Lewis-base Adducts of Main Group 1 Metal Compounds. Part 3.[1] Synthesis and Structural Systematics* of $[LiXL_3]$ and $[L'_2LiX_2LiL'_2]$ Systems (X = Cl, Br, or I; L = 3,5-$Me_2C_5H_3N$, L′ = 2-MeC_5H_4N)*

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Complexes $[LiXL_3]$ and $[L'_2LiX_2LiL'_2]$ (X = Cl, Br, or I; L = 3,5-dimethylpyridine, L′ = 2-methylpyridine) have been synthesized by recrystallization of the anhydrous lithium halide from the parent base and their stoicheiometries and structures confirmed and defined by single-crystal *X*-ray structure determination at 295 K; the structures are closely related to those of their copper(I) analogues. $[LiClL_3]$ and $[LiBrL_3]$ are rhombohedral, space group *R*3*c*, with $a \approx 10.3$ Å, $\alpha \approx 96°$, $Z = 2$, the molecules being disposed on three-fold crystallographic axes. $[LiIL_3]$ is monoclinic, space group *Cc*, with $a = 13.260(6)$, $b = 15.178(8)$, $c = 11.625(5)$ Å, $\beta = 97.49(3)°$, $Z = 4$. The structures were refined to residuals of 0.044, 0.036, 0.033 for 406, 302, and 1 307 independent observed reflections respectively. Li–Cl, –Br, –I are 2.320(9), 2.51(2), and 2.80(1) Å respectively. $[L'_2LiX_2LiL'_2]$ are all triclinic, space group $P\bar{1}$, with $a \approx 9.5$, $b \approx 9.2$, $c \approx 8.9$ Å, $\alpha \approx 107$, $\beta \approx 117$, $\gamma \approx 95°$ (chloride, bromide), $\alpha \approx 68$, $\beta \approx 85$, $\gamma \approx 75°$ (iodide), $Z = 1$ dimer. Residuals were 0.064, 0.041, 0.041 for 1 399, 1 846, 2 030 independent observed reflections respectively. $\langle$Li–X$\rangle$ are 2.38, 2.56, 2.80 Å (average) respectively.

With pyridine bases substituted in the 2- and 6-positions, steric control of the co-ordination number of *e.g.* copper(I) in its complexes may be effected by the degree and nature of substitution. Thus, for the perchlorate, the copper in $[CuL_n][ClO_4]$ may be four-,[2] three-,[3] or two-co-ordinate[4] depending on whether the base is pyridine, 2-methylpyridine, or 2,6-dimethylpyridine, if synthesis is effected by recrystallization of copper(I) perchlorate from neat base. Similar control over the nature of the halide adducts $[CuXL_n]$ may be achieved: with no substituent in the 2-position, *e.g.* with 3-methyl- or 3,5-dimethyl-pyridine, $n = 3$, while with 2-methylpyridine $n = 2$[5–7] with copper four-co-ordinate in a bridged-dimer configuration. With 2,6-dimethylpyridine, n is still 2 but discrete three-co-ordinate monomers are obtained,[6] and $n = 1$ may be achieved with very bulky bases.[8] The present studies demonstrate that parallel behaviour may be achieved on a wide-ranging scale with lithium rather than copper(I) halides as substrate. The lithium halides yield compounds $[LiXL_3]$ (X = Cl, Br, or I) on crystallization from 3,5-dimethylpyridine (3,5Me_2-py), and compounds $[L'_2LiX_2LiL'_2]$ from 2-methylpyridine (2Me-py). The present paper describes their synthesis and structural characterization.

Experimental

Synthesis.—All complexes described in this paper are simply (but not necessarily easily) prepared by recrystallization of the lithium halide from the parent base under standard Schlenk procedures; the chief difficulty encountered concerns the isolation of partially hydrated species introduced by incomplete drying of chemicals. In synthesis of the present compounds, *absolute dryness is essential*, and not easily achieved.

Materials. Solid LiCl, LiBr, and LiI were ground up and heated at 180 °C for two days under vacuum and stored under dry argon. 3,5-Dimethylpyridine was dried under argon using sodium pieces, freeze degassed, filtered and stored under argon; 2-methylpyridine was treated similarly. The compounds were prepared as colourless crystals by recrystallization of the lithium halide from a solution in the hot base. They were mounted in capillaries for the *X*-ray work.

$[LiCl(3,5Me_2\text{-}py)_3]$, m.p. 151—152 °C (decomp.) (Found: C, 69.2; H, 7.6; Cl, 10.0; N, 11.6. Calc. for $C_{21}H_{27}ClLiN_3$: C, 69.3; H, 7.5; Cl, 9.7; N, 11.6%).

