

Expanding the Scope of Lithium Coordination Chemistry by Placing Sodium Nearby: A Mixed Lithium–Sodium Benzyl Compound Having TMEDA-Chelated Li⁺ Cations in an Unprecedented Tetrameric Environment

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Summary: Mixed-alkali-metal metalation of toluene in the presence of TMEDA produces the benzyl complex $[(\text{PhCH}_2)_4\text{Li}_{2-x}\text{Na}_{2+x}(\text{TMEDA})_4]$, which has an octagonal ring structure that, in spite of the 4-fold aggregation, contains Li⁺ cations complexed by bidentate TMEDA, a situation normally sterically forbidden in homometallic lithium tetramers.

This paper reveals that the eight-membered-ring structure of crystalline tetrakis(benzylsodium)·4TMEDA,¹⁵ $[(\text{PhCH}_2\text{Na})_4\cdot 4\text{TMEDA}]$, reported by Schleyer *et al.* in 1986^{1,2} provides the template for the crystal structure of the mixed lithium-sodium analogue $[(\text{PhCH}_2)_4\text{Li}_{2-x}\text{Na}_{2+x}\cdot 4\text{TMEDA}]$ (**1**), synthesized in our laboratory. Substituting Li⁺ for Na⁺ in an organic environment usually leads to pronounced differences,³ at the most, in the aggregation state, and at the least, in the number of coordination contacts with the carbanion and/or complexant, attributable in the main to the size inequality between the cations (*i.e.*, ionic radii: Li⁺, 0.76 Å; Na⁺, 1.02 Å).⁴ Furthermore, structures of organic derivatives containing both Li and Na have hitherto exhibited distinct chemical environments for each; therefore, their indistinguishable nature in **1** (by X-ray structure determination) is both unique and surprising. It is the synthetic potential of such mixed-metal formulations that provides the major stimulus for their study. The presence of a second alkali metal can alter (enhance!) the chemical reactivity of an organolithium. Mixed organo(lithium/potassium) alkoxides, increasingly utilized as “superbases”⁵ in organic synthesis, work on this principle.

Structural types of mixed Li/Na organics that have been identified prior to **1** are illustrated in Figure 1. Derived from benzene and a guanidine, respectively, **a**⁶

and **b**,⁷ related by a 1:3 Li:Na stoichiometry, differ in other respects, with **a** based on a Li-capped Na₃ equilateral triangle and **b** based on a distorted (LiNa₃N₄) cubane. Conversely, the ketimide **c**⁸ has a Li-rich (4:2) stoichiometry. Equimolar amounts of Li and Na, captured in a range of stoichiometries (1:1, 2:2, 4:4), are found in the remaining structures **d**–**h**. Quasi-dimeric (NLiNNa) rings are common to iminoaminosulfinate **d**⁹ and silylamide **e**.¹⁰ Bis(pyridyl)methane derivative **f**¹¹ is a clear-cut example of a sodium lithiate. Amide **g**¹² displays a step ladder appearance. Tetramer **h**,¹³ a model RLi/NaOR “superbase”, has an (OLi)₄ pseudocubane body with benzyl Na arms.

Air-sensitive **1** was prepared under argon by metalation of toluene. Specifically, a mixture of BuⁿLi/BuⁿNa (10 mmol each) in hexane was treated with an excess of toluene (50 mmol) and stirred for 10 min before TMEDA (20 mmol) was introduced. A yellow precipitate formed. Further addition of toluene (125 mmol) and vigorous heating were required for redissolution. A large crop of yellow needle crystals (yield based on consumption of BuⁿLi, 56%, 5.00 g) were subsequently deposited. Alternatively, the product may be synthesized by stepwise metallation of toluene (*i.e.*, adding BuⁿNa, followed by BuⁿLi). A series of melting point determinations (result consistently 93–95 °C to an orange liquid) established the product's homogeneity. Bands at 3680 and 3620/3580 cm⁻¹ in the IR spectrum of the *air-exposed* product associated with LiOH and NaOH, respectively, confirmed the presence of Li and Na, later quantified by AAS. These and C,H,N analyses¹⁶ agree well with that predicted from the empirical formula deduced by the X-ray diffraction study, which conclusively identified the yellow crystals as **1**.¹⁷

