Lewis-base Adducts of Main Group 1 Metal Compounds. Part 2.[1] Syntheses and Structures of $[Li_4Cl_4(pmdien)_3]$ and $[LiI(pmdien)]$ *

Colin L. Raston, Brian W. Skelton, Claire R. Whitaker, and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009

Crystallization of lithium chloride from its solution in excess *NNN'N'N''*-pentamethyldiethylenetriamine (pmdien) in hydrocarbon yields a 4:3 adduct, characterised crystallographically as $[Li_4Cl_4(pmdien)_3]$, crystals of which are monoclinic, space group $P2_1/n$, with a = 9.318(7), b = 34.91(2), c = 13.578(7) Å, β = 97.08(5)°, Z = 4 oligomers; R = 0.077 for 2 286 observed reflections. Lithium iodide yields a 1:1 mononuclear species, $[LiI(pmdien)]$, crystals of which are orthorhombic, space group *Pbam*, with a = 14.895(8), b = 14.815(8), c = 13.550(8) Å, Z = 8; R = 0.063 for 913 observed reflections. In the iodide, there are two independent molecules, each with *m* symmetry and four-co-ordinate lithium [Li–I 2.75(3), 2.67(3) Å], whereas the chloride contains both four- and five-co-ordinate lithium atoms.

Permethylated polydentate tertiary amines such as *NNN'N'*-tetramethylethylenediamine (tmen) and *NNN'N'N''*-pentamethyldiethylenetriamine (pmdien) render Group 1 metal halides readily soluble in organic solvents[2,3] by the formation of metal N-chelate complexes. Solution studies[2] have suggested these to be 1:1 mononuclear, *e.g.* $[LiX(pmdien)]$, but recent work has shown the bromide to be a novel $[LLiBr_2LiL]$ (L = pmdien) dimer with five-co-ordinate lithium,[1] while a novel chlorine-centred cation $[LLi(\mu\text{-}Cl)LiL]^+$ with four-co-ordinate lithium has been isolated as its $[Li\{C(SiMe_3)_3\}_2]^-$ salt.[4]

In this paper we record the syntheses and structural characterisation of solid adducts of lithium chloride and iodide from solution with excess pmdien in hydrocarbon solvents; the chloride is a 4:3 species, $[Li_4Cl_4(pmdien)_3]$, while the iodide is mononuclear, $[LiI(pmdien)]$.

Experimental

Synthesis.—The present routes, similar to that adopted for the bromide analogue,[1] have been used as a convenient method of ensuring moisture-free conditions; crystalline compounds were obtained only with difficulty and those proportions appropriate to successful synthesis are given.

$[Li_4Cl_4(pmdien)_3]$. To hexane (30 cm³) at 0 °C was added standardized $LiBu^n$ solution (2.8 cm³, 1.68 mol dm⁻³ in hexane, 4.7 mmol) and excess of pmdien (0.81 g, 1 cm³, 5.8 mmol). $SiMe_3Cl$ (0.6 cm³, 4.7 mmol) was then added dropwise to the resulting yellow solution. The solution became colourless. After storage in the refrigerator overnight crystals formed; the supernatant liquid was removed and the crystals dried under vacuum (m.p. 81—86 °C) (Found: C, 46.8; H, 10.0; Cl, 21.6; N, 17.9. Calc. for $C_{27}H_{69}Cl_4Li_4N_9$: C, 47.0; H, 10.1; Cl, 20.6 N, 18.3%).

$[LiI(pmdien)]$. n-Butyl-lithium (2.8 cm³, 1.68 mol dm⁻³ in hexane, 4.7 mmol) was added to excess of pmdien (0.81 g, 1 cm³, 5.8 mmol) at 0 °C, giving a yellow solution. Methyl iodide (0.3 cm³, 4.8 mmol) was added dropwise to the cold solution without stirring giving a violent exothermic reaction and immediate formation of a white precipitate, insoluble in hexane, but eventually found to be soluble in toluene (10 cm³) on heating, depositing large needles on cooling. The solvent was removed and the product (0.86 g) dried under vacuum (m.p. 170—176 °C) (Found: C, 35.2; H, 7.6; I, 42.6; N, 13.6. Calc. for $C_9H_{23}ILiN_3$: C, 34.9; H, 7.5; I, 40.9; N, 13.6%).

The crystals of both compounds are hygroscopic, and were mounted in capillaries for the *X*-ray work.