$[LiBr(3.5Me_2\text{-}py)_3]$, m.p. 169—170 °C (decomp.) (Found: C, 61.0; H, 6.6; Br, 20.7; N, 10.2. Calc. for $C_{21}H_{27}BrLiN_3$: C, 61.8; H, 6.7; Br, 19.6; N, 10.3%).

$[LiI(3.5Me_2\text{-}py)_3]$, m.p. 190—196 °C (decomp.) (Found: C, 54.0; H, 5.9; I, 27.6; N, 8.8. Calc. for $C_{21}H_{27}ILiN_3$: C, 55.4; H, 6.0; I, 27.9; N, 9.2%).

$[\{LiCl(2Me\text{-}py)_2\}_2]$, m.p. 80—81 °C (decomp.) (Found: C, 62.4; H, 6.1; Cl, 16.0; N, 12.1. Calc. for $C_{24}H_{28}Cl_2Li_2N_4$: C, 63.0; H, 6.2; Cl, 15.5; N, 12.3%).

$[\{LiBr(2Me\text{-}py)_2\}_2]$, m.p. 121—126 °C (decomp.) (Found: C, 52.2; H, 5.1; Br, 28.5; N, 10.1. Calc. for $C_{24}H_{28}Br_2Li_2N_4$: C, 52.8; H, 5.2; Br, 29.3; N, 10.3%).

$[\{LiI(2Me\text{-}py)_2\}_2]$, m.p. 140—146 °C (decomp.) (Found: C, 45.1, H, 4.5; I, 39.5; N, 8.8. Calc. for $C_{24}H_{28}I_2Li_2N_4$: C, 45.0; H, 4.4; I, 39.6; N, 8.8%).

In most cases the crystals melted at the temperatures specified above but losing ligand in the process; it is expected that phases $[LiXL_n]$ with diminishing n are formed.

Structure Determination.—Unique data sets were measured at 295 K on specimens mounted in capillaries, 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 ($\lambda = 0.710\,69$ Å) and operating in conventional 2θ—θ scan mode. N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered observed and used in the full-matrix least-squares refinement after solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; estimated values of (x, y, z) and $(U_{\text{iso}})_H$ were used. Residuals on $|F|$, R and R', at convergence are quoted, statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{\text{diff.}} + 0.000n[\sigma^4(I)_{\text{diff.}}]$ being used. Neutral complex scattering

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* Chloro-, bromo-, and iodo-tris(3,5-dimethylpyridine)lithium(I) and di-μ-chloro-, di-μ-bromo-, and di-μ-iodo-bis[(2-methylpyridine)-lithium(I)] respectively.

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

factors were used;[9] computation used the XTAL program system,[10] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Crystal data for [LiCl(3,5Me$_2$-py)$_3$] (**1**). $C_{21}H_{27}ClLiN_3$, M = 363.9, rhombohedral, space group $R3c$ (C^6_{3v}, no. 161), a = 10.270(6) Å, α = 95.65(5)°, U = 1 066(1) Å^3, D_c (Z = 2) = 1.13 g cm^{-3}, F(000) = 388, μ_{Mo} = 1.8 cm^{-1} (no absorption correction); $2\theta_{max.}$ = 50°, N = 635, N_o = 406, R = 0.044, R' = 0.041 (n = 5) (both chiralities). Specimen: 0.4 × 0.3 × 0.7 mm.

Crystal data for [LiBr(3,5Me$_2$-py)$_3$] (**2**). $C_{21}H_{27}BrLiN_3$, M = 408.3, rhombohedral, space group $R3c$, a = 10.392(10) Å^3, α = 95.93(8)°, U = 1 103(1) Å^3, D_c (Z = 2) = 1.23 g cm^{-3}, F(000) = 424, μ_{Mo} = 18.4 cm^{-1} (no absorption correction); $2\theta_{max.}$ = 45°, N = 478, N_o = 302, R = 0.036, R' = 0.037 (n = 3) (both chiralities). Specimen: 0.4 × 0.25 × 0.4 mm.

Crystal data for [LiI(3,5Me$_2$-py)$_3$] (**3**). $C_{21}H_{27}ILiN_3$, M = 455.3, monoclinic, space group Cc (C^4_s, no. 9), a = 13.260(6), b = 15.178(8), c = 11.625(5) Å, β = 97.49(3)°, U = 2 311(2) Å^3, D_c (Z = 4) = 1.31 g cm^{-3}, F(000) = 920, μ_{Mo} = 13.1 cm^{-1}, $A^*_{min.,max.}$ = 1.23, 1.45; $2\theta_{max.}$ = 50°, N = 2 043, N_o = 1 307, R = 0.033, R' = 0.037 (n = 7) (both chiralities). Specimen: 0.35 × 0.2 × 0.9 mm.

