Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Bis[$\mu$-2-(phenylamido)pyridine]bis{[2-(phenylamino)pyridine]lithium(I)}

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**Key indicators**

Single-crystal X-ray study
$T$ = 160 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.040
$wR$ factor = 0.102
Data-to-parameter ratio = 13.0

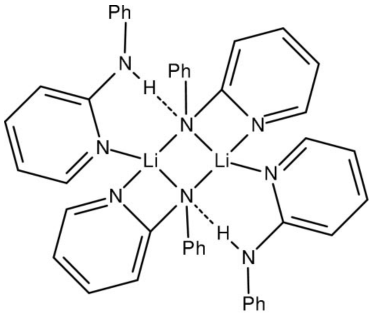
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 29 September 2004
Accepted 1 October 2004
Online 9 October 2004

The title complex, [Li(PhN-2-$C_5H_4N$)(PhNH-2-$C_5H_4N$)]$_2$ or [$Li_2(C_{11}H_9N_2)_2(C_{11}H_{10}N_2)_2$], is centrosymmetric with a central $Li_2N_2$ ring formed by two amide ligands bridging the two $Li^+$ centres. Each amide ligand also coordinates through its pyridine N atom to one of the $Li^+$ cations, giving LiNCN chelate four-membered rings. Each neutral amine ligand coordinates terminally to one $Li^+$ cation and forms an intramolecular N—H···N hydrogen bond by donation from its amine group to the bridging amido N atom of one of the amide ligands. The coordination of Li is distorted tetrahedral by two bridging amido and two pyridyl N atoms. The complex is the product of partial deprotonation of 2-phenylaminopyridine by alkyllithium reagents, the remaining amine NH groups being sterically inaccessible even to strong bases.

## Comment

The anion $L^-$ of 2-phenylaminopyridine (H$L$) has been extensively used as a ligand in transition metal chemistry. Its two N atoms can be used to bridge pairs of metal ions or to chelate a single metal ion. The Cambridge Structural Database (CSD, Version 5.25, with updates to April 2004; Allen, 2002) contains over 30 examples of the former type of complex and ten of the latter. Its use in complexes of main-group metals has been more restricted. The 20 structures in the CSD include three with aluminium, nine with alkali metals, and the others contain two metals (Li and Zn, or Li and Al). In these complexes, the ligand displays a variety of chelating and bridging modes, with attachment to as many as four metal centres. Some of the lithium complexes are fascinating clusters encapsulating hydride anions (Armstrong *et al.*, 1999). We have recently reported some structures in which the anion remains uncoordinated to alkali metal cations, which are sandwiched by crown ethers to generate separated ion-pair complexes (Liddle *et al.*, 2004).



(I)

In our previous work with this ligand, we found that it was surprisingly difficult to deprotonate it fully by treatment with

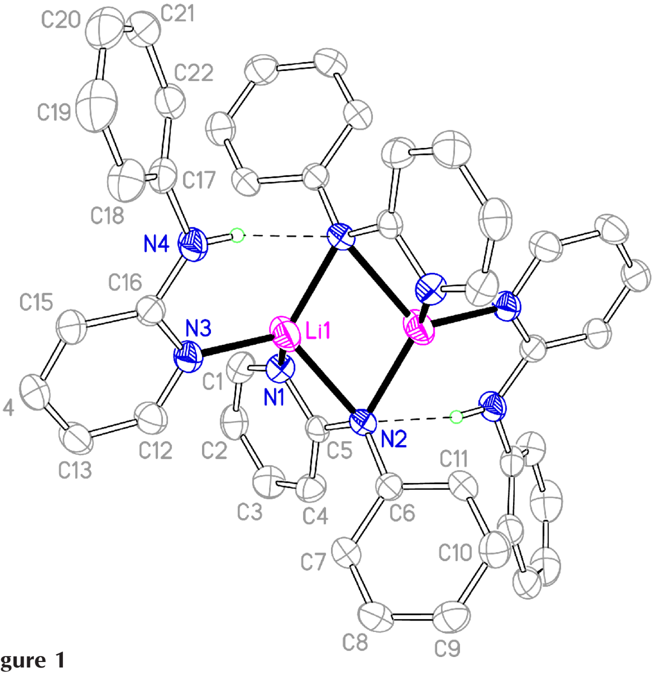


**Figure 1**
The molecular structure of (I) with atom labels and 50% probability ellipsoids. H atoms, except for those involved in hydrogen bonding, have been omitted. Hydrogen bonds are shown as dashed lines. Unlabelled atoms are related to the labelled atoms by the symmetry code (1 − *x*, 1 − *y*, 1z − *z*.

