2,2′-Bipyridine Complexes of the Lithium Chalcogenolates Li(EPh) and Li(NC_5H_4E-2) (E = S or Se)†

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2,2′-Bipyridine (bipy) forms stable crystalline co-ordination complexes with lithium benzeneselenolate and lithium pyridine-2-selenolate. The compounds are insoluble in aromatic hydrocarbons, slightly soluble in pyridine, and extremely soluble in tetrahydrofuran, from which they can be crystallized in *ca.* 70% yield. Both complexes have been characterized by elemental analysis, NMR, IR, and single-crystal X-ray diffraction. Compound [{Li(bipy)(SePh)}$_2$] **1** [space group $P2_1/m$, a = 9.493(4), b = 16.866(5), c = 10.112(9), β = 114.53(6)° and Z = 4] is a dimer containing two lithium ions bridged by a pair of symmetric benzeneselenolate ligands, with bidentate bipy ligands bound to each lithium ion. In compound [{Li(bipy)(NC_5H_4Se-2)}$_2$] **2** [space group $P2_1/n$, a = 10.361(5), b = 13.521(4), c = 11.062(5) Å, β = 117.21(4)° and Z = 4] each lithium ion is bound to a bidentate bipy ligand, one bridging selenium atom, and the nitrogen atom from the second bridging pyridine-2-selenolate ligand, thus forming an eight-membered Li–Se–C–N–Li–Se–C–N ring. The analogous lithium thiolates have also been prepared in 70% yield; they are not isostructural with the selenolates.

The synthesis and characterization of metal chalcogenolate complexes continues to be an area of considerable interest, because the thermolysis of such complexes offers a low-temperature route to the synthesis of novel solid-state chalcogenide materials.[1,2] While structure and bonding studies of transition-metal chalcogenolates are well documented, analogous studies with the more electropositive elements (*i.e.* alkali,[3] alkaline earths,[4] and the f elements[2,5]) are less well defined, and of these ionic metals Li and Mg are unique from a structure and bonding perspective, as well as being the most useful as reagents in synthetic chemistry. Structural studies of ionic chalcogenolates are generally hampered by thermal sensitivity of isolated crystalline compounds, due to the tendency of these compounds to dissociate neutral donor solvents. This problem can be overcome by co-ordinating non-volatile, neutral donor ligands, or by covalently attaching the neutral donor functionality to the chalcogenolate, *e.g.* pyridine-2-selenolate.

In the course of studying the chemistry of the lanthanide chalcogenolates, we found examples where stoichiometric metathesis reactions of trivalent lanthanide halides with alkali-metal arenechalcogenolates gave bimetallic lanthanide–alkali metal products as either discrete molecules[2a] or as bimetallic co-ordination polymers.[2c] In each case, the chalcogenolate ligands bridge alkali and lanthanide metal centres. While bridging benzenechalcogenolates are well documented in transition-metal chemistry,[6] the structure and bonding in more electropositive systems is relatively unexplored. In order to assess the Li–Se bond and the effect of the lithium ion on lanthanide–selenium bonding, it would be helpful to compare such compounds with related lithium-containing compounds.

In this paper, we describe our initial efforts in studying the chemistry of the pyridine-2-selenolate ligand with the more ionic metals, and describe the synthesis and characterization of the lithium chalcogenolates [{Li(bipy)(NC_5H_4E-2)}$_2$] and [{Li(bipy)(EPh)}$_2$] (bipy = 2,2′-bipyridine, E = S or Se). In all four compounds, co-ordination of a bipy ligand to the lithium ion imparts stability with respect to ligand dissociation at room temperature, and so the compounds are useful reagents in metal chalcogenolate synthesis when precise stoichiometries and ultrapure starting materials are necessary. The molecular structures of the selenolate complexes, [{Li(bipy)(NC_5H_4-Se-2)}$_2$] and [{Li(bipy)(SePh)}$_2$] are also presented, in order to establish the proper resonance description of the pyridine-2-selenolate compound.

