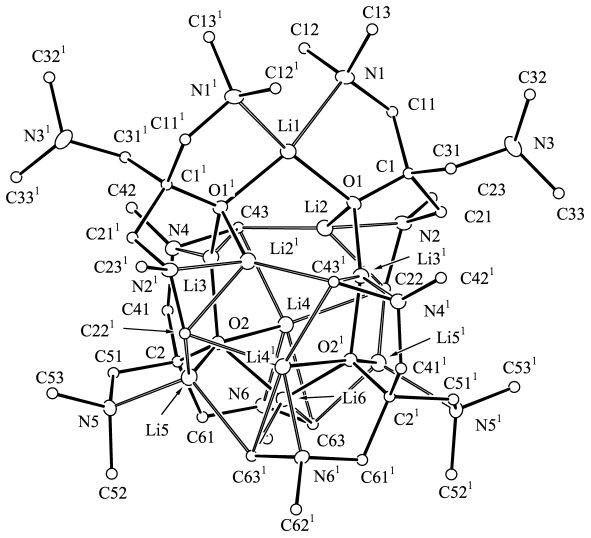


Fig. 4. Molecular structure of **5** in the crystal and crystallographic numbering scheme used (ORTEP-III). For clarity, the Li, N, and O atoms were drawn as ellipsoids at the 20% probability level, the C atoms are spheres with arbitrary radius, and the H atoms were omitted. Symmetry code as superscript: 1: $-x, 1-y, z$.

In the solid state **5** is a large dimeric aggregate with crystallographic $2\,(C_2)$ symmetry (Fig. 4, Table 5) as two dimers are accomodated in the cell (space group $P2_12_12$). Details of the highly complicated molecular structure can be obtained by careful (and slow) inspection of Fig. 4 where the lithium bonds to nitrogen and (deprotonated) carbon atoms are highlighted as open bonds while all others have been drawn as solid bonds. In the upper part of Fig. 4 there are two symmetry-related doubly deprotonated ligands. Their oxygen atoms (O1) and lithium-coordinated neutral aminomethyl arms (N1) are held together by Li1 which resides on a crystallographic two-fold axis. The methyl lithiation of these ligands occured at N2-C22 as could be clearly inferred from the two located hydrogen atoms and the coordination by additional lithium atoms which is explained further below. The aminomethyl group N3 is uncoordinated and extends to the outside of the aggregate. In the lower part of Fig. 4 the triply deprotonated ligands reside where in addition to oxygen the methyl groups N4-C43 and N6-C63 are lithiated. Their neutral aminomethyl arm N5 is also lithium-coordinated to Li5. Of altogether six crystallographically independent lithium atoms two reside on two-fold axes (Li1, Li6) so that a total of ten lithium atoms required for the charge neutrality of the entire aggregate is crystallographically generated. Their coordination numbers are four (Li1, Li2, Li3, Li5, Li6) and five (Li4).

Important other structural details are visualized in Fig.'s 5 and 6 and shall be briefly explained here. The deprotonated oxygen atoms O1 (Fig. 5) and O2 (Fig. 6) are coordinated to three and four lithium counterions, respectively. Of particular interest are the details of the lithium coordination to the deprotonated methyl groups also shown in Fig.'s 5 and 6. As can be clearly seen, each of these $N\text{-}CH_2^-$ groups is lithium-bridged

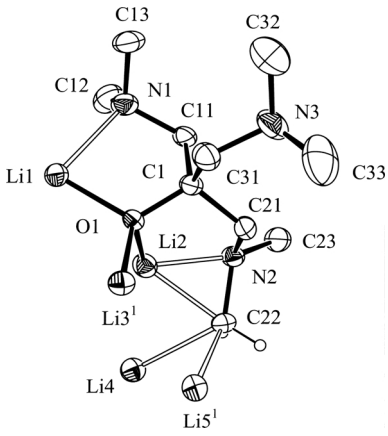


Fig. 5. Molecular structure of the dimetallated ligand in the crystal structure of **5** including the coordinated lithium cations (ORTEP-III. Displacement ellipsoids at the 50% probability level). The H atoms were omitted for clarity except those at the metallated carbon atom. Symmetry code as superscript: 1: $-x, 1-y, z$.

