An Unprecedented Mixed Alkali Metal Organonitrogen Ladder: Synthesis, NMR Spectroscopic Studies, and X-ray Crystallographic Studies of the Dilithium Disodium Amide [{LiNa[N(CH₂Ph)₂]₂·OEt₂}₂]

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If the small number of mixed alkali metal organic formulations[1] being increasingly utilized in proton abstraction applications[2] are typical, then a group of such compounds would be of considerable value to the synthetic chemist. Indeed, a new class of mixed Li/Na and Li/K organic compounds could offer a range of reactivities and selectivities even surpassing that of conventional organolithium reagents. However, as yet, species of this type are rare. We are therefore attempting to develop this area synthetically and to elucidate the structural makeup of any new mixed metal aggregate formed. The few mixed Li/Na structures so far identified are based on four-membered rings, either remaining discrete (e.g., (LiNNaN) in the monolithium monosodium silylamide [LiNa{N(SiMe₃)₂}₂·3THF])[3] or combining in a vertical face-to-face manner to give clusters ("stacks") (e.g., (LiNLiN)-(NNaNNa)(LiNLiN) in the tetralithium disodium guanidino triple stack [Li₄Na₂{N═C(NMe₂)₂}₆][4]). In this communication we report an unprecedented structure, a heterobimetallic ladder, arising from the lateral combination of two (LiNNaN) rings in the new dilithium disodium amide [{LiNa[N(CH₂Ph)₂]₂·OEt₂}₂] (1). This novel arrangement, established in the crystal by an X-ray diffraction study, appears to remain intact in arene solution on the basis of NMR spectroscopic data.

In the preparation of compound 1, a chilled, stirred suspension of an *n*-butyllithium/*n*-butylsodium (10 mmol:10 mmol) mixture in hexane under a protective argon atmosphere was injected with small aliquots of dibenzylamine (20 mmol in total). A pink solid formed almost immediately. After 1 h, ether (5 mL) was introduced, causing firstly partial dissolution of this solid and secondly precipitation of a second (red) solid. Mild heating and addition of toluene (15 mL) effected complete dissolution. Standing the solution overnight afforded a large crop of deep-red crystalline 1.[5]

The ladder structure of the molecule in the solid state (Figure 1)[6] has four M–N rungs: M = Li in the inner rungs and M = Na in the outer ones. In common with ladders having four Li–N rungs, complexation occurs at outer M⁺ sites, not inner M⁺ sites due to steric factors.[7] Here, therefore, only the Na⁺ cations are complexed by ether molecules. Attachment of such additional ligands is known to distort ladder frameworks from a planar arrangement. The distortion is exaggerated in this case by the different sizes of the Li⁺ and Na⁺ cations. The approximately planar (rms deviation 0.084 Å) NaN(1)LiN(2) ring forms an envelope with the exactly planar (by crystallographic symmetry) LiN(1)Li'N(1') ring with a flap angle of 167.6°. The Li–N rungs measure 2.067(5) Å in length. Significantly, Li–N edges in the central [LiN(1)Li'N(1')] ring are decidedly longer [2.126-(5) Å], but those belonging to outer [LiN(2)NaN(1), Li'N(2')-Na'N(1')] rings are decidedly shorter [2.021(5) Å, *cf.* 2.024(6) Å for the Li–N ring bonds in [LiNa{N(SiMe₃)₂}₂·3THF][3]]. This pattern fits the idea that the ladder results from the lateral combination of two (LiNNaN) "dimeric" rings, with Li–N(1'), Li'–N(1) representing long "interdimer" bonds, Li–N(1), Li'–N(1') representing intermediate "intradimer" bonds, and Li–N(2), Li'–N(2') representing short "intradimer" bonds. Internal bond angles at Li vary from 106.2(2)° in the central (LiN)₂ ring to 117.6(2)° in the larger, more distorted (LiNNaN) ring. The Na–N rung is substantially shorter than the Na–N edge [2.398-(3) and 2.539(3) Å, respectively, *cf.* 2.509(4) Å for the Na–N ring bonds in [LiNa{N(SiMe₃)₂}₂·3THF][3], while the bond angle in between [N(1)NaN(2)] is very small [90.14(8)°]. Both Li (with respect to N) and Na (with respect to N and O) are three-coordinate. Hitherto, dibenzylamido anions have always assumed μ₂-bonding roles in alkali metal structures.[8] This again is evident in the outer rungs [NaN(2)Li internal bridge angle 77.38(14)°]; N(2) is therefore four-coordinate. However, those positioned in the inner rungs are μ₃-bonded [NaN(1)Li, Li'N(1)Li, internal bridge angles 73.4(2)° and 73.9(2)°, respectively]; N(1) is therefore five-coordinate. This novel bonding mode is facilitated by the long length of the Na–N ladder edges [Na–N(1), Na'–N(1')], which provides the attached benzyl rings with enough room to avoid proximate ether molecules. The stereochemistry of these μ₃-bonding anions also brings their benzylic carbon atoms within bonding distance of a Li⁺ cation [Li'–C(12), 2.701(5) Å; Li'–C(11), 2.826(5) Å]. A plethora of contacts, similar to these, was noted in the crystal structure of trimeric dibenzylamidolithium

