THE MOLECULAR STRUCTURE OF $[(C_5H_3NMeNH_2)_2Li(\mu\text{-}Br)_2Li[(C_5H_3NMeNH_2)_2]$, ($C_5H_3NMeNH_2$ = 6-methyl-2-aminopyridine)

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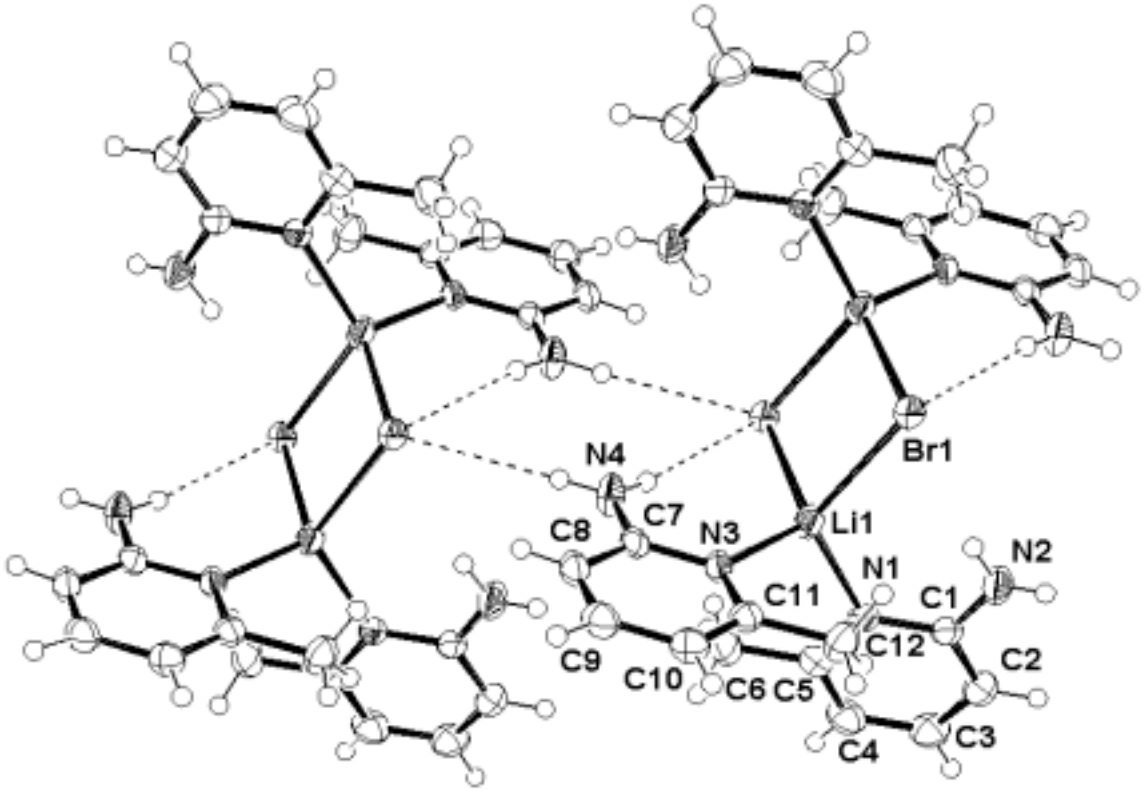

Figure 1. Molecular structure of $[(C_5H_3NMeNH_2)_2Li(\mu\text{-}Br)_2Li[(C_5H_3MeNH_2)_2]$. Selected bond lengths (Å) and angles (°): Li1-Br1 2.614(5), Li1-Br1#1 2.616(5), Li1-N1 2.116(5), Li1-N3 2.100(5), Li1...Li1#1 3.544(5), Br1...Br1#1 3.846(5), H2NA-Br1 2.54(5), H4A-Br1#1 2.65(5), H4B-Br1#2 2.76(5), N2-Br1 3.469(3), N4-Br1#1 3.504(2), N4-Br1#2 3.632(2), N1-Li1-Br1 119.20(19), N3-Li1-Br1 105.65(19), N1-Li1-Br1#1 103.90(19), N3-Li1-Br1#1 119.98(19), N1-Li1-N3 112.9(2), Li1-Br1-Li1#1 85.32(15), Br1-Li1-Br1#1 94.68(15). Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+2, #2 x+1,y,z