Results and Discussion

Diphenyl diselenide and di-2-pyridyl diselenide can be reduced cleanly to selenolate anions *via* the stoichiometric reaction of the diselenide with lithium triethylhydroborate in tetrahydrofuran (thf). The reactions, which proceed at room temperature, give colourless solutions of selenolate anions within minutes. The route is considerably faster and cleaner than reduction of the diselenides with Na, K, or Na/K in thf. Upon taking these colourless solutions to dryness to remove the borane, a white amorphous powder forms; solids of this type have been described as base-free Li(ER) (E = S, Se or Te).[7] This white solid can be redissolved in thf to give colourless homogeneous solutions. Addition of 2,2′-bipyridine then results in the immediate appearance of a red colour to the lithium pyridine-2-selenolate solution and no colour change to the lithium benzeneselenolate solution; filtering and layering the thf with hexane gives light yellow crystals of both compounds in 60–70% yield. The compounds redissolve readily in thf, but are sparingly soluble in pyridine, and insoluble in hydrocarbon solvents. Since thf is the usual choice of solvent in a metathesis reaction, these compounds have utility as easily prepared, crystalline, thermally stable chalcogenolating reagents. They are slightly air-sensitive, but can be handled in air for a few seconds with no observable decomposition. The potential utility of these compounds prompted us to prepare the analogous lithium thiolates in 70% yield. The thiolate derivatives appear to be air-stable over a period of hours.

Initial characterization of the crystalline selenolates by NMR and elemental analysis indicated that 1 : 1 bipy : Li(SeR) complexes precipitate from solution. For the benzeneselenolate compound a molecular 1 : 1 complex would give a three-co-ordinate lithium ion, and so some sort of chalcogenolate bridge between metal centres to give either a dimeric or polymeric

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† *Supplementary data available* (No. SUP 57051, 7 pp.): calculated X-ray powder diffraction patterns for **1** and **2** and X-ray powder diffraction patterns for **3** and **4**. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{16}H_{13}LiN_2Se$	$C_{15}H_{12}LiN_3Se$
M	319.18	320.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/n$
a/Å	9.493(4)	10.361(5)
b/Å	16.866(5)	13.521(4)
c/Å	10.112(9)	11.062(5)
α/°	90.00(6)	90.00(4)
β/°	114.53(6)	117.21(4)
γ/°	90.00(3)	90.00(4)
U/Å^3	1473(2)	1378(1)
Z	4	4
D_c/g cm^{-3}	1.439	1.543
μ/cm^{-1}	25.4	27.1
Crystal dimensions/mm	0.12 × 0.18 × 0.22	0.15 × 0.16 × 0.20
F(000)	640	640
No. of independent reflections	2111	2857
No. of observed reflections	1510	1888
$R(F)^a$	0.050	0.045
$wR(F^2)^b$	0.076	0.098

[a] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o^2) + A_1P^2 + A_2P]$ and $P = [0.333\,33\max(0, F_o^2) + 0.666\,67F_c^2]$.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Li	−1006(13)	1571(5)	−2698(11)
C(1)	−250(6)	−89(3)	−2310(6)
N(2)	190(6)	576(3)	−2789(5)
C(3)	1309(7)	501(4)	−3243(6)
C(4)	2013(8)	−214(4)	−3290(7)
C(5)	1570(8)	−878(4)	−2784(7)
C(6)	423(7)	−823(4)	−2275(6)
C(7)	−1563(6)	29(3)	−1877(5)
N(8)	−2222(5)	747(3)	−2142(5)
C(9)	−3414(7)	882(4)	−1778(6)
C(10)	−3991(7)	315(4)	−1161(6)
C(11)	−3321(7)	−423(4)	−889(6)
C(12)	−2084(7)	−577(3)	−1238(6)
Se(1)	−2203(1)	2500	−4874(1)
C(13)	−4312(11)	2500	−5050(8)
C(14)	−5112(7)	1792(4)	−5205(6)
C(15)	−6660(8)	1791(4)	−5407(6)
C(16)	−7430(14)	2500	−5522(9)
Se(2)	123(1)	2500	−464(1)
C(17)	2178(10)	2500	−369(8)
C(18)	3425(10)	2500	987(8)
C(19)	4950(10)	2500	1118(9)
C(20)	5210(10)	2500	−148(9)
C(21)	3989(10)	2500	−1490(8)
C(22)	2483(9)	2500	−1589(8)