Crystal data for [(2Me-py)$_2$LiCl$_2$Li(2Me-py)$_2$] (**4**). $C_{24}H_{28}Cl_2Li_2N_4$, M = 457.3, triclinic, space group $P\bar{1}$ (C^1_i, no. 2), a = 9.526(8), b = 9.148(8), c = 8.942(8) Å, α = 107.01(7), β = 116.29(6), γ = 95.12(7)°, U = 646(1) Å^3, D_c (Z = 1 dimer) = 1.18 g cm^{-3}, F(000) = 240, μ_{Mo} = 2.6 cm^{-1} (no absorption correction); $2\theta_{max.}$ = 50°, N = 2 280, N_o = 1 399, R = 0.064, R' = 0.057 (n = 1). Specimen: 0.3 × 0.25 × 0.4 mm.

Crystal data for [(2Me-py)$_2$LiBr$_2$Li(2Me-py)$_2$] (**5**). $C_{24}H_{28}Br_2Li_2N_4$, M = 546.2, triclinic, space group $P\bar{1}$, a = 9.556(3), b = 9.234(2), c = 9.077(2) Å, α = 107.29(2), β = 116.94(2), γ = 94.28(2)°, U = 660.8(3) Å^3, D_c (Z = 1 dimer) = 1.37 g cm^{-3}, F(000) = 276, μ_{Mo} = 30.3 cm^{-1}, $A^*_{min.,max.}$ = 1.7, 2.4; $2\theta_{max.}$ = 50°, N = 2 282, N_o = 1 846, R = 0.041, R' = 0.041 (n = 2). Specimen: 0.4 × 0.2 × 0.8 mm.

Crystal data for [(2Me-py)$_2$LiI$_2$Li(2Me-py)$_2$] (**6**). $C_{24}H_{28}I_2Li_2N_4$, M = 640.2, triclinic, space group $P\bar{1}$, a = 10.553(6), b = 9.243(5), c = 8.138(4) Å, α = 68.32(4), β =

Table 1. Non-hydrogen atom co-ordinates for [LiX(3,5Me$_2$-py)$_3$]

	(1) (X = Cl)			(2) (X = Br)		
Atom	x	y	z	x	y	z
X	0.650 0(–)	*	*	0.650 0(–)	*	*
Li	0.504 5(9)	*	*	0.493(2)	*	*
N(1)	0.393 2(5)	0.373 9(5)	0.599 0(5)	0.383(1)	0.369(1)	0.594(1)
C(2)	0.325 0(6)	0.262 4(6)	0.544 9(6)	0.317(1)	0.257(1)	0.541(1)
C(3)	0.240 1(6)	0.186 1(6)	0.609 1(7)	0.233(1)	0.184(1)	0.606(2)
C(31)	0.164 3(9)	0.060 4(7)	0.539 6(9)	0.163(2)	0.062(2)	0.542(2)
C(4)	0.223 5(7)	0.232 2(8)	0.735 8(7)	0.220(2)	0.232(2)	0.734(2)
C(5)	0.291 7(6)	0.346 9(6)	0.796 6(6)	0.286(1)	0.343(2)	0.789(1)
C(51)	0.272 0(8)	0.398 9(8)	0.933 1(7)	0.270(2)	0.402(2)	0.926(2)
C(6)	0.376 5(6)	0.412 1(5)	0.723 4(6)	0.372(1)	0.411(1)	0.716(1)

* Symmetry constraint: $x = y = z$; X atom defines origin.

Table 2. Non-hydrogen atom co-ordinates for [LiI(3,5Me$_2$-py)$_3$] (**3**)