Comment

The 2:1 adduct of 6-methyl-2-aminopyridine and LiBr crystallizes as a centrosymmetric dimer with doubly bridging bromides. This structure is reminiscent of the related 2:1 complexes formed between 2-methylpyridine and LiCl, LiBr or LiI.[1] Perhaps surprisingly, the present complex is not isostructural with the isoelectronic adducts of 2,6-dimethylpyridine and LiBr where a 1.5:1 complex crystallizes as a tetranuclear ladder type structure.[2] The over-riding influence affecting the overall structure in the present dimer may be the inter- and intra-molecular hydrogen bonds formed between N-H donors and Br acceptors forming polymeric strands between adjacent dimers. The intramolecular hydrogen bond formed between

N4-H and Br1' does not significantly affect the Li-N and Li-Br bond lengths within the Li_2Br_2 core where the Li-Br bond lengths are almost identical, a feature that contrasts the 2:1 adducts of 2-methylpyridine and LiX.[1]

Experimental

Preparation of $[(C_5H_3NMeNH_2)_2Li(\mu\text{-}Br)_2Li[(C_5H_3NMeNH_2)_2]$:

To anhydrous LiBr (0.33g, 3.8 mmol) in thf (20 cm^3) was added to a solution of 6-methyl-2-aminopyridine (0.80 g, 7.2 mmol) in thf (20 cm^3) and the solution stirred for 2h. The solution was reduced in volume to the point of crystallization and placed at -35°C overnight, yielding colourless crystals. Yield 0.90 g, 79%, mp 63-5°C. ^{1}H-NMR (400MHz, $CDCl_3$, 298K) δ 2.30 (s, 12H, CH_3), 4.37 (s, 8H, NH_2), 6.22 - 7.25 (m, 12H, H_{arom}) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$, 298K) δ 25.98 (*C*H_3), 105.77, 113.60, 138.47, 157.21, 158.27 (aromatic *C*) ppm. IR (Nujol, NaCl plates, ν): 3220, 2971, 2360, 1348, 1281, 1164, 1049, 993, 894, 784 cm^{-1}.

Crystallography:

Table 1. Crystal data for of $[(C_5H_3NMeNH_2)_2Li(\mu\text{-}Br)_2Li[(C_5H_3NMeNH_2)_2]$

Formula	$C_{24}H_{32}Br_2Li_2N_8$	Formula weight	606.28
Crystal system	triclinic	Crystal size, mm	0.30 x 0.24 x 0.24
Space Group	*P*bar1	*a*, Å	8.2173(6)
b, Å	8.5030(6)	*c*, Å	11.5074(8)
α, °	92.635(2)	β, °	108.650(1)
γ, °	112.086(1)	*V*, Å^3	693.15(9)
Z	1	Diffractometer	Siemens SMART 1000
Temperature, K	223(2)	μ(Mo-K$_\alpha$), mm^{-1}	2.951
D_{calcd}, g cm^{-3}	1.452	*F*(000)	308
θ_{max}, °	27.07	Reflns meas.	3719
Reflns unique	2642	Reflns with $I > 2\sigma(I)$	2333
$R(F^2)$ [$I > 2\sigma(I)$]	0.030	$R_w(F^2)$ (all data)	0.078
ρ, e Å^{-3}	0.49	G.O.F	1.01
No. parameters	209		
Weighting scheme	$w=1/[\sigma^2(Fo^2)+(0.0491P)^2+0.0966P]$ where $P=(Fo^2+2Fc^2)/3$		
Programs used	SHELX-97 [3], XSEED [4], SADABS [5]		
Deposition number	CCDC 168987		

Acknowledgements

We gratefully acknowledge financial support from the Australian Research Council and The University of Leipzig for collection of X-ray data.

References

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Received: August 20, 2001 - Accepted: September 10, 2001 – Accepted in publishable format: September 14, 2001