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Li	1390(8)	−703(6)	−196(7)
C(1)	4014(5)	−1135(3)	−521(4)
N(2)	3417(4)	−1389(3)	291(3)
C(3)	4204(5)	−1964(3)	1365(5)
C(4)	5565(5)	−2315(3)	1664(5)
C(5)	6175(6)	−2042(3)	843(5)
C(6)	5390(5)	−1431(3)	−266(4)
C(7)	3096(5)	−487(3)	−1689(4)
N(8)	1837(4)	−194(3)	−1748(3)
C(9)	981(6)	399(4)	−2769(5)
C(10)	1340(6)	702(4)	−3772(5)
C(11)	2618(6)	382(4)	−3720(5)
C(12)	3510(6)	−214(3)	−2673(5)
Se	2051(1)	445(1)	1916(1)
C(13)	1409(5)	1717(3)	1158(4)
N(14)	−31(4)	1862(3)	419(3)
C(15)	−472(5)	2771(3)	−113(4)
C(16)	441(5)	3547(3)	47(4)
C(17)	1895(5)	3395(3)	816(4)
C(18)	2391(5)	2492(3)	1385(4)

Table 4 Selected bond lengths (Å) and angles (°) for compound **1**

Li–N(8)	2.029(11)	Se(1)–C(13)	1.924(10)
Li–N(2)	2.049(10)	Se(1)–Li′	2.552(9)
Li–Se(1)	2.552(9)	Se(2)–C(17)	1.913(9)
Li–Se(2)	2.588(10)	Se(2)–Li′	2.588(10)
N(8)–Li–N(2)	80.9(4)	Se(1)–Li–Li′	52.1(2)
N(8)–Li–Se(1)	123.9(5)	Se(2)–Li–Li′	52.7(2)
N(2)–Li–Se(1)	121.4(5)	C(13)–Se(1)–Li	99.5(3)
N(8)–Li–Se(2)	104.4(4)	C(13)–Se(1)–Li′	99.5(3)
N(2)–Li–Se(2)	119.9(5)	Li–Se(1)–Li′	75.8(4)
Se(1)–Li–Se(2)	104.8(3)	C(17)–Se(2)–Li	95.0(3)
N(8)–Li–Li′	133.2(3)	C(17)–Se(2)–Li′	95.0(3)
N(2)–Li–Li′	145.0(3)	Li–Se(2)–Li′	74.6(4)

Symmetry transformation used to generate equivalent atoms: $x, -y + \frac{1}{2}, z$.

Table 5 Selected bond lengths (Å) and angles (°) for compound **2**

Li–N(14′)	2.044(9)	Li–Se	2.622(8)
Li–N(8)	2.089(8)	Se–C(13)	1.896(4)
Li–N(2)	2.127(9)	N(14)–Li′	2.044(9)
N(14′)–Li–N(8)	123.6(4)	N(8)–Li–Se	118.1(3)
N(14′)–Li–N(2)	104.0(4)	N(2)–Li–Se	101.9(3)
N(8)–Li–N(2)	77.7(3)	C(13)–Se–Li	104.3(2)
N(14′)–Li–Se	116.5(3)		

Symmetry transformation used to generate equivalent atoms: $-x, -y, -z$.

structure was assumed. For the pyridine-2-selenolate complex both a molecular structure containing a chelating pyridine-2-selenolate, and a bridging chalcogenolate structure similar to the phenyl derivative, were considered structural possibilities. To establish the correct description of both compounds the molecular structures of [{Li(bipy)(SePh)}$_2$] **1** and [{Li(bipy)(NC$_5$H$_4$Se-2)}$_2$] **2** were determined by single-crystal X-ray diffraction. Table 1 lists the crystallographic data, Tables 2 and 3 the positional parameters for compounds **1** and **2**, respectively, and Tables 4 and 5 the important bond geometries for **1** and **2**, respectively.

In compound **1**, the benzeneselenolate ligand bridges the two lithium ions to form a symmetric four-membered ring (Fig. 1). The structure is similar in geometry to the majority of structures with benzeneselenolate ligands spanning two metal centres. The Li–Se bonds are statistically equivalent, and the Li–Se and Li–N bond distances are similar to previously reported values.[2a,4] The symmetry of the Li_2Se_2 core contrasts with the asymmetry observed in the $LiMSe_2$ cores of [(py)$_2$Li(μ-SePh)$_2$Yb(SePh)$_2$(py)] (py = pyridine),[2a] and the organometallic compound [(C$_5$H$_5$)$_2$Lu(μ-SePh)$_2$Li(thf)$_2$].[3e]

