

A Mixed Aggregate of Lithium Diisopropylamide and Lithium Chloride: Synthesis and Crystal Structure

Francis S. Mair^{*†}

University Chemical Laboratory
Lensfield Road, Cambridge CB2 1EW, U.K.

William Clegg and Paul A. O'Neil

Department of Chemistry, University of Newcastle
Newcastle upon Tyne NE1 7RU, U.K.

Received December 29, 1992

With the realization that reaction selectivity is dependent upon reagent structure¹ has come a burgeoning of activity in structural studies of lithium diisopropylamide (LDA) and related systems, both in the solution² and solid^{2d,3} states. Recent synthetic, mechanistic, and NMR spectroscopic studies of lithium amide/lithium halide aggregates^{2a,4} have shown that such species have superior stereoselectivity over pure amide bases in enolization reactions. While these careful investigations have provided many clues as to the nature of mixed aggregates in solution, the complementary solid-state structural data necessary for supporting and differentiating between proposed solution structures have until now been almost completely lacking.⁵ Herein we report a method for synthesis,⁶ isolation, and structural characterization⁷ of (LDA)₂LiCl(TMEDA)₂ (**1**) (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) as a three-runged ladder.

Synthesis of **1** could not be effected by mixing LiCl, LDA, and TMEDA, presumably due to the high lattice energy of LiCl. More surprisingly, the "ammonium salt route", so successful in preparing crystalline Lewis base complexes of lithium halides and pseudohalides,⁸ and in the synthesis of a lithium phenoxide/

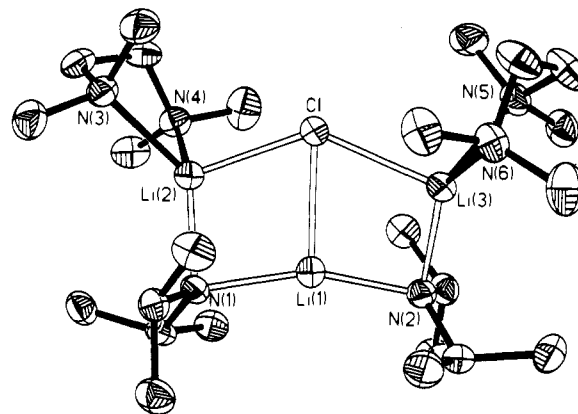
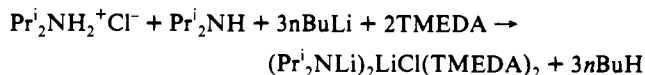


Figure 1. Thermal ellipsoid plot (50% probability) of the molecular structure of **1**. Selected bond distances (Å) and angles (deg): Li(1)–Cl = 2.478(3); Li(2)–Cl = 2.364(3); Li(3)–Cl = 2.384(3); Li(1)–N(1) = 2.021(3); Li(1)–N(2) = 2.022(3); Li(2)–N(1) = 2.070(3); Li(3)–N(2) = 2.074(3); Li(2)–Cl–Li(3) = 136.47(9); Li(2)–Cl–Li(1) = 68.63(9); Li(3)–Cl–Li(1) = 67.94(9); N(1)–Li(1)–Cl = 99.22(11); N(2)–Li(1)–Cl = 100.86(11); N(1)–Li(1)–N(2) = 159.9(2).

thiocyanate mixed aggregate,⁹ also failed. A new synthetic methodology was developed.¹⁰ By using the hydrochloride of the amine to be metalated (plus a further equivalent of the amine), the generation of LiCl was possible in the immediate vicinity of the amide at low temperature.



The fact that the reaction with butyllithium of the amine-hydrochloride was so different from that of the amine plus ammonium chloride is significant.¹¹ It suggests that the lithium amide units generated *in situ* are acting as strong complexants, trapping a fragment of LiCl in a partial R₂N–Li⁺ "lattice", thus preventing the fragment from further association into (LiCl)_n.

Inspection of the molecular structure (Figure 1) seems to support this view of **1** as a LiCl "monomer" trapped between two LDA·TMEDA "monomers". However, the longest Li–Cl distance is that of the supposed monomer unit Li(1)–Cl. Two shorter contacts to Li(2) and Li(3) complete the near-planar (root mean square deviation 0.029 Å) three-coordinate chloride geometry. The geometry around Li(1) is even nearer planarity [N(1), N(2), Cl, and Li(1), root mean square deviation 0.008 Å], Li(2) and Li(3) lying above and below this plane, respectively. A non-crystallographic 2-fold axis lies coincident with the Li–Cl bond. All these features characterize **1** as a three-runged ladder. Thus **1** constitutes, to our knowledge, the first odd-number-runged ladder in alkali-metal chemistry, and the first in which a chloride ion forms a component.¹² While the planar μ₃-chloride is very unusual, the LDA·TMEDA units are also of note. The η² chelating mode of TMEDA was not observed in two different crystal structures from^{2d,3a} and detailed NMR investigations of^{2d} the LDA/TMEDA system. It was postulated as a transient intermediate in exchange processes, but is here to be found in the solid state, stabilized by the sterically undemanding LiCl unit. Thus while LDA itself is too bulky to ladder^{3a} or be chelated by TMEDA,^{2d} lithium chloride is not bulky enough, preferring to

(9) Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1011.

(10) A similar method has recently been used to produce solutions containing some 1:1 bromide/amide aggregates among other species, ref 4.

(11) Reaction of 2 equiv of amine and TMEDA with 3 equiv of butyllithium and 1 equiv of ammonium chloride required strong heating to go to completion, producing a fine precipitate (LiCl).