Ligand	1			2			3		
Atom	x	y	z	x	y	z	x	y	z
I*	0.25	0.247 50(6)	0.5						
Li	0.081(1)	0.250(1)	0.329(1)						
N(1)	0.086 9(8)	0.137 0(6)	0.229(1)	−0.048 1(7)	0.255 9(8)	0.411 0(8)	0.087 7(9)	0.355 0(7)	0.223(1)
C(2)	0.013(1)	0.117(9)	0.149(1)	−0.139(1)	0.280 7(9)	0.358(1)	0.035(1)	0.364 8(10)	0.117(1)
C(3)	0.023(1)	0.045 4(9)	0.071(1)	−0.226(1)	0.282 8(10)	0.411(1)	0.040(1)	0.439 3(11)	0.049(1)
C(31)	−0.066(2)	0.020 0(13)	−0.018(2)	−0.325(1)	0.314 3(19)	0.349(2)	−0.024(1)	0.449(15)	−0.069(1)
C(4)	0.115(1)	0.007 0(9)	0.070(1)	−0.214(1)	0.257 4(13)	0.525(1)	0.102(1)	0.506 7(12)	0.096(2)
C(5)	0.196(1)	0.033 5(9)	0.151(1)	−0.123(1)	0.226 6(9)	0.583(1)	0.158(1)	0.499 0(10)	0.202(1)
C(51)	0.301(1)	−0.002(1)	0.152(2)	−0.113(2)	0.196 9(18)	0.706(2)	0.226(2)	0.571 4(12)	0.253(2)
C(6)	0.175(1)	0.098 2(9)	0.230(1)	−0.042(1)	0.230 3(8)	0.522(1)	0.147(1)	0.421 0(9)	0.261(1)

* Defines origin.

Table 3. Non-hydrogen atom co-ordinates for [(2Me-py)$_2$LiX$_2$Li(2Me-py)$_2$]

	(4) (X = Cl)			(5) (X = Br)			(6) (X = I)		
Atom	x	y	z	x	y	z	x	y	z
X	0.618 0(2)	0.352 4(2)	0.539 6(2)	0.627 19(6)	0.341 76(6)	0.543 95(7)	−0.098 36(4)	0.928 08(5)	0.748 69(5)
Li	0.367 0(10)	0.375 5(10)	0.328 3(11)	0.357 5(9)	0.366 9(9)	0.315 7(10)	0.141 5(10)	0.837 1(12)	0.585 1(13)
N(1)	0.366 9(5)	0.309 0(5)	0.084 4(5)	0.362 8(4)	0.307 2(4)	0.078 0(5)	0.299 9(5)	0.839 9(6)	0.717 0(7)
C(12)	0.285 4(6)	0.358 3(6)	−0.049 4(7)	0.280 1(6)	0.354 7(6)	−0.055 3(7)	0.424 1(7)	0.801 7(9)	0.667 3(10)
C(121)	0.155 0(7)	0.435 6(7)	−0.040 7(8)	0.151 6(8)	0.432 1(7)	−0.045 1(8)	0.448 7(8)	0.764 0(13)	0.500 9(13)
C(13)	0.316 3(8)	0.335 5(8)	−0.192 4(8)	0.310 6(9)	0.331 5(8)	−0.194 4(8)	0.526 1(8)	0.800 2(13)	0.763 1(14)
C(14)	0.434 3(9)	0.257 9(8)	−0.197 4(9)	0.430 0(10)	0.258 5(9)	−0.196 9(9)	0.499 6(8)	0.830 2(13)	0.916 3(14)
C(15)	0.514 5(7)	0.209 9(7)	−0.061 5(9)	0.512 0(7)	0.208 0(8)	−0.063 3(9)	0.372 3(8)	0.866 7(11)	0.969 4(12)
C(16)	0.482 5(7)	0.237 1(6)	0.078 6(7)	0.476 8(6)	0.234 8(6)	0.070 1(7)	0.276 2(7)	0.871 3(8)	0.867 8(10)
N(2)	0.161 4(5)	0.245 3(6)	0.307 4(5)	0.155 1(4)	0.241 6(4)	0.298 3(5)	0.167 0(5)	0.607 4(6)	0.578 5(6)
C(22)	0.129 5(7)	0.093 5(7)	0.288 2(7)	0.126 7(6)	0.091 6(6)	0.279 5(7)	0.175 4(6)	0.476 3(7)	0.725 9(8)
C(221)	0.239 5(8)	0.000 2(7)	0.250 9(9)	0.234 3(7)	0.002 3(7)	0.237 2(9)	0.183 0(8)	0.494 9(9)	0.897 8(9)
C(23)	−0.000 7(8)	0.026 4(7)	0.298 7(8)	0.002 1(7)	0.026 6(6)	0.295 5(8)	0.177 7(7)	0.329 0(8)	0.716 8(10)
C(24)	−0.101 6(7)	0.115 6(9)	0.325 7(9)	−0.096 5(7)	0.114 1(8)	0.329 1(8)	0.172 4(7)	0.314 6(9)	0.556 9(11)
C(25)	−0.071 8(7)	0.268 8(8)	0.345 6(8)	−0.070 2(6)	0.265 6(7)	0.344 9(7)	0.162 8(7)	0.446 5(10)	0.408 1(10)
C(26)	0.060 5(7)	0.329 2(6)	0.334 9(7)	0.056 6(6)	0.325 2(6)	0.332 1(7)	0.161 0(7)	0.590 5(9)	0.423 5(9)

