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 (R₂NCH₂)₃COH (R = Me: 1) was synthesized by reaction of 1-chloro-2,3-epoxy-2-chloromethylpropane with a large excess of 40% aqueous HNMe₂ in 95% yield as colorless liquid (b.p. 87 °C/1 mbar). Similar syntheses led to the respective amino alcohols with R = Et, CH₂Ph. The dimethylamino alcohol 1 was characterized crystallographically as hydrochloride salt 2. Reaction of 1 with elemental sodium in toluene gave the tetrameric alcoholate [(Me₂NCH₂)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 LiNMe₂ afforded the lithium alcoholate which crystallized as dimeric mixed-anion aggregate [(Me₂NCH₂)₃COLi-LiNMe₂]₂ (4). It has a four-rung ladder structure consisting of two four-membered Li(NMe₂)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 LiBu 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 [(−H₂CN(Me)CH₂)(Me₂NCH₂)₂CO⁻·5 Li⁺·(−H₂CN(Me)CH₂)₂(Me₂NCH₂)CO⁻]₂ (5) having a core of 10 Li⁺ cations, 4 alcoholate oxygen atoms, and 6 N(Me)⁻-CH₂⁻ groups.

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