The structure of compound **2** is also dimeric and is unique in following sense: (*a*) instead of the chalcogen atom bridging both metal centres, or (*b*) instead of the intermolecular interaction of N and Se of the single pyridine-2-selenolate ligand to a single metal ion, the Se and N atoms of the ligand are bound to different Li atoms, forming an eight-membered ring (Fig. 2). Co-ordination of the pyridine-2-selenolate nitrogen to the lithium can be accounted for by noting the resonance description of the pyridine-2-selenolate anion that places a partial negative charge on the nitrogen atom, which would be

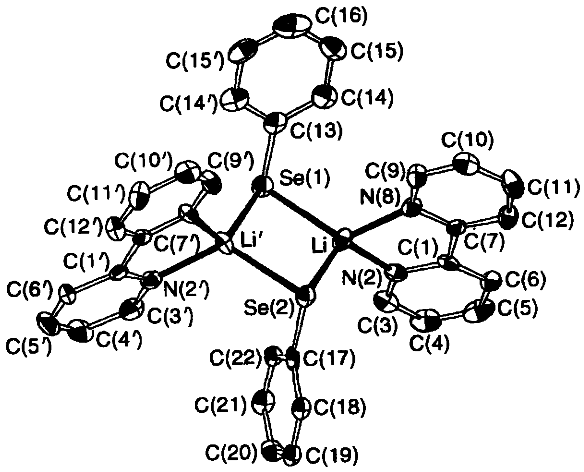

Fig. 1 Molecular structure of $[\{Li(bipy)(SePh)\}_2]$ **1**. Thermal ellipsoids are drawn at the 50% probability level

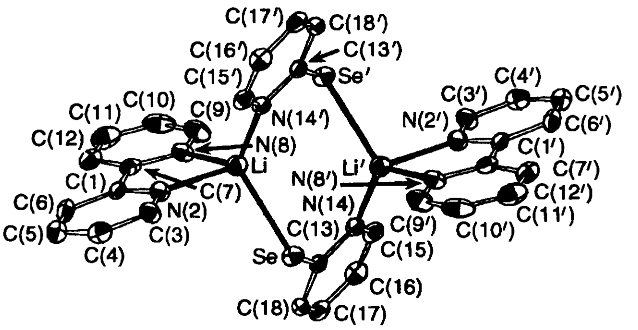

Fig. 2 Molecular structure of $[\{Li(bipy)(NC_5H_4Se\text{-}2)\}_2]$ **2**. Thermal ellipsoids are drawn at the 50% probability level

reflected in a shortening of the Li–N bond distance and a lengthening of Li–Se. At first glance this is not obviously reflected in the structures; the Li–N bond lengths to the bipy ligand are shorter than the Li–N distance to the anionic pyridine-2-selenolate ligand, and there are no differences in C–C distances throughout the pyridine ring. However, if we compare the Li–Se bond distance in compound **2** [2.622(8) Å] with the few reported compounds containing direct Li–Se bonds, we find a significant but small lengthening of the Li–Se bond in **2**. The distance is longer than the Li–Se bonds reported for trimeric $[\{Li(thf)(SeC_6H_2Bu^t\text{-}2,4,6)\}_3]$ [2.47(1) Å],[3c] dimeric $[\{Li(dme)[SeSi(SiMe_3)_3]\}_2]$ (2.57, 2.61 Å) (dme = 1,2-dimethoxyethane),[3c] and monomeric $[Li(thf)_3(SeC_6H_2Me_3\text{-}2,4,6)]$ (2.57 Å).[3d] Molecular $[Li(thf)_3(SeC_6H_2Me_3\text{-}2,4,6)]$ offers the most appropriate structural comparison with compound **2**, because both contain identical Se and Li co-ordination numbers. From the Li–Se bond lengths in **2** and $[Li(thf)_3(SeC_6H_2Me_3\text{-}2,4,6)]$ we conclude that there is a small but significant lengthening of the Li–Se bond in **2**. This lengthening can be attributed to either a contribution of the selenoketone resonance structure, or a decrease in the electrostatic attraction between Li and Se, due to the co-ordination of stronger pyridine donor ligands, rather than thf. The latter possibility can be discounted by noting that the Li–Se bond lengths in **1** are 0.02 Å shorter than the related distances in $[\{Li(dme)[SeSi(SiMe_3)_3]\}_2]$.