Table 4. $LiXN_3$ geometries in $[LiX(3,5Me_2\text{-}py)_3]$[a]

Compound	(**1**) (X = Cl)	(**2**) (X = Br)	(**3**) (X = I)
Distances (Å)			
Li–X	2.320(9)	2.51(2)	2.80(1)
	[2.412(9)]	[2.51(1)]	[2.683(3)]
Li–N	2.054(11)	2.07(2)	2.07(2), 2.06(2), 2.02(2)
	[2.08(1)]	[2.02(1)]	[2.01(1), 2.15(4), 1.98(2)]
H(6) • • • X	3.09	3.10	3.1_8, 3.2_0, 3.1_9
	[2.8_3]	[3.0_7]	[3.20, 3.13, 3.2_6]
H(6) • • • X (Pauling[b])	3.0_0	3.1_5	3.3_5
Angles (°)			
X–Li–N	112.4(4)	110.1(8)	107.6(7), 107.8(7), 110.2(7)
	[104.8(6)]	[107.1(5)]	[106.8(9), 107.4(5), 104.3(4)]
N–Li–N′	106.4(5)	108.8(9)	113.1(9), 110.6(9), 107.4(8)
	[113.7(6)]	[111.7(5)]	[109(1), 122(2), 106(1)]

[a] Equivalent values for the corresponding copper(I) derivatives are given in square brackets below those for the lithium derivatives. [b] L. A. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1962, p. 262.

84.58(4), γ = 74.70(4)°, U = 711.6(6) Å^3, D_c = 1.49 g cm^{-3}, $F(000)$ = 312, μ_{Mo} = 34.5 cm^{-1}, $A^*_{min.,max.}$ = 1.45, 2.20; $2\theta_{max.}$ = 50°, N = 2 250, N_o = 2 030, R = 0.041, R' = 0.046 (n = 7). Specimen: cuboid, *ca.* 0.3 mm.

Abnormal features and variations in procedure. No satisfactory untwinned specimen could be obtained for (**4**) and the data set used was deconvoluted from that of a twinned specimen, 12 reflections badly affected by reflection overlap being deleted. Compounds (**4**) and (**5**) are isomorphous, and also isomorphous with their previously studied copper(I) analogues;[7] cell and co-ordinate settings of the latter were used for the present work.[7] Compounds (**1**) and (**2**) are isomorphous with their copper(I) bromide analogue (the chloride is $R3m$ rather than $R3c$), while the iodide is isomorphous with its copper(I) iodide analogue;[5] similar cells and settings were used for the lithium analogues. For the copper(I) iodide analogue, refinement problems were experienced because of the pseudo-symmetric relation to the related $R3c$ structures; this was not the case with the (lighter atom) lithium analogue which refined relatively smoothly. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Discussion

Synthesis of the adducts $[LiX(3,5Me_2\text{-}py)_3]$ and $[(2Me\text{-}py)_2\text{-}LiX_2Li(2Me\text{-}py)_2]$ as air-sensitive (*i.e.* moisture-sensitive) crystalline solids has been achieved by recrystallization of the lithium halide LiX (X = Cl, Br, or I) from the parent base. Single-crystal *X*-ray structure determination has been used to establish the mononuclear, four-co-ordinate nature of the complexes $[LiX(3,5Me_2\text{-}py)_3]$ (Figure 1), and the binuclear $[(2Me\text{-}py)_2LiX_2Li(2Me\text{-}py)_2]$ species (Figure 2), also with four-co-ordinate lithium and dihalogeno-bridges. Surprisingly strong parallels with the analogous copper(I) systems have been established.