The molecule (Figure 2) has crystallographic C₂ symmetry, the axis running perpendicular to the eight-membered ring. It has the same basic structure as the all-sodium analogue, although the space group and, hence, the crystal packing are different. There are no

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(3) Crystal structure reviews are as follows. Li: Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. Na: Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169. General: Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

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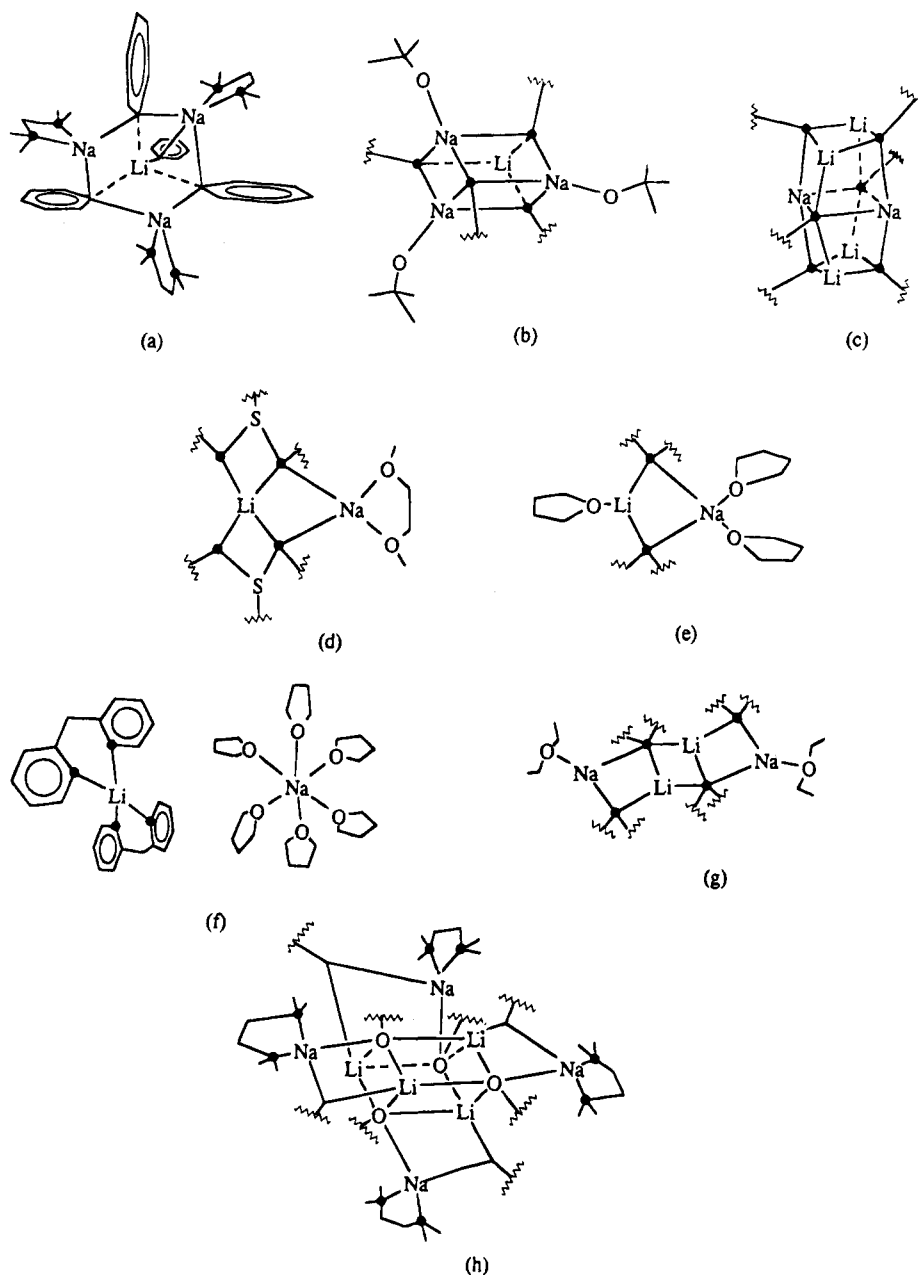