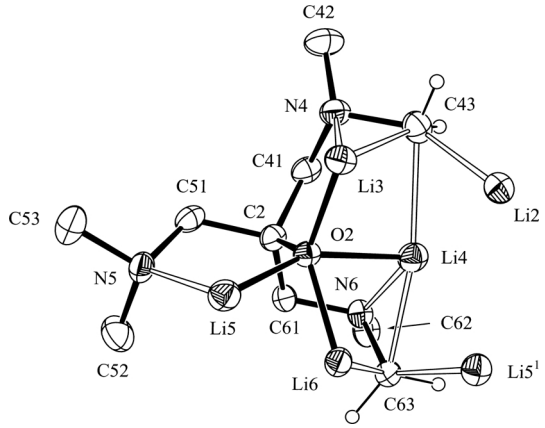


Fig. 6. Molecular structure of the trimetallated ligand in the crystal structure of **5** including the coordinated lithium cations (ORTEP-III. Displacement ellipsoids at the 50% probability level). The H atoms were omitted for clarity except those at the metallated carbon atoms. Symmetry code as superscript: 1: $-x, 1-y, z$.

(η^2 bonding) by one lithium atom coordinated to the lone pairs at carbon and nitrogen under concomitant formation of a three-membered LiCN ring. The carbon atoms of each of the three N-CH_2^- groups are further coordinated by two other lithium atoms resulting in a hexacoordination made up of one nitrogen, two hydrogen, and three lithium atoms. Closer inspection of the N-C bond lengths and C-N-C bond angles (Table 5) reveals that the N-CH_2^- bonds (N2-C22 1.499(5), N4-C43 1.505(5), N6-C63 1.500(4) Å) are slightly elongated with respect to the other nitrogen alkyl bonds which range between 1.455 (5) and 1.472(5) Å. No striking differences are observed in the respective bond angles at nitrogen no matter whether the metallated carbon atoms are involved or not. Simple lone-pair considerations suggest that N-CH_2^- bonds should be longer than N-C bonds with non-metallated carbon atoms due to strong repulsion of the lone pairs at nitrogen and carbon. A complexation of lithium to these lone pairs, as is amply observed in **5** by coordination of three Li atoms to each N-CH_2^- bond, should reduce the lone-pair repulsion and counterbalance the bond elongation. In **5** a slight elongation prevails apparently. Much attention has been drawn to these effects in other α-lithiated amines but the number of crystal structures is still small [25, 26]. The arguments have been augmented by computational studies [25, 27]. In $[(C_5H_{10}NCH_2)_4Li_4(THF)_2]$ [26c] and especially in $[(Me_2NCH_2)_2Li_2(THF)_2]_2$ [26b] similar trends have been observed as in **5** but the effects are generally small so that they are often blurred by the standard deviations.

Finally it should be noted that α-lithiated amines, whose utility in organic synthesis has long been established [25], have recently found important application also in synthetic heteroelement chemistry [28]. It should also be mentioned that α-lithiated organophosphines show a completely different behavior, as do lithiated carbon atoms with other α substituents from the third row (second long row) of the Periodic Table. Most notably, $R_2P\text{-}CH_2^-$ bonds are generally shorter than their non-metallated counterparts, and their η^2-coordination to lithium (and other electropositive metals) with concomitant formation of three-membered rings is very rare [29, 30].

Conclusions

The tris(dimethylaminomethyl)-substituted alcohol $(Me_2NCH_2)_3COH$ (**1**) seems to have a varied coordination chemistry to the alkali metals after deprotonation at oxygen. It may be further lithiated at N-CH_3 groups under drastic conditions forming doubly and triply charged anions. Methylene carbon atoms α to nitrogen are not subjected to deprotonation under these conditions. This behavior is drastically different from the respective phosphinomethyl-substituted alcohol $(Me_2PCH_2)_3COH$ where deprotonation at PCH_2 groups has been observed [13]. Furthermore, although

both tertiary alcohols were found to form mixed-anion aggregates, they do so in completely different ways. $(Me_2PCH_2)_3CO^-$ is capable to bind three Li^+ cations *via* its oxygen atoms and phosphino groups in a very appealing symmetrical fashion [13] with subsequent formation of a mixed-anion aggregate. It belongs to the polyhedral structures often encountered for lithium alkyls. In the mixed-anion aggregate $(Me_2NCH_2)_3CO^-$ binds only to two Li^+ cations in a much less symmetrical way. The aggregate **4** formed with $LiNMe_2$ has a ladder structure typical for lithium organoamides.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 250109 (**2**), 250110 (**3**), 250111 (**4**), 250112 (**5**). Copies of the data can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: (int. Code) +44 (1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.deposit@ccdc.cam.ac.uk

Acknowledgement

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[1] The term “atom-centered anion” is used here for convenience, as the encountered anions are rather diverse making the use of a more precise nomenclature cumbersome.

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