$[CuX(3,5Me_2\text{-}py)_3]$ comprise a structurally related series of compounds based on the $R3m$ array of $[CuCl(3,5Me_2\text{-}py)_3]$,[5] in which one molecule in the unit cell achieves its potential $3m$ symmetry, being disposed on the crystallographic three-fold axis with the ligands lying in the three intersecting mirror planes. By a slight concerted twist of the three ligands about their Cu–N co-ordination axes, this symmetry is degraded to 3 and, by stacking molecules of alternating chirality in a polar array along the three-fold axis, the cell size is doubled, with symmetry $R3c$, as found in $[CuBr(3,5Me_2\text{-}py)_3]$.[5] Loss of true three-fold symmetry within the structure may lead to a similar,

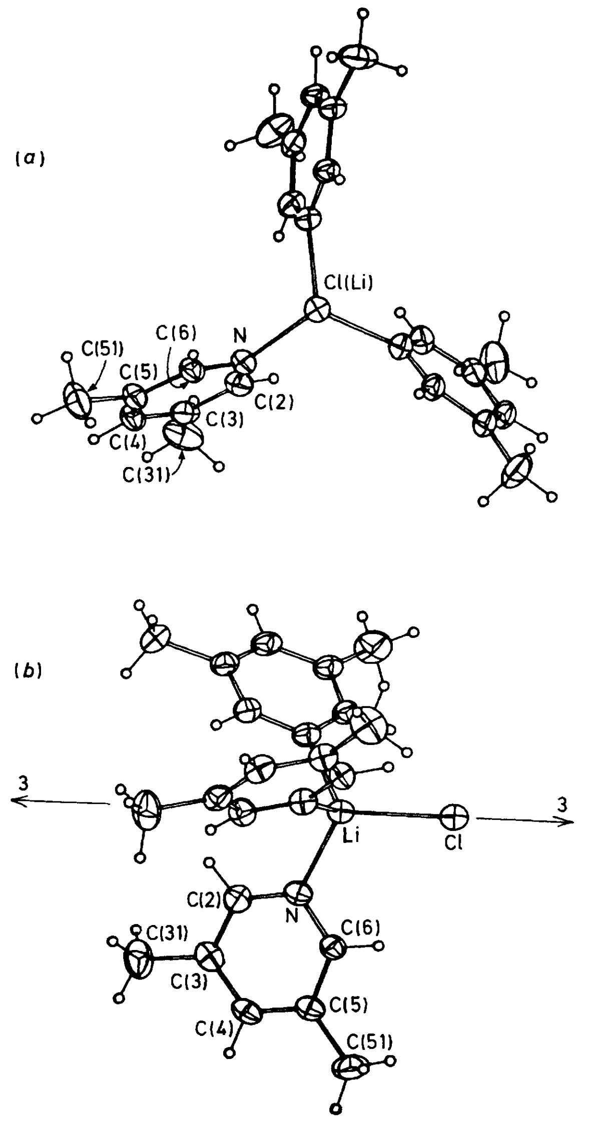

Figure 1. A single molecule of $[LiCl(3,5Me_2\text{-}py)_3]$ (**1**), projected (*a*) down and (*b*) normal to the three-fold axis. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, together with atom labelling. Hydrogen atoms have an arbitrary radius of 0.1 Å

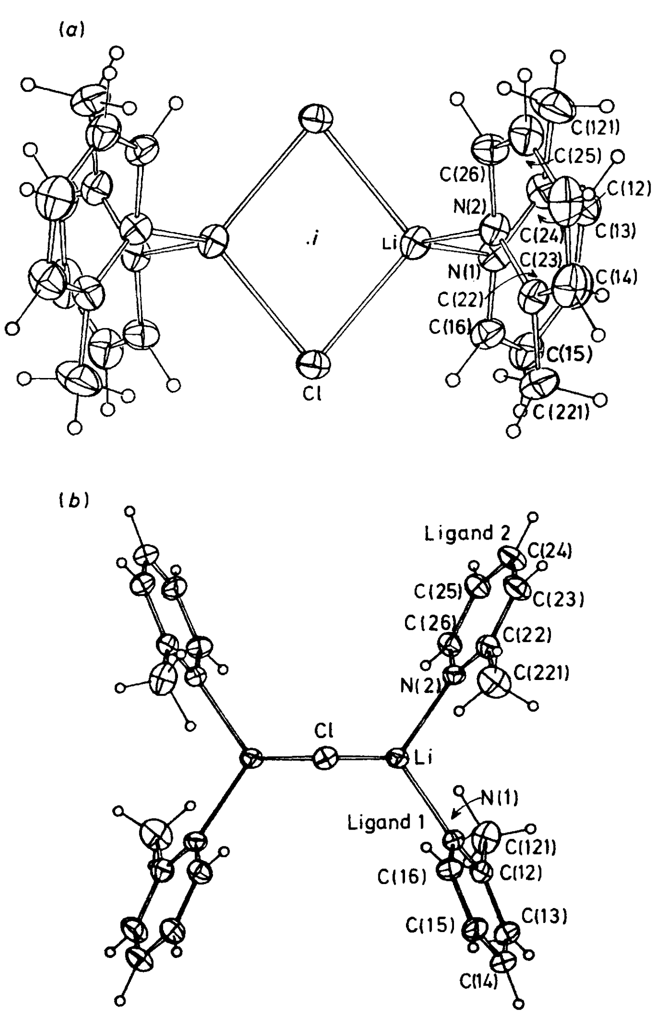

Figure 2. A single dimer of [(2Me-py)$_2$LiCl$_2$Li(2Me-py)$_2$], projected (*a*) normal to the Li$_2$Cl$_2$ plane, (*b*) through the Cl $\cdots$ Cl direction