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(3) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671.

(4) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1992**, *11*, 2809. For related mixed Li/Na crystal structures, see: Clegg, W.; Mulvey, R. E.; Snaith, R.; Toogood, G. E.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1740. Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1989**, 57.

(5) Yield (based on consumption of alkyllithium), 56%; mp 83–85 °C. Anal. (C₆₄H₇₆Li₂N₄Na₂O₂) C, H, Li, N, Na. When isolated from solution and stored in an argon-filled drybox, the air- and moisture-sensitive crystals are prone to turning black and oily.

(6) Crystal data for 1: C₆₄H₇₆Li₂N₄Na₂O₂, *M* = 993.2, monoclinic, *P*2₁/*c*, *a* = 9.890(6), *b* = 16.870(12), and *c* = 18.283(10) Å, *β* = 105.59(6)°, *V* = 2938(3) Å³, *Z* = 2, *D*calcd = 1.123 g cm⁻³, λ(Mo Kα) = 0.710 73 Å, μ = 0.079 mm⁻¹, *F*(000) = 1064. Measurements were made at 200 K on a Stoe-Siemens diffractometer with an Oxford Cryostream cooler from a crystal of size 0.96 × 0.46 × 0.35 mm³. Structure solution was by direct methods, and all 5134 independent reflections were used for full-matrix least-squares refinement on *F*². H atoms were constrained; other atoms were assigned anisotropic atomic displacement parameters, and restraints were imposed on disordered ether molecules. At convergence, *R*w² = (Σ[*w*(*F*o² − *F*c²)²]/Σ[*w*(*F*o²)²])^{1/2} = 0.1719, conventional *R* [on *F* values for 2580 reflections with *I* > 2σ(*I*)] = 0.0551, goodness of fit on *F*² = 1.02 for 356 parameters. All features in a final difference synthesis were within ±0.36 eÅ⁻³. Program systems: SHELXTL/PC, SHELXL-92 (G.M. Sheldrick, University of Göttingen, Germany). Key dimensions: Li–N(1) 2.067(5), Li–N(1') 2.126(5), Li–N(2) 2.021(5), Na–N(1) 2.539(3), Na–N(2) 2.398(3), and Na–O 2.299(3) Å; N(1)–Li–N(1') 106.2(2), N(1)–Li–N(2) 117.6(2), N(2)–Li–N(1') 132.1(2), Li–N(1)–Na 73.4(2), Li'–N(1)–Na 145.9(2), Li–N(2)–Na 77.38(14), N(1)–Na–N(2) 90.14(8), N(1)–Na–O 128.51(11), and N(2)–Na–O 130.68(10)°.

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(8) For lithium, see: Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. For sodium in the crystal structure of [{NaN(CH₂Ph)₂·TMEDA}₂]: Andrews, P. C.; Clegg, W.; Mulvey, R. E.; O'Neil, P. A., unpublished data.