The formation of a dimeric **2**, rather than a monomeric structure containing a chelating pyridine-2-selenolate, can be attributed to strain associated with the non-ideal geometry at the lithium ion bound to two potentially chelating ligands with little bonding flexibility.[7] The formation of a dimeric structure alleviates some strain associated with the non-ideal tetrahedral geometry. Similar strain in the analogous thiolates $[\{Li(bipy)(SPh)\}_n]$ **3** and $[\{Li(bipy)(NC_5H_4S\text{-}2)\}_n]$ **4** should also lead to the formation of molecular compounds, but comparison of the powder X-ray diffraction patterns of **3** and **4** with the calculated powder diffraction patterns of the selenolates indicates that in both pairs of related compounds the thiolates are not isostructural with the selenolates.* While this may result from crystallization of dimeric units in a different space group, it is also possible that the thiolates crystallize as one-dimensional polymers (as in the structure of $[\{Li(py)_2(SPh)\}_\infty]$).[3f]

Experimental

General.—All synthetic work was carried out under ultrapure N_2 using standard Schlenk techniques. Chemicals were purchased from Aldrich and used as received, with the exception of Ph_2Se_2, which was recrystallized from hexane. Solvents (Fisher) were freshly distilled from molten alkali metals. Di-2-pyridyl diselenide was prepared according to the reported procedure.[6f] The ^1H NMR spectra were recorded on a Varian XL 200 MHz instrument at 24.5 °C in $[^2H_8]$thf and are reported in ppm with a $SiMe_4$ reference. The IR spectra were taken on a Mattus Cygnus 100 FTIR spectrometer and recorded from 4000 to 450 cm^{-1}. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were performed by Quantitative Technologies Inc. (Salem, NJ).

$[\{Li(bipy)(SePh)\}_2]$ **1**.—A yellow solution of diphenyl diselenide (0.624 g, 2.00 mmol) in thf (10 cm^3) was treated dropwise with $LiBHEt_3$ (4.0 cm^3 of a 1.0 mol dm^{-3} solution in thf, 4.0 mmol), and the solution immediately turned colourless. The reaction mixture was stirred for 4 h and evaporated to dryness. The white solid was washed with hexane (2 × 10 cm^3), pumped to dryness, and then treated with bipy (0.624 g, 4.00 mmol) in thf (10 cm^3). After 4 h the solvent was removed and the yellow solid was redissolved in thf (20 cm^3). The solution was filtered, and then layered with hexane to yield yellow crystals of **1** (0.84 g, 61%), m.p. 250–252 °C (decomp.) (Found: C, 59.7; H, 4.20; N, 8.55. Calc. for $C_{16}H_{13}LiN_2Se$: C, 60.2; H, 4.05; N, 8.75%). IR: 1593m, 1571s, 1487w, 1438s, 1315w, 1260s, 1174w, 1152m, 1010s, 758m, 739s, 665w, 623w cm^{-1}. ^1H NMR: δ 8.64 (2 H, d, *J* 8.6), 8.50 (2 H, d, *J* 8), 7.83 (2 H, d of t, *J* 15), 7.5 (2 H, m, *J* 4), 7.34 (2 H, m, *J* 4) and 6.66 (3 H, m, *J* 2 Hz).

$[\{Li(bipy)(NC_5H_4Se\text{-}2)\}_2]$ **2**.—A yellow solution of di-2-pyridyl diselenide (0.320 g, 1 mmol) in thf (10 cm^3) was treated dropwise with $LiBHEt_3$ (2.0 cm^3 of a 1.0 mol dm^{-3} solution in thf, 2.0 mmol). The solution turned colourless. After 4 h the solvent was removed and the colourless solid was washed with hexanes (2 × 10 cm^3), pumped to dryness, and then treated with bipy (0.312 g, 2.00 mmol) in thf (10 cm^3). After 4 h the solution was taken to dryness and the yellow solid dissolved in thf (20 cm^3). The solution was filtered and then layered with hexane to yield yellow crystals of **2** (0.530 g, 81%), m.p. 245–247 °C (decomp.) (Found: C, 56.0; H, 3.80; N, 13.0. Calc. for $C_{15}H_{12}LiN_3Se$: C, 56.3; H, 3.75; N, 13.1%). IR: 1591w, 1574m, 1544w, 1402s, 1258m, 1170m, 1154w, 1116m, 1106m, 1077m, 1047w, 756s, 740m, 696m, 633m cm^{-1}. ^1H NMR; δ 8.71 (2 H, d, *J* 5), 8.45 (2 H, d, *J* 8), 7.85 (2 H, t, *J* 15), 7.74 (1 H, d, *J* 8), 7.33 (2 H, t, *J* 12), 6.91 (1 H, t, *J* 15) and 6.55 (2 H, t, *J* 12 Hz).