Structure Determination.—Unique data sets were measured at 295 K within the specified $2\theta_{max.}$ limit using a Syntex $P\bar{1}$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 69 Å) and operating in conventional 2θ–θ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block-diagonal (chloride) or 2-block (iodide) least-squares refinement after solution of the structures by direct and vector methods as appropriate. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z) and $(U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$, R and R', at convergence are quoted; statistical reflection weights used were derived from $\sigma^2(I) = \sigma^2(I)_{diff.} + 0.000n[\sigma^4(I)_{diff.}]$. Neutral atom complex scattering factors were used;[5] computation used the XTAL 83 program system[6] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Final non-hydrogen atomic co-ordinates are given in Tables 1 and 2, and structural parameters in Tables 3—5.

Crystal data for $[Li_4Cl_4(pmdien)_3]$. $C_{27}H_{69}Cl_4Li_4N_9$, M = 689.5, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), a = 9.318(7), b = 34.91(2), c = 13.578(7) Å, β = 97.08(5)°, U = 4 383(5) Å³, D_c (Z = 4) = 1.05 g cm⁻³, $F(000)$ = 1 496, μ_{Mo} = 2.9 cm⁻¹ (no absorption correction); $2\theta_{max.}$ = 40°, N = 4 054, N_o = 2 286, R = 0.077, R' = 0.084 (n = 2.8). Specimen: *ca.* 0.2 mm.

Crystal data for $[LiI(pmdien)]$. $C_9H_{23}ILiN_3$, M = 307.2, orthorhombic, space group *Pbam* (D_{2h}^9, no. 55), a = 14.895(8), b = 14.815(8), c = 13.550(8) Å, U = 2 990(3) Å³, D_c (Z = 8) = 1.37 g cm⁻³, $F(000)$ = 1 232, μ_{Mo} = 19.7 cm⁻¹, $A^*_{min., max.}$ (Gaussian correction) 1.22, 1.85; $2\theta_{max.}$ = 45°, N = 2 029, N_o = 913, R = 0.063, R' = 0.057 (n = 2.3). Specimen: 0.36 × 0.36 × 0.10 mm.

Abnormal features. Crystals of the chloride were badly twinned; data were measured on one component deconvoluted from the diffraction pattern of such a specimen. Reciprocal lattice overlap on $3kl$ was severe and 29 reflections were deleted; $0kl$ were refined with a scale factor of 0.5. Both independent molecules of the iodide lie on crystallographic mirror planes;

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* 2,3,4-μ_3-Chloro-1,2;1,2;3,4-tri-μ-chloro-μ-[*NNN'N'N''*-pentamethyldiethylenetriamine-*N*(Li²),*N'N''*(Li³)]-1,4-bis(*NNN'N'N''*-pentamethyldiethylenetriamine-*N*,*N'*,*N''*)tetralithium(I) and iodo(*NNN'N'N''*-pentamethyldiethylenetriamine-*N*,*N'*,*N''*)lithium(I) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Non-hydrogen atom co-ordinates for [$Li_4Cl_4(pmdien)_3$]