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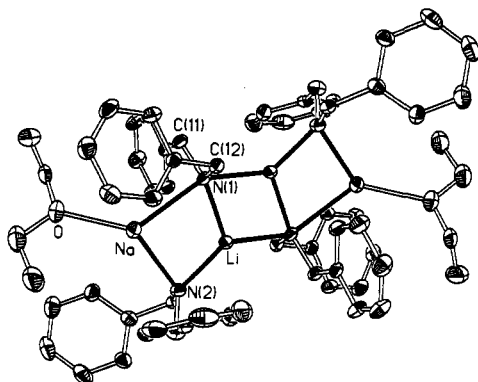
Figure 1. Thermal ellipsoid plot (30% probability) of the ladder structure of **1**. Hydrogen atoms are omitted for clarity.

(Li–C bond lengths: mean, 2.81 Å; shortest, 2.69 Å), as well as additional contacts to *ipso*- and *o*-C atoms of the phenyl rings and to nearby H atoms, all of which supplement the formally low coordination number (2 *cf.* 3 in **1**) of its Li^+ centers.[9]

NMR spectroscopic studies[10] suggest that the ladder structure is retained in arene solution. Most significantly, even at room temperature, two distinct (1:1) benzylic–CH_2 resonances are clearly visible in the ^{1}H spectrum of a benzene-d_6 solution, consistent with the two different types of dibenzylamido bridges (μ_2- or μ_3-bonded) within the solid-state ladder. Only one such resonance would be expected if the ladder were broken up into its constituent dimeric rings. The [7]Li spectrum of a toluene-d_8 solution supports the ^{1}H data in showing only one sharp, single resonance, which can be assigned to the sole lithium environment in the ladder.[10]

In a developing theme in the literature, rings have been identified as the fundamental units from which the structures of organolithium and other lithium compounds are constructed. Structures can be categorized as discrete rings, stacked rings, and laddered rings, on this basis.[11] With the discovery of **1**, all of these options have now been demonstrated in mixed Li/Na organonitrogen aggregates.[3,4]

Further studies are in progress to test the reactivity of the new mixed metal amide in relation to that of its homometallic lithium and sodium analogues.

Supplementary Material Available: Details of the X-ray analysis and tables of atomic coordinates, bond lengths and angles, and atomic displacement parameters (13 pages); listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

(9) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 287.

(10) NMR spectra: [1]H (400 MHz; benzene-d_6 solution; 298 K) Et_2O-(CH_3), 6H, t, 1.12 ppm; $Et_2O(CH_2)$, 4H, quart, 3.26 ppm; CH_2, 4H, s, 3.56 ppm; CH_2', 4H, s, 3.57 ppm; *Ph*, 20H, m, 7.20 ppm (relative to TMS, 0.00 ppm); [7]Li (139 MHz; toluene-d_8; 298 K) s, –0.28 ppm (relative to PhLi, 0.00 ppm) (Ξ value, 38.863 882 MHz)).

(11) For a review of ring-stacking and ring-laddering concepts, see: Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167. For key papers, see: (a) Barr, D.; Snaith, R.; Clegg, W.; Mulvey, R. E.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 295. (b) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869. (c) Geissler, M.; Kopf, J.; Schubert, B.; Weiss, E.; Neugebauer, W.; Schleyer, P. v. R. *Angew. Chem.* **1987**, *99*, 569; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 587. (d) Armstrong, D. R.; Barr, D.; Snaith, R.; Clegg, W.; Mulvey, R. E.; Wade, K.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1987**, 1071. (e) Barr, D.; Snaith, R.; Clegg, W.; Mulvey, R. E.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1987**, 2141. (f) Clegg, W.; MacGregor, M.; Mulvey, R. E.; O'Neil, P. A. *Angew. Chem.* **1992**, *104*, 74; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 93. (g) Hey-Hawkins, E.; Sattler, E. *J. Chem. Soc., Chem. Commun.* **1992**, 775.