alkyllithium reagents. In many reactions, the product contained equal amounts of the desired anion and the parent amine, often linked together by an N—H···N hydrogen bond. Various attempts to overcome this reluctance of the amine to full stoichiometric deprotonation included metathesis reactions in which a complex of the fully deprotonated ligand with a different alkali metal was treated with a compound of lithium. In order to generate the complex $[(15\text{-crown-}5)_2\text{Li}]^+\cdot L^-$, the corresponding potassium salt was treated with lithium iodide in THF solution. The title complex was the unexpected solid product, in low yield (*ca* 20%), indicating that other unidentified products remained in solution.

After determining its crystal structure, we discovered that the same complex had been prepared previously by Polamo & Leskelä (1996), who also determined its structure. It is of interest that their synthesis was also unintentional (in an attempt to produce a zirconium complex), and that it represents another half-deprotonation of H*L* by butyllithium. We report the results of our work here because the structure is of significantly higher precision and in order to compare the structure with those of related compounds, some of which have only recently been published.

The title complex, (I), is dimeric and centrosymmetric (Fig. 1). Two $L^-$ ligands act as bridges between two $\text{Li}^+$ cations, through their amido N atoms, to give a central four-membered $\text{Li}_2\text{N}_2$ ring, a common feature in structural lithium amide chemistry. The pyridine N atom of each bridging ligand coordinates to one lithium centre, generating a four-membered LiNCN chelate ring. Distorted tetrahedral coordination of each $\text{Li}^+$ is completed by terminal attachment of the

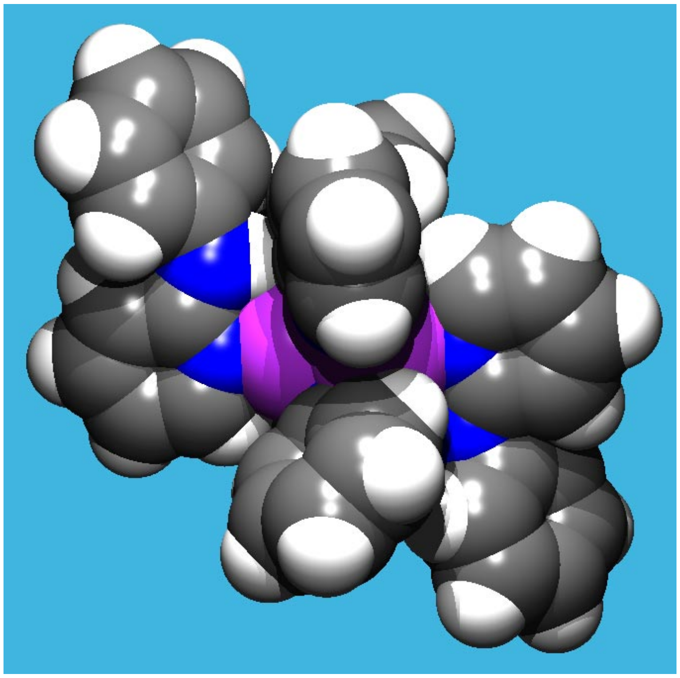


**Figure 2**
Space-filling representation of (I), including H atoms. The amine H atom is barely visible, next to its N atom and an Li atom.

pyridine N atoms of a neutral *L*H molecule, the NH group of which is hydrogen bonded to one of the bridging amido N atoms (Tables 1 and 2).

The combined chelating and bridging functions of the anionic ligand $L^-$ and the combination of coordination and hydrogen bonding for the neutral ligand H*L* bring both of these ligands into a *syn* arrangement of the two N atoms, in contrast to the preferred *anti* arrangement for the uncomplexed anion (Liddle *et al.*, 2004). The *syn* arrangement, unlike the *anti* arrangement, does not permit coplanarity of the two rings, because of unfavourable steric interaction of H atoms, so the phenyl ring is twisted around the N—C bond, well out of the mean plane of the rest of the ligand [dihedral angles are 51.39 (3) and 53.45 (4)° for $L^-$ and H*L*, respectively, in the title complex]. A similar effect has been seen for other chelate complexes of $L^-$ (Liddle *et al.*, 2004) and for uncomplexed H*L* (Polamo *et al.*, 1997), which forms a hydrogen-bonded dimer.