monoclinic *Cc* array with three independent ligands in the molecule as in [CuI(3,5Me$_2$-py)$_3$].[5]

In the three copper(I) structures, Cu–Cl, –Br, –I are 2.412(9), 2.51(1), 2.683(3) Å; Cu–N in each case are 2.08(1), 2.02(1), 1.98(2)—2.15(4) Å,[5] the precision of the last (iodide) value being adversely affected by correlation problems in the refinement associated with loss of symmetry. In the lithium analogues, we find both chloride and bromide to adopt the *R*3*c* structure, while the iodide is *Cc*. The structures of the lithium analogues are based on closely similar arrays to those of the copper derivatives, with the variation that the chloride and bromide adducts are both of the *R*3*c* structure, while the iodide is *Cc*.

Comparison of metal–ligand distances (Table 4) is of considerable interest, showing a shorter lithium–halogen bond, by *ca.* 0.1 Å, while the less-precisely determined metal–nitrogen distances, although scattered more widely, suggest no significant trend (especially at the 0.1 Å level) either in respect of change of halide or metal. Although some erratic variations are observed, the results concerning the angles in the metal-atom co-ordination sphere suggest Cl–Li–N to be unusually large compared with the remainder. As with the copper(I) complexes, the H(6) $\cdots$ X interactions lie at, or close to, the van der Waals distances and may be a significant determinant of the structural characteristics of the species.

Table 5. N$_2$LiX$_2$LiN$_2$ geometries in [(2Me-py)$_2$LiX$_2$Li(2Me-py)$_2$]*

Compound	(4) (X = Cl)	(5) (X = Br)	(6) (X = I)
Distances (Å)			
Li–X	2.378(8) [2.433(2)]	2.555(7) [2.581(2)]	2.821(10) [2.714(3)]
Li–X′	2.383(9) [2.476(2)]	2.573(8) [2.607(2)]	2.768(9) [2.663(3)]
Li–N(1)	2.09(1) [2.026(4)]	2.09(1) [2.027(7)]	2.08(1) [2.05(1)]
Li–N(2)	2.10(1) [2.031(4)]	2.09(1) [2.030(6)]	2.09(1) [2.06(1)]
Li $\cdots$ Li	3.004(9) [3.145(3)]	3.242(8) [3.351(3)]	3.589(12) [3.083(3)]
X $\cdots$ X	3.694(3) [3.769(2)]	3.972(1) [3.962(2)]	4.285(2) [4.407(3)]
Angles (°)			
Li–X–Li	78.2(3) [79.68(6)]	78.5(2) [80.45(6)]	79.9(3) [69.95(6)]
X–Li–X′	101.8(2) [100.32(5)]	101.5(2) [99.56(5)]	100.1(3) [110.05(6)]
X–Li–N(1)	105.8(4) [103.1(1)]	105.7(4) [103.2(1)]	111.2(5) [107.9(3)]
X–Li–N(2)	114.6(5) [114.2(1)]	113.7(4) [112.2(2)]	110.7(4) [106.5(3)]
X′–Li–N(1)	115.6(5) [111.9(1)]	114.0(4) [111.5(2)]	113.5(5) [104.6(3)]
X′–Li–N(2)	106.6(5) [103.4(1)]	106.2(4) [103.8(2)]	111.9(5) [109.7(4)]
N(1)–Li–N(2)	112.2(3) [122.1(1)]	115.0(3) [124.0(2)]	109.2(4) [117.9(2)]

* Equivalent values for the corresponding copper(I) compounds are given in square brackets below those for the lithium derivatives.

