

The Remarkable Structural Diversity of Alkali Metal Pyridine-2-thiolates with Mismatched Crown Ethers

Scott Chadwick and Karin Ruhlandt-Senge*

Abstract: The metathesis reaction of butyllithium or sodium or potassium hydride with pyridine-2-thiol is effected in ethereal or hydrocarbon media, where the addition of crown ether (which is essential in the case of sodium hydride) facilitates the metalation step. The reaction is driven forward irreversibly by the evolution of a volatile component (C_4H_{10} or H_2). It is shown that the choice of crown ether is of paramount importance in determining the solid-state structural outcome. When the cavity size of the crown ether is matched with the alkali metal ionic radius, simple monomeric formulations are identified in $[Li(12C4)(NC_5H_4S-2)]$ (**1**) ($12C4 = [12]crown-4$), $[Na(15C5)-$

$(NC_5H_4S-2)]$ (**2**) ($15C5 = [15]crown-5$), and $[K(18C6)(NC_5H_4S-2)]$ (**3**) ($18C6 = [18]crown-6$), although the geometrical relationship between cation and anion in this series has proven to be more complex than was anticipated. The complexes resulting from the pairing of crown ethers that are either too small or too large relative to the alkali metal exhibit a rich structural diversity that is a direct function of the macrocyclic donor: dimeric $[[Li(NC_5H_4S-2)]_2\{18C6\}]$

(**4**) and monomeric $[Na(18C6)(NC_5H_4S-2)]$ (**5**) are formed in the presence of $18C6$; the unprecedented metalloanionic $[[Na(12C4)_2]\{Na(NC_5H_4S-2)(thf)\}\{Na(NC_5H_4-\mu-S-2)(NC_5H_4S-2)\}_2]$ (**6**), with two hitherto unknown metallates, is obtained when $12C4$ is employed; and the unusual polymeric $[[K(\mu-NC_5H_4-\mu-S-2)]_2\{15C5\}]_\infty$ (**7**) results from the templating ability of $15C5$. All complexes reported have been identified primarily through single-crystal X-ray structural analysis together with 1H and ^{13}C NMR (solubility permitting), IR spectroscopy, and melting point determination.

Keywords: alkali metals • coordination modes • crown compounds • metallacycles • solid-state structures • thiolates

Introduction

Alkali metal and alkaline earth metal chalcogenolates based on oxygen have been extensively investigated for decades. Complexes of the general formula $[M(OR)_n]_m$ ($M = \text{Group I or II cation}$; $R = \text{alkyl, vinyl, aryl, silyl}$) incorporating a metal–oxygen bond have found application in such diverse fields as organic and inorganic synthesis, biochemistry, and the production of solid-state materials.^[1] Despite the extensive literature on alkali metal and alkaline earth metal alkoxides, aryloxides, enolates, and other related species, new results on the synthesis and especially the structural identification of these complexes are continually being disseminated.^[2] Moreover, the impetus behind much of the current research into these oxygen-containing metal complexes is the wish to elucidate the parameters influencing the observed solid-state

structural chemistry, and based on this information, to apply the data in developing (where appropriate) solution structural models to explain the chemical reactivity.

An analogous program of synthesis and structural identification is emerging for the complexes of alkali metal and alkaline earth metal chalcogenolates of the heavier chalcogen elements sulfur, selenium, and tellurium. For the putative metal complexes, a broad array of applications in organic and inorganic synthesis, biochemistry, and solid-state technology are also known.^[3] It is only recently, however, that detailed analyses of the solid-state structures of these metal chalcogenolates have started coming to light. As part of a larger research effort into the synthesis, solution, and solid-state structural identification of alkali and alkaline earth metal thiolates and their applications, we have been interested in elucidating the parameters affecting their structural chemistry through a program of stepwise reagent modification in the synthesis of families of target compounds.