A relatively strong hydrogen bond between H*L* and $L^-$ occurs also in the complexes $[(12\text{-crown-}4)_2M]^+[L\cdot\text{H}L]^-$, with $M$ = Li, Na, K (Liddle & Clegg, 2003). The lithium complex in this series was also obtained as an unexpected product of partial lithiation of H*L* and has the hydrogen-bonded $[L\cdot\text{H}L]^-$ unit as an uncoordinated anion; the sodium and potassium complexes were generated from it by metathesis reactions. The same behaviour was observed 20 years ago by Barr *et al.* (1984*a*), also in a lithium complex, $[\{(\text{Me}_2\text{N})_3\text{PO}\}\text{Li}(L)(\text{H}L)]$, which was first obtained as a minor product in the synthesis of $[\{(\text{Me}_2\text{N})_3\text{PO}\}\text{Li}(L)]_2$ (Barr *et al.*, 1984*b*) and subsequently in a targeted synthesis with reagents in the appropriate stoichiometry. As in the title complex, the hydrogen-bonded combination of coordinated $L^-$ and H*L* ligands here necessarily involves a short Li···H contact, but this should probably not be regarded as a direct interaction, of the agostic kind or otherwise. The apparent tendency of H*L* and $L^-$ to associate by hydrogen bonding does, however, seem to be linked to the failure of organolithium reagents to deprotonate H*L* completely in these reactions, and may be the cause rather than a result of this, the N—H···N proton being thereby shielded from attack by the base. The inaccessibility of this site is demonstrated by the space-filling representation in Fig. 2, where the amine H atom is barely visible; this is true in all directions of view.

## Experimental

A solution of $[(15\text{-crown-5})_2K]L$ (Liddle *et al.*, 2004) (0.89 g, 1.38 mmol) in THF (50 ml) was added to solid LiI (0.18 g, 1.38 mmol), giving a turbid yellow solution, which was stirred for one day. The solution was filtered and volatile materials removed *in vacuo*, to give a dark orange oil. Recrystallization from toluene yielded crystals of the title compound (0.05 g, 21%).

*Crystal data*

$[Li_2(C_{11}H_9N_2)_2(C_{11}H_{10}N_2)_2]$
$M_r = 692.70$
Triclinic, $P\overline{1}$
$a = 8.7031\ (8)$ Å
$b = 10.3718\ (10)$ Å
$c = 11.5289\ (11)$ Å
$\alpha = 116.715\ (2)^\circ$
$\beta = 92.739\ (2)^\circ$
$\gamma = 91.216\ (2)^\circ$
$V = 927.46\ (15)$ Å$^3$
$Z = 1$
$D_x = 1.240$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3543 reflections
$\theta = 2.2$–$28.5^\circ$
$\mu = 0.08$ mm$^{-1}$
$T = 160\ (2)$ K
Plate, yellow
0.70 × 0.52 × 0.08 mm

*Data collection*

Bruker SMART 1 K CCD diffractometer
Thin-slice $\omega$ scans
Absorption correction: none
5683 measured reflections
4165 independent reflections
2868 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 28.6^\circ$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 11$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 0.92$
4165 reflections
321 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.20$ e Å$^{-3}$
Extinction correction: *SHELXTL*
Extinction coefficient: 0.011 (3)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Li—N1 | 2.036 (3) | Li—N2$^{\rm i}$ | 2.022 (3) |
| Li—N2 | 2.187 (3) | Li—N3 | 2.002 (3) |
| | | | |
| N1—Li—N2 | 65.19 (8) | N2—Li—N2$^{\rm i}$ | 110.67 (12) |
| N1—Li—N2$^{\rm i}$ | 118.30 (13) | N2—Li—N3 | 120.85 (13) |
| N1—Li—N3 | 112.43 (13) | N2$^{\rm i}$—Li—N3 | 118.54 (12) |

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4N···N2$^{\rm i}$ | 0.900 (16) | 2.288 (17) | 3.1763 (16) | 169.1 (13) |

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

All H atoms were located in a difference Fourier synthesis and refined with individual isotropic displacement parameters. C—H distances are in the range 0.916 (17)–0.992 (17) Å, and the unique N—H distance is 0.900 (16) Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC for financial support.

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