Multidentate Aminoalkoxides. Synthesis and Complexation Behavior to Lithium and Sodium

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Z. Naturforsch. **59b,** 1400 – 1410 (2004); received August 18, 2004

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