Figure 1. X-ray crystallographically characterized structural types found in mixed lithium-sodium organic derivatives.

significant intermolecular contacts. If size variations are disregarded, both Na(1) and Li(2) are enclosed within the same type of coordination polyhedron, comprising two C and two N atoms arranged tetrahedrally. As a result, the metal cations are interchangeable in the bulk crystal (an example of mutual substitution disorder) with the Na(1) site partially populated by Li (27%) and the Li(2) site by Na (43%), giving an actual overall stoichiometry of $\text{Li}_{1.67}\text{Na}_{2.33}$, *i.e.*, $x = 0.33$ in the formula of **1** shown above. This means that the observed geometries of the metal sites represent a weighted average for Li and Na, so that a comparison of the dimensions involving these atoms with those in related structures would be of little significance; we note, however, that bonds are shorter to the site richer in Li, as should be expected. Irrespective of that, the four metal centers clearly approach a square, with each Li-Na edge bisected by an approximately perpendicularly orientated benzyl group with a trigonal-bipyramidal α -C atom. TMEDA molecules bite the metal corners

in their usual bidentate manner, causing the central, eight-membered ring to pucker to minimize repulsions with the benzyl groups. Thus, replacing some Na^+ centers by Li^+ centers does not, as might have been expected, alter the gross structure, as all of these features also appear in the congener containing Na^+ exclusively.¹ Minor variations show up when comparing (benzyl) C-C distances in the two structures, but the basic pattern (long $\text{C}_\alpha\text{-C}_{\text{ipso}}$, $\text{C}_{\text{ipso}}\text{-C}_{\text{ortho}}$; short $\text{C}_{\text{ortho}}\text{-C}_{\text{meta}}$, $\text{C}_{\text{meta}}\text{-C}_{\text{para}}$), remains the same.

In a regular octagon (model C-Li tetramer) the endocyclic angle is 135° , whereas this falls to 90° in a square (model C-Li dimer); therefore, the less aggregated structure is greatly preferred for complexation, as it provides a larger exocyclic angle (ideally, 270° vs 225°) for the complexant to occupy. Increasing the denticity of the complexant (*e.g.*, from mono to di) would make the more aggregated structure yet more unfavorable sterically. For this reason, TMEDA complexes of molecular lithium compounds tend to be dimers or even