Atom	*x*	*y*	*z*
Li(1)	1.302(2)	0.684 3(4)	0.185 5(11)
Li(2)	1.141(2)	0.604 4(5)	−0.318 9(10)
Li(3)	1.213(2)	0.596 7(4)	0.165 7(12)
Li(4)	1.065(2)	0.624 4(4)	−0.103 6(9)
Cl(1)	1.247 9(4)	0.631 89(8)	0.306 0(2)
Cl(2)	1.023 3(4)	0.662 97(7)	−0.242 9(2)
Cl(3)	1.221 3(3)	0.642 41(7)	0.042 0(2)
Cl(4)	1.136 8(3)	0.566 98(6)	−0.171 3(2)
Ligand A			
N(1)	1.526(1)	0.690 1(1)	0.235 2(7)
C(11)	1.594(1)	0.656 4(4)	0.212(1)
C(12)	1.566(2)	0.696 3(5)	0.341(1)
C(1)	1.573(2)	0.721 4(6)	0.184(2)
C(2)	1.508(1)	0.740 9(4)	0.114(1)
N(0)	1.354(1)	0.734 6(2)	0.087 5(6)
C(01)	1.327(2)	0.728 1(3)	−0.022 0(8)
C(2′)	1.260(2)	0.764 7(3)	0.116(1)
C(1′)	1.181(2)	0.759 5(4)	0.183(2)
N(1′)	1.159(1)	0.726 4(2)	0.236 8(7)
C(11′)	1.194(2)	0.735 6(4)	0.341(1)
C(12′)	1.016(1)	0.713 2(5)	0.218(1)
Ligand B			
N(1)	0.969 5(8)	0.591 8(2)	−0.430 5(5)
C(11)	0.941(2)	0.622 2(4)	−0.502 4(8)
C(12)	0.836(1)	0.584 6(5)	−0.384 4(9)
C(1)	1.008(1)	0.557 9(3)	−0.477 6(7)
C(2)	1.157(1)	0.556 5(3)	−0.498 6(7)
N(0)	1.259 0(9)	0.561 6(2)	−0.411 0(5)
C(01)	1.292(2)	0.524 7(3)	−0.359 9(8)
C(2′)	1.384(1)	0.581 9(4)	−0.435 2(8)
C(1′)	1.439(1)	0.608 0(5)	−0.369(1)
N(1)	1.338 7(9)	0.635 7(2)	−0.331 7(6)
C(11′)	1.401(1)	0.649 1(4)	−0.232 7(9)
C(12′)	1.313(1)	0.668 6(3)	−0.395 2(9)
Ligand C			
N(1)	0.861 4(9)	0.620 2(2)	−0.047 3(5)
C(11)	0.806(1)	0.659 6(3)	−0.046 4(8)
C(12)	0.760(1)	0.596 5(3)	−0.114 7(7)
C(1)	0.875(1)	0.604 0(3)	0.050 9(6)
C(2)	0.944(1)	0.565 2(2)	0.055 9(6)
N(0)	1.035 0(9)	0.559 2(2)	0.149 7(5)
C(01)	0.945(1)	0.559 7(4)	0.232 2(7)
C(2′)	1.107(1)	0.521 3(3)	0.145 8(8)
C(1′)	1.240(2)	0.522 3(3)	0.106(1)
N(1′)	1.348(1)	0.551 5(2)	0.146 9(7)
C(11′)	1.442(2)	0.555 6(4)	0.070(1)
C(12′)	1.430(2)	0.539 4(5)	0.236(1)

Table 2. Non-hydrogen atom co-ordinates [LiI(pmdien)]

	Molecule A			Molecule B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
I	0.194 7(1)	0.092 2(1)	0	0.097 9(1)	0.715 9(1)	0.5
Li	0.036(2)	0.187(2)	0	0.186(2)	0.559(2)	0.5
N(1)	−0.030(1)	0.198(1)	0.133(1)	0.195(1)	0.485(1)	0.633(1)
C(11)	−0.126(1)	0.184(2)	0.136(2)	0.146(2)	0.527(2)	0.708(2)
C(12)	0.002(2)	0.137(2)	0.207(2)	0.171(2)	0.392(2)	0.629(3)
C(1)	−0.012(2)	0.284(2)	0.163(2)	0.281(2)	0.493(4)	0.650(3)
C(2)	−0.002(2)	0.352(1)	0.094(2)	0.349(2)	0.509(2)	0.594(2)
N(0)	0.046(1)	0.328(1)	0	0.330(1)	0.561(2)	0.5
C(01)	0.133(2)	0.362(2)	0	0.363(2)	0.650(2)	0.5

thermal anisotropy was very high, and although not resolvable in terms of disorder or a lower symmetry space group, may nevertheless be a foil for either of these phenomena. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Discussion

[$Li_4Cl_4(pmdien)_3$].—Lithium chloride, formed under strictly anhydrous conditions from $SiMe_3Cl$ and $LiBu^n$, in the presence of excess of pmdien in hexane solution has yielded the novel oligomer [$Li_4Cl_4(pmdien)_3$], the stereochemistry being as shown in Figure 1. The oligomer is the asymmetric unit of the structure with no intrinsic crystallographically imposed symmetry, and no potential non-crystallographic symmetry elements. The four lithium centres within the oligomer each have different environments (Table 3): Li(1) is five-co-ordinate as is Li(2), with a tridentate pmdien ligand and a pair of bridging halogens, one of those in the environment of Li(1) being μ_3 [Cl(3)]. As with the lithium environments in the

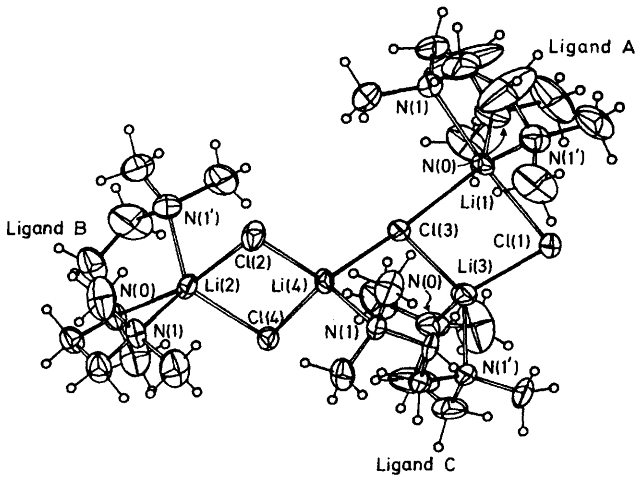

Figure 1. The molecule of [$Li_4Cl_4(pmdien)_3$]; 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with the atom labelling