During the course of our investigations we have focused our attention on the role that crown ether ligation plays in the solid-state structural chemistry of alkali metal pyridine-2-thiolates. The premise of this work is based on a very simple question: How will the crown ether/alkali metal pairing affect

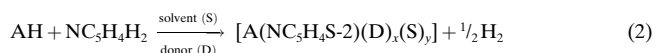
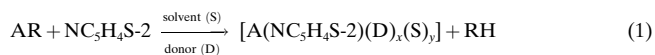
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the observed structural chemistry in a homologous thiolate series? It was assumed that matching the crown ether to the cationic radius would stabilize the formation of simple monomeric structures. This has been realized in the synthesis of [Li(12C4)(NC₅H₄S-2)] (**1**) (12C4 = [12]crown-4), [Na(15C5)(NC₅H₄S-2)] (**2**) (15C5 = [15]crown-5), and [K(18C6)(NC₅H₄S-2)] (**3**) (18C6 = [18]crown-6), although the specific geometrical details of these complexes belie an underlying complexity in the relationship between cation and anion. In the case of mismatched crown ether/cation pairings, the structures of the alkaline earth metal siloxides [M(15C5)(OSiPh₃)₂(thf)] (M = Sr and Ba) were the first to be elucidated.^[4] The crown ether occupies a coordination hemisphere of the strontium or barium, thereby stabilizing monomeric formulations. In the alkali metal pyridine-2-thiolate series in which crown ethers that are either too small or too large coordinate the cation, however, simple monomeric formulations are not observed. A fascinating array of structural diversity has subsequently been identified in the crown ether-templated dimer [[Li(NC₅H₄S-2)]₂{18C6}] (**4**), the asymmetrically coordinated monomer [Na(18C6)(NC₅H₄S-2)] (**5**), the novel solvent-separated ion quadruple containing sodium-centered anions [[Na(12C4)]₂{Na(NC₅H₄S-2)₂(thf)}{Na(NC₅H₄-μ-S-2)(NC₅H₄S-2)}₂] (**6**), and the crown ether-templated polymer [[K(μ-NC₅H₄-μ-S-2)]₂{15C5}]_∞ (**7**).

Results

An efficient synthetic route to the crown ether-coordinated alkali metal pyridine-2-thiolate complexes **1–7** is the metathesis reaction (alkane/H₂ elimination) of an organometal or metal-hydride reagent with the thiol in the presence of an appropriately chosen macrocyclic donor [Eqs. (1) and (2), in

which AR = *n*BuLi; AH = NaH, KH; S = tetrahydrofuran (thf), toluene; D = 12C4, 15C5, 18C6]. Various benefits



distinguish the alkane/H₂ elimination reaction from other routes to the target complexes: there is significant latitude in the choice of solvent—both ethereal and hydrocarbon media have been employed; the reagents are commercially available in acceptable purity and at reasonable cost; the reaction is driven towards completion by the evolution of a volatile molecule, resulting in cleaner products (the absence of this advantage is a major limitation in the salt-forming metathesis protocol); and reaction times are relatively brief at room temperature, allowing for parallel studies and incremental modifications to the components of the system.

The metalation of pyridine-2-thiol in the presence of various crown ether molecules was verified initially through crystallization and subsequent solid-state structural identification. Compounds **1–3** display similar molecular topologies overall—their monomeric formulations are attributed to the favorable crown ether/cation pairing. In contrast, **4–7** display a variety of unexpected structural motifs (especially the unprecedented disodate **6**) as a result of mismatching the cationic radius with the size of the crown ether cavity.

Crystallographic information and data collection parameters for **1–7** are provided in Table 1 and the Experimental Section.^[5] A compilation of pertinent bond lengths and angles for all compounds is given in Table 2. In each complex, geometrical data for the respective crown ether molecule (bond lengths and angles) were unexceptional and can be found among the crystal structure data.^[5]

Table 1. Crystallographic data for compounds **1–7**.