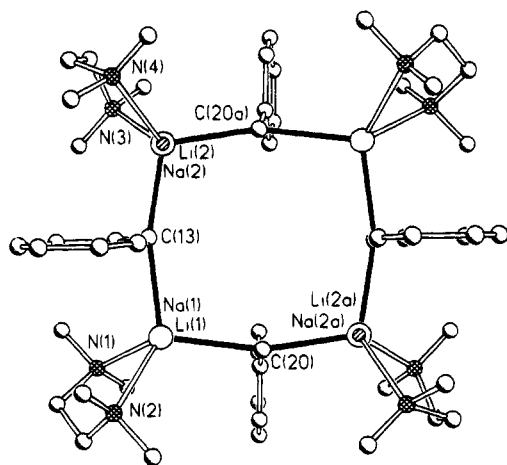


Figure 2. Molecular structure of **1** without hydrogen atoms and with important atoms labeled, showing the mutual substitution disorder components [Li(1), Na(2), Na(2a)]. Key dimensions: Na(1)–C(13) = 2.515(6), Na(1)–C(20) = 2.544(6), Li(2)–C(13) = 2.394(6), Li(2)–C(20a) = 2.406(6), Na(1)–N(1) = 2.434(5), Na(1)–N(2) = 2.407(5), Li(2)–N(3) = 2.328(5), Li(2)–N(4) = 2.313(5) Å; C(13)–Na(1)–C(20) = 103.2(2), C(13)–Li(2)–C(20a) = 107.9(2), Na(1)–C(13)–Li(2) = 162.8(3), Na(1)–C(20)–Li(2a) = 162.0(3)°. The appended “a” denotes an atom related by the 2-fold rotation axis perpendicular to the eight-membered ring.

monomers. Even in $[\{(MeLi)_4 \cdot 2TMEDA\}_n]^{14}$ an extreme case having the smallest organic substituent (Me), the tetrameric subunits survive intact only because TMEDA adopts an alternative monodentate bridging role, instead of its normal bidentate role. Therefore, the structure of **1** is rare, perhaps unique, within the vast literature of molecular organolithium structures

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(15) Abbreviation used: TMEDA = *N,N,N',N'*-tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$.

(16) Anal. Calcd for **1** ($C_{52}H_{92}Li_{1.67}N_8Na_{2.33}$): C, 69.9; H, 10.3; Li, 1.3; N, 12.5; Na, 6.0. Found: C, 70.2; H, 10.1; Li, 1.3; N, 12.1; Na, 5.9.

(whether rings or cages),³ for having bidentate complexant molecules bound to Li^+ cations in a high aggregate (“tetramer”).

Why is this new structural feature, sterically forbidden generally, possible here? In short, it is allowed by the presence of the larger sodium cation, which creates more room for the ring-attached substituents, as heterometallic LiCNa triads are considerably longer than homometallic LiCLi ones (*i.e.*, the $(LiCNaC)_2$ octagon would be expanded relative to a corresponding $(LiCLiC)_2$ octagon).

The wider implication of this discovery is intriguing. Placing Na^+ near Li^+ could open the way to realizing new structures/unconventional coordination modes in organolithium compounds, and as structure and reactivity are inherently linked, this could lead to synthetic reagents with improved performance, much in the same way that metallic Li with traces of Na is superior to pure Li in reactions with organic halides.

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Supplementary Material Available: Text giving details of the crystal structure determination and tables of atomic coordinates, bond distances, bond angles, and atomic displacement parameters (8 pages). Ordering information is given on any current masthead page.

OM940636X

(17) Crystal data for **1**: $C_{52}H_{92}Li_{1.67}N_8Na_{2.33}$, $M_r = 894.4$, monoclinic, $a = 26.109(4)$ Å, $b = 8.653(5)$ Å, $c = 27.853(14)$ Å, $\beta = 111.07(3)^\circ$, $V = 5872(6)$ Å³, $Z = 4$, $D_{calc} = 1.012$ g cm⁻³, $\mu = 0.074$ mm⁻¹ (Mo K α , $\lambda = 0.71073$ Å), $F(000) = 1962$, space group $C2/c$. A total of 7692 reflections were measured at 160 K on a Stoe-Siemens diffractometer, to $2\theta_{max} = 45^\circ$, yielding the 3846 unique data ($R_{int} = 0.048$). The structure was solved by direct methods and refined on F^2 values for all measured data, with anisotropic displacement parameters and constrained isotropic hydrogen atoms. Disorder was refined for mixed Li/Na site occupancy and also for alternative positions of the TMEDA CH_2CH_2 links, with restraints on displacement parameters. At convergence, $R^1 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2} = 0.229$ for all data, conventional $R = 0.066$ on F values of 1825 reflections with $F_o^2 > 2\sigma(F_o^2)$, and goodness of fit = 1.035 on F^2 . Programs were of the SHELX family (G. M. Sheldrick, University of Göttingen).