(12) Mulvey, R. E. *Chem. Soc. Rev.* 1991, 20, 167. A recent review of laddered and stacked alkali-metal structures.

[†] Octel/Queens' College Research Fellow.

(1) Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1624.

(2) (a) Galiano-Roth, A. S.; Kim, Y.-J.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* 1991, 113, 5053. (b) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* 1992, 114, 794. (c) Hall, P. L.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* 1991, 113, 9575. (d) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* 1992, 114, 5100. (e) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* 1989, 111, 6722.

(3) (a) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* 1991, 113, 8187. (b) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* 1990, 112, 8602. (c) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* 1987, 109, 5539.

(4) Hall, P. L.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* 1991, 113, 9571.

(5) One 1:1 lithium amide/chloride structure has been published, containing a planar, cyclic secondary amide: Engelhardt, L. M.; Jacobsen, G. E.; White, A. H.; Raston, C. L. *Inorg. Chem.* 1991, 30, 3978.

(6) To a toluene solution (4 mL) of butyllithium (6.9 mmol) and TMEDA (0.69 mL, 4.6 mmol) were added Pr₂NH₂Cl (0.316 g, 2.3 mmol) and Pr₂NH (0.32 mL, 2.3 mmol) at 77 K under dry nitrogen. Storage of the clear solution layered with *n*-hexane (1 mL) at 273 K for 2 days produced a first crop of air-sensitive, pale yellow crystals of **1** (0.45 g, 40%): ¹H NMR (250 MHz, C₆D₆, 298 K) δ 3.7 (br unresolved multiplet, 2 H, Me₂CH), δ 2.1 (s, 12 H, Me₂N), δ 2.0 (s, 4 H, NCH₂CH₂N), δ 1.5 (br unresolved multiplet, 12 H, Me₂CH); mp = 69.5–70.0 °C. Satisfactory C, H, N, and Cl analyses were obtained.

(7) Crystal data for **1**: C₂₄H₆₀ClLi₃N₆, *M* = 489.1, monoclinic, *P*2₁/*n*, *a* = 9.126(3) Å, *b* = 17.538(6) Å, *c* = 20.470(7) Å, β = 98.02°, *V* = 3244.2(19) Å³, *Z* = 4, *D*_{calc} = 1.001 g cm⁻³, λ(Mo Kα) = 0.710 73 Å, μ = 0.138 mm⁻¹, *F*(000) = 1088. Measurements were made at 160 K on a Stoe-Siemens diffractometer with an Oxford Cryostream cooler from a crystal of size 0.77 × 0.69 × 0.61 mm. Structure solution was by direct methods, and all 5693 independent reflections were used for least squares refinement on *F*². H atoms were constrained. Other atoms were assigned anisotropic displacement parameters. At convergence, *wR* 2 = [Σ(*w*(*F*_o² – *F*_c²)²)/Σ(*w*(*F*_o²))]^{1/2} = 0.1367, conventional *R* [on *F* values for 4593 reflections with *I* > 2σ(*I*)] = 0.0470, goodness of fit on *F*² = 1.06 for 323 parameters. All features in a final difference synthesis were within ±0.42 e Å⁻³. Program systems: SHELXTL/PC, SHELXL-92 (G. M. Sheldrick, University of Göttingen, Germany).

(8) Barr, D.; Snaith, R.; Wright, D. S.; Mulvey, R. E.; Wade, K. *J. Am. Chem. Soc.* 1987, 107, 7891.

stack¹³ or associate infinitely to the ionic lattice. Careful combination of the two allows isolation of a ladder where two lithiums attain four-coordination instead of the maximum of three found for solvated LDA ring dimers.^{2d} One three-coordinate lithium remains in the central rung of the ladder, perhaps stabilized partially by CH...Li interactions (the shortest H-Li distances are 2.54 and 2.53 Å).¹⁴

Returning to the enolization studies of Collum, maximum *E/Z* selectivities were obtained where species akin to **1** were the most abundant in tetrahydrofuran solution.^{2a,4} While it is not possible in solution to differentiate between a cyclic trimer with each lithium coordinated by one Lewis base and a three-rung ladder with one "bare" lithium, the observed structure of **1** strongly suggests the second of these proposed structures to be correct. This is entirely consistent with *ab initio* calculations¹⁵ and the dearth of solvated trimers known in the solid state.¹⁶ Consequently, **1** may be used as a structural model for the species

(13) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79.

(14) Li-H distances of this magnitude have been correlated with CH...Li interactions before: Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 287. Such interactions would also explain the broadness of the isopropyl signals in the NMR spectrum, and an infrared absorption at 2570 cm⁻¹.

present in Collum's studies, and indeed for one of the species involved in the Corey-Gross enolization protocol.¹⁷ Approach of a ketone to the unsolvated, but highly sterically crowded, Li(1) offers a rationalization of the observed high stereoselectivity, at least at low percent conversions. The solution behavior and reactivity of **1** are currently under investigation.

Acknowledgment. We thank the Associated Octel Company, the Royal Society, and the SERC for financial support.

Supplementary Material Available: Details of the diffraction analysis, fully labeled plot of the molecular structure of **1**, and tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1** (12 pages); listing of observed and calculated structure factors for **1** (13 pages). Ordering information is given on any current masthead page.

(15) (a) Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719. (b) For a recent review of structural trends in lithium amides, see: Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(16) There are no complexed lithium amide trimers known in the solid state. One alkoxide trimer stabilized by anchimeric coordination has recently been reported: van der Schaaf, P. A.; Hogerheide, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1703.

(17) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495.