| Compound | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|----------------------------------------------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| formula | C ₁₃ H ₂₀ LiNO ₄ S | C ₁₅ H ₂₄ NNaO ₅ S | C ₁₇ H ₂₈ KNO ₆ S | C ₂₂ H ₃₂ Li ₂ N ₂ O ₆ S ₂ | C ₁₇ H ₂₈ NNaO ₆ S | C ₅₆ H ₈₈ N ₄ Na ₄ O ₁₇ S ₄ | C ₂₀ H ₂₈ K ₂ N ₂ O ₅ S ₂ |
| fw | 293.30 | 353.40 | 413.56 | 498.5 | 397.45 | 1309.50 | 518.76 |
| crystal size [mm] | 0.35 × 0.15 × 0.15 | 0.30 × 0.08 × 0.08 | 0.40 × 0.20 × 0.05 | 0.60 × 0.30 × 0.08 | 0.35 × 0.30 × 0.02 | 0.35 × 0.25 × 0.08 | 0.20 × 0.20 × 0.05 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic | monoclinic |
| <i>a</i> [Å] | 8.7156(1) | 13.5757(4) | 8.2304(1) | 12.8329(3) | 12.8581(3) | 8.261(1) | 12.7656(3) |
| <i>b</i> [Å] | 14.0409(4) | 8.8741(1) | 17.935(1) | 8.4037(2) | 18.2125(2) | 13.1684(3) | 9.6624(3) |
| <i>c</i> [Å] | 12.0892(3) | 15.3303(4) | 14.3530(1) | 14.737(1) | 8.7456(2) | 31.7086(1) | 19.8051(4) |
| <i>α</i> [°] | 90 | 90 | 90 | 90 | 90 | 88.191(1) | 90 |
| <i>β</i> [°] | 93.624(2) | 110.099(1) | 92.636(1) | 98.231(1) | 101.499(1) | 83.903(1) | 91.856(1) |
| <i>γ</i> [°] | 90 | 90 | 90 | 90 | 90 | 73.478(1) | 90 |
| <i>V</i> [Å ³] | 1476.46(6) | 1734.40(7) | 2116.48(3) | 1572.94(5) | 2006.92(7) | 3288.30(8) | 2441.60(1) |
| <i>Z</i> | 4 | 4 | 4 | 4 | 4 | 2 | 4 |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>I</i> <i>a</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>C</i> <i>c</i> | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ / <i>c</i> |
| <i>ρ</i> _{calcd} [g cm ⁻³] | 1.319 | 1.353 | 1.298 | 1.053 | 1.315 | 1.323 | 1.411 |
| lin.abs.coeff. [mm ⁻¹] | 0.229 | 0.235 | 0.380 | 0.200 | 0.214 | 0.239 | 0.592 |
| min/max transmission | 0.722/0.964 | 0.807/0.928 | 0.627/0.962 | 0.718/0.928 | 0.68/0.96 | 0.621/0.977 | 0.72/0.94 |
| 2 θ range [°] | 4–56 | 5–56 | 3–56 | 3–56 | 3–56 | 2–45 | 3–56 |
| total refl./Rint | 6339 (0.0938) | 5419 (0.0285) | 12647 (0.0620) | 9509 (0.0456) | 6339 (0.0310) | 13073 (0.0871) | 14089 (0.0803) |
| indep. refl. | 3430 | 2746 | 4876 | 3709 | 3798 | 8008 | 5563 |
| obs. refl. (>2 σ) | 1835 | 2446 | 3262 | 2440 | 3185 | 4023 | 2906 |
| no. parameters | 181 | 208 | 235 | 154 | 235 | 764 | 280 |
| <i>R</i> 1, <i>wR</i> 2 (all data) ^[a] | 0.1305, 0.1186 | 0.0470, 0.0769 | 0.1049, 0.1590 | 0.0945, 0.1269 | 0.0589, 0.0880 | 0.1878, 0.1914 | 0.1665, 0.1541 |
| <i>R</i> 1, <i>wR</i> 2 (>2 σ) ^[a] | 0.0568, 0.1008 | 0.0377, 0.0720 | 0.0647, 0.1403 | 0.0567, 0.1139 | 0.0417, 0.0801 | 0.0938, 0.1566 | 0.0769, 0.1256 |
| peak and hole [e Å ⁻³] | 0.254 and –0.265 | 0.202 and –0.222 | 0.565 and –0.897 | 0.222 and –0.215 | 0.233 and –0.266 | 0.405 and –0.322 | 0.363 and –0.423 |

$$[a] \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR2 = [\Sigma w(F_o)^2 - (F_c)^2] / \Sigma w(F_o)^2]^{1/2}$$