Table 3. Lithium environments in $[Li_4Cl_4(pmdien)_3]$*

Li(1)

Atom	*r*	N(A0)	N(A1′)	Cl(1)	Cl(3)
N(A1)	2.12(2)	80.8(6)	117.1(7)	97.5(6)	119.9(7)
N(A0)	2.29(2)		81.3(6)	175.5(7)	93.5(5)
N(A1′)	2.16(2)			95.9(6)	121.0(7)
Cl(1)	2.55(2)				90.9(5)
Cl(3)	2.48(1)				

Li(2)

Atom	*r*	N(B0)	N(B1′)	Cl(2)	Cl(4)
N(B1)	2.11(2)	81.1(6)	128.6(8)	97.3(7)	113.4(8)
N(B0)	2.31(2)		79.5(6)	167.8(8)	99.2(6)
N(B1′)	2.16(2)			92.3(6)	116.4(7)
Cl(2)	2.60(2)				92.6(5)
Cl(4)	2.40(1)				

Li(3)

Atom	*r*	Cl(3)	N(C0)	N(C1′)
Cl(1)	2.26(2)	102.8(6)	117.1(9)	119.8(8)
Cl(3)	2.33(2)		116.7(8)	111.3(9)
N(C0)	2.10(2)			89.9(7)
N(Cl′)	2.05(2)			

Li(4)

Atom	*r*	Cl(3)	Cl(4)	N(Cl)
Cl(2)	2.32(1)	123.1(7)	101.9(5)	105.3(7)
Cl(3)	2.39(1)		112.1(7)	101.5(6)
Cl(4)	2.34(2)			113.1(7)
N(Cl)	2.14(2)			

Chlorine environment angles (°)

Li(1)–Cl(1)–Li(3)	82.4(5)	Li(2)–Cl(4)–Li(4)	84.1(5)
Li(2)–Cl(2)–Li(4)	80.1(5)	Li(3)–Cl(3)–Li(4)	110.2(6)
Li(1)–Cl(3)–Li(3,4)	82.6(5), 154.3(5)		

* *r* = Li–Cl or Li–N distance (Å). Other entries are the angles (°) subtended at the lithium by the relevant atoms at the head of the associated row and column.

Table 4. Non-hydrogen atom distances (Å) for [LiI(pmdien)]. The two values in each entry are for molecules A and B

Li–I	2.75(3), 2.67(3)
Li–N(1)	2.07(2), 2.12(2)
Li–N(0)	2.09(3), 2.14(4)
N(1)–C(11)	1.44(3), 1.39(4)
N(1)–C(12)	1.43(3), 1.42(3)
N(1)–C(1)	1.36(3), 1.30(4)
C(1)–C(2)	1.37(3), 1.29(5)
C(2)–N(0)	1.50(2), 1.52(3)
N(0)–C(01)	1.40(3), 1.40(4)

Table 5. Non-hydrogen interbond angles (°) for [LiI(pmdien)]. The two values in each entry are for molecules A and B; italicized atoms are related by the intramolecular mirror plane

I–Li–N(1)	116.9(9), 118.8(9)
I–Li–N(0)	117.2(15), 118.8(13)
N(1)–Li–N(0)	87.3(9), 87.0(11)
N(1)–Li–*N*(*1*)	121.8(18), 117.0(14)
Li–N(1)–C(1)	103(2), 99(2)
Li–N(1)–C(11)	119(2), 111(2)
Li–N(1)–C(12)	113(2), 117(2)
C(1)–N(1)–C(11)	109(2), 110(3)
C(1)–N(1)–C(12)	109(2), 110(3)
C(11)–N(1)–C(12)	103(2), 110(2)
N(1)–C(1)–C(2)	121(2), 134(4)
C(1)–C(2)–N(0)	117(2), 116(3)
Li–N(0)–C(2)	102(1), 100(1)
Li–N(0)–C(01)	115(2), 111(2)
C(2)–N(0)–C(01)	111(1), 114(1)
C(2)–N(0)–*C*(*2*)	117(2), 114(1)