The 1:2 adducts of the copper(I) halides with 2-methylpyridine are all binuclear dihalogeno-bridged species, [(2Me-py)$_2$-CuX$_2$Cu(2Me-py)$_2$] (X = Cl or Br), with four-co-ordinate CuX$_2$N$_2$ copper, crystallizing in triclinic ($P\bar{1}$) cells with $a \approx 9.6$, $b \approx 9.1$, $c \approx 9.0$ Å, $\alpha \approx 108$, $\beta \approx 117$, $\gamma \approx 95°$, $Z = 1$ dimer.[7] The copper iodide cell is similar [$a = 10.229(8)$, $b = 9.084(5)$, $c = 8.270(5)$ Å, $\alpha = 105.45(4)$, $\beta = 96.24(5)$, $\gamma = 102.36(5)°$], but the array is *not* isostructural, although the constituent component is still the centrosymmetric dimer.[7] The lithium chloride and bromide adducts are isostructural with their copper(I) counterparts, the iodide again being a different but similar triclinic cell, and in all cases the structural unit, likewise, is the centrosymmetric dimer. Details of the molecular core geometries for the two series are given in Table 5. Again we note the dissimilarities (consistent between the two independent values for each structure) in metal–halide distances, Li–Cl being shorter than Cu–Cl by *ca.* 0.1 Å, Li–Br and Cu–Br very similar, and Li–I longer than Cu–I by *ca.* 0.1 Å, while M–X–M and X–M–X angles are very similar for all halogens and metals *except* in the copper–iodide system where the Cu $\cdots$ Cu distance is unexpectedly small with concomitant angular distortions. Metal–nitrogen distances in these systems are generally more precise than in the MXL$_3$ series, and here we find Li–N substantially constant [2.08(1)—2.10(1) Å] over six different estimates, while Cu–N are generally shorter, particularly for the chloride.

The above variations in Li–X across both series are interesting and suggest that a parallel should be found in the parent metal–halide structures, from which, it has been argued, structures such as the above are the ultimate result of solvation and fragmentation by the base. Regrettably, such an exercise is futile since the structures of the copper(I) halides are zinc-blended at room temperature, while the lithium halides all have the rock-salt structure, and hence, different co-ordination environments. For the lithium halides, Li–Cl, –Br, –I are 2.57, 2.75, 3.03 Å, in the crystal.

Although there have been many reports of complexes of lithium halides with nitrogen bases, particularly of the polydentate variety, we are only aware of one structure determination of a pure monodentate nitrogen base–lithium halide adduct, $[\mathrm{LiCl(py)}]_{\infty}$.[11] This stereochemistry is essentially that of the 'stair polymer' system, well known for adducts of monodentate nitrogen bases with transition-metal Group 1 halides, and, in particular, for the 1:1 pyridine adducts of copper(I) chloride,[12] bromide,[12,13] and iodide,[14] and also silver(I) bromide.[15] In total, although the body of systematic and sporadic structural information is not large at present, it suggests a very close parallel between the isomeric possibilities of the nitrogen base adducts with coinage metal(I) halides, and their lithium counterparts, a theme to be explored in future studies in this area.

References

1 Part 2, C. L. Raston, B. W. Skelton, C. R. Whitaker, and A. H. White, preceding paper.

2 A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore, and G. Avitabile, *Chem. Commun.*, 1971, 1400; K. Nilsson and A. Oskarsson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 605.

3 A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 1972, 661.

4 L. M. Engelhardt, C. Pakawatchai, A. H. White, and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 117.

5 J. C. Dyason, L. M. Engelhardt, P. C. Healy, and A. H. White, *Aust. J. Chem.*, 1986, **39**, 1043.

6 J. C. Dyason, P. C. Healy, C. Pakawatchai, V. A. Patrick, and A. H. White, *Inorg. Chem.*, 1985, **24**, 1957.

7 J. C. Dyason, L. M. Engelhardt, P. C. Healy, C. Pakawatchai, and A. H. White, *Inorg. Chem.*, 1985, **24**, 1950.

8 P. C. Healy, J. D. Kildea, and A. H. White, *Aust. J. Chem.*, submitted for publication.

9 J. A. Ibers and W. C. Hamilton (eds.), 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

10 J. M. Stewart and S. R. Hall (eds.), 'The XTAL System,' Technical Report TR-1364, Computer Science Center, University of Maryland, U.S.A., 1983.

11 F. Durant, J. Verbist, and M. van Meerssche, *Bull. Soc. Chim. Belg.*, 1966, **75**, 806.

12 J. A. Campbell, C. L. Raston, and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937.

13 P. C. Healy, J. D. Kildea, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, submitted for publication.

14 E. Eitel, D. Oelkrug, W. Hiller, and J. Strahle, *Z. Naturforsch., Teil B.*, 1980, **35**, 1247.

15 L. M. Engelhardt, S. Gotsis, P. C. Healy, J. D. Kildea, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, submitted for publication.

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