$[\{Li(bipy)(SPh)\}_n]$ **3**.—A solution of benzenethiol (0.513 cm^3, 5.00 mmol) in thf (10 cm^3) was treated dropwise with phenyllithium (2.8 cm^3 of a 1.8 mol dm^{-3} solution, 5.0 mmol) in cyclohexane–diethyl ether. The reaction mixture was stirred for 4 h and evaporated to dryness. The colourless solid was washed

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* X-Ray powder diffraction patterns of the lithium thiolates are available as supplementary material, along with the calculated powder X-ray diffraction patterns for **1** and **2** (SUP No. 57051).

with hexane (2 × 10 cm^3), pumped to dryness, and then treated with a solution of bipy (0.780 g, 5.00 mmol) in thf (10 cm^3). The solution was stirred for 4 h and evaporated to dryness. The pale yellow product was dissolved in thf (*ca.* 20 cm^3), the solution was filtered, and then layered with hexane to yield pale yellow crystals of **3** (0.72 g, 52%), m.p. 248–250 °C (decomp.) (Found: C, 70.2; H, 4.85; N, 10.1. Calc. for $C_{16}H_{13}LiN_2S$: C, 70.6; H, 4.75; N, 10.3%). IR: 1591m, 1576m, 1315w, 1259m, 1174w, 1152m, 759w, 739m, 697m, 645w, 623w cm^{-1}. ^1H NMR: δ 8.7 (2 H, d, *J* 5), 8.5 (2 H, d, *J* 8), 7.85 and 7.84 (4 H, t, *J* 17), 7.32 (2 H, t, *J* 13), 6.79 (2 H, t, *J* 15) and 6.62 (1 H, d, *J* 8 Hz).

[{Li(bipy)(NC_5H_4S-2)}$_n$] **4**.—A solution of pyridine-2-thiol (0.445 g, 4.00 mmol) in thf (10 cm^3) was treated dropwise with phenyllithium (2.3 cm^3 of a 1.8 mol dm^{-3} solution, 4.0 mmol) in cyclohexane–diethyl ether. The solution remained colourless. After 4 h the solvent was removed and the colourless solid was washed with hexanes (2 × 10 cm^3), pumped to dryness, and treated with bipy (0.624 g, 4.00 mmol) in thf (10 cm^3). The solvent was removed and the pale yellow solid was dissolved in thf (20 cm^3), the solution was filtered, and then layered with hexane to yield pale yellow crystals of **4** (0.85 g, 71%), m.p. 283–285 °C (decomp.) (Found: C, 65.7; H, 4.35; N, 15.2. Calc. for $C_{15}H_{12}LiN_3S$: C, 65.9; H, 4.40; N, 15.4%). IR: 1539m, 1405m, 1378m, 1168m, 1149m, 1130s, 1003w, 753s, 640m cm^{-1}. ^1H NMR: δ 8.65 (1 H, d, *J* 3), 8.47 (2 H, d, *J* 8), 7.85 (2 H, t, *J* 16), 7.75 (1 H, d, *J* 5), 7.32 (2 H, d, *J* 12), 7.15 (1 H, d, *J* 8), 6.9 (1 H, t, *J* 15) and 6.55 (2 H, t, *J* 12 Hz).

Crystal Structure Determinations.—All data were collected at −120(5) °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). Cell data were based upon the setting angles of 25 reflections with 10 < θ < 12° for both **1** and **2**. A numerical absorption correction (SHELX 76,[8] transmission factor range 0.63–0.75) was used for **1** whose ψ-scan data indicated small absorption effects; no absorption correction was used for **2** whose ψ-scan data indicated negligible absorption effects. Structure solutions were accomplished with the SHELXS 86[9] program; structure refinements were completed with the SHELXL 93 program.[10] Hydrogen atoms were fixed at idealized positions (C–H 0.93 Å).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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