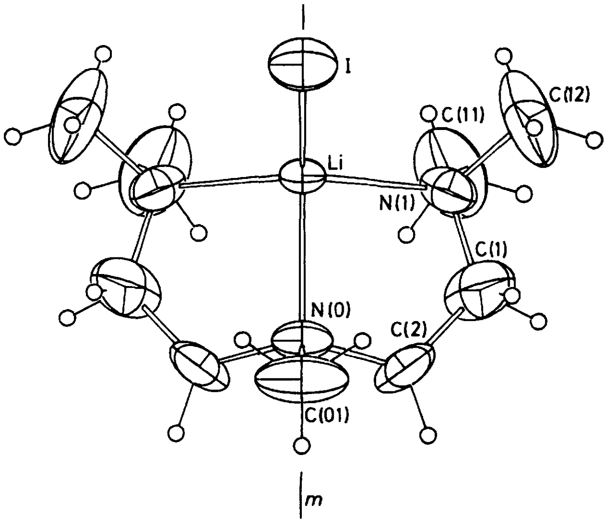

Figure 2. Molecule A of [LiI(pmdien)]; molecule B is similar

bromide, the environments of Li(1) and Li(2) in this compound were fairly close to *fac*-trigonal bipyramidal with the central nitrogen atom of the tridentate ligand at one apex and opposed by one of the halogen atoms; the local symmetry about the Li approximates to *m*.

Parameter changes are largely confined to the LiX_2L ring; Li–Cl distances are more unsymmetrical about Li(2), in spite of the similar nature of the chlorine atoms, those about Li(1) being μ [Cl(1)] and μ_3 [Cl(3)]. Li(3) and Li(4) are both four-co-ordinate, with larger angles generally and, in particular, between the halogen atoms in the $LiCl_2Li$ rings, compared with their five-co-ordinate counterparts. About Li(3), the N(0)–Li–N(1) angle of ligand C approaches 90°, *ca.* 10° larger than its counterparts in the five-co-ordinate environments. It is of interest to note that the Li–X,X′ asymmetry about the metal atoms of the bromide is greater than that at either of the five-co-ordinate metal atoms in the chloride, probably a consequence of *trans*-$LiBr_2Li$ annular methyl contacts. The only other structurally authenticated tetranuclear lithium halide species are $[LiCl\{OP(NMe_2)_3\}]_4$,[7] $[Li_4Cl_2(OEt_2)_{10}]^{2+}$,[8] and $(Et_2OLiPh)_3LiBr$, which contain only triply bridging halogens.

[LiI(pmdien)]. In the situation where three co-ordination sites about the lithium are occupied by the tridentate ligand with bulky N-substituents, the achievement of five-co-ordination by the attachment of a pair of bridging halogen atoms becomes increasingly difficult to sustain as halide size increases. Consequently, the increased asymmetry in Li–X distances found in the bromide reaches its logical culmination in the iodide, where reversion to a novel mononuclear four-co-ordinate lithium halide species occurs (Figure 2). The two independent molecules of the iodide both lie on crystallographic mirror planes; both molecules have very high thermal motion anisotropy at their periphery, perhaps, not surprisingly, a consequence of their pseudo-spheroidal profiles librating in the lattice, but also perhaps a result of unresolved disorder or lower symmetry consequent upon the different conformational arrays which might be present. Although the precision of the lithium environment is low, it is of interest to compare it with the

$LiIN_3$ environment found in tris(3,5-dimethylpyridine)iodolithium(I).[10] In that compound Li–I is 2.80(1) Å,[10] slightly longer than the present values of 2.75(3) and 2.67(3) Å (all values uncorrected for libration), and Li–N [2.02(2)—2.07(2) Å],[10] slightly shorter than the present values, in keeping with the larger N–Li–N angles [107.4(8)—113.1(9)°].[10]

Formation of a 4:4:3 complex containing four different lithium environments, rather than a 1:1:1 complex, as proposed in $[Li_2(\mu\text{-}Cl)(pmdien)_2]Cl$,[4] in the presence of excess amine is noteworthy. Its ^7Li n.m.r. (116.64 MHz) spectrum in toluene consisted of a single line down to −73 °C (δ 0.75 relative to 0.1 mol dm^{-3} $LiNO_3$) due to rapid exchange and/or self dissociation–association. This contrasts with a related amido complex $[Li_6\{\overline{N(CH_2)_3C}H_2\}_6(pmdien)_2]$ which shows magnetically distinct lithiums at low temperature.[11] Not surprisingly the 1:1:1 iodide complex gave a single line down to −73 °C (δ 0.77). Both of the lithium halide complexes and the bromide analogue have a substantially constant ^7Li chemical shift over a wide range of concentrations.[3]

Acknowledgements

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