Table 2. Selected bond lengths [Å] and angles [°] for compounds 1–7.

| Compound 1 | | | | | | | |
|-------------------|-----------|-------------------|-----------|-------------------|-----------|------------------|-----------|
| Li(1)–S(1) | 2.894(5) | Li(1)–O(1) | 2.189(5) | Li(1)–O(3) | 2.237(5) | S(1)–C(1) | 1.741(3) |
| Li(1)–N(1) | 2.002(5) | Li(1)–O(2) | 2.061(5) | Li(1)–O(4) | 2.066(5) | N(1)–C(1) | 1.358(3) |
| Li(1)–S(1)–C(1) | 69.15(13) | S(1)–Li(1)–O(1) | 99.0(2) | N(1)–Li(1)–O(1) | 110.9(2) | Li(1)–N(1)–C(1) | 111.2(2) |
| S(1)–Li(1)–O(2) | 163.4(2) | N(1)–Li(1)–O(2) | 101.7(2) | | | | |
| S(1)–Li(1)–N(1) | 62.41(14) | S(1)–Li(1)–O(3) | 104.3(2) | | | | |
| N(1)–Li(1)–O(3) | 98.9(2) | S(1)–C(1)–N(1) | 117.0(2) | S(1)–Li(1)–O(4) | 101.4(2) | N(1)–Li(1)–O(4) | 162.0(3) |
| Compound 2 | | | | | | | |
| Na(1)–S(1) | 3.038(1) | Na(1)–O(2) | 2.621(2) | Na(1)–O(4) | 2.515(2) | S(1)–C(1) | 1.735(3) |
| Na(1)–N(1) | 2.429(3) | Na(1)–O(3) | 2.433(2) | Na(1)–O(5) | 2.500(2) | N(1)–C(1) | 1.358(4) |
| Na(1)–O(1) | 2.481(2) | | | | | | |
| Na(1)–S(1)–C(1) | 76.41(1) | S(1)–Na(1)–O(2) | 127.75(7) | N(1)–Na(1)–O(2) | 84.47(8) | Na(1)–N(1)–C(1) | 107.9(2) |
| S(1)–Na(1)–O(3) | 102.00(6) | N(1)–Na(1)–O(3) | 120.12(8) | | | | |
| S(1)–Na(1)–N(1) | 56.98(7) | S(1)–Na(1)–O(4) | 88.38(6) | | | | |
| N(1)–Na(1)–O(4) | 145.14(9) | S(1)–C(1)–N(1) | 118.3(2) | S(1)–Na(1)–O(5) | 95.24(6) | N(1)–Na(1)–O(5) | 110.33(8) |
| S(1)–Na(1)–O(1) | 149.98(6) | N(1)–Na(1)–O(1) | 105.27(8) | | | | |
| Compound 3 | | | | | | | |
| K(1)–S(1) | 3.2558(1) | K(1)–O(2) | 2.956(2) | K(1)–O(5) | 2.898(2) | S(1)–C(1) | 1.744(3) |
| K(1)–N(1) | 2.854(3) | K(1)–O(3) | 2.908(2) | K(1)–O(6) | 2.911(2) | N(1)–C(1) | 1.363(4) |
| K(1)–O(1) | 2.878(2) | K(1)–O(4) | 2.884(2) | | | | |
| K(1)–S(1)–C(1) | 82.72(1) | S(1)–K(1)–O(3) | 91.78(5) | N(1)–K(1)–O(2) | 132.35(7) | K(1)–N(1)–C(1) | 106.4(2) |
| S(1)–K(1)–O(4) | 127.53(5) | N(1)–K(1)–O(3) | 116.30(7) | S(1)–K(1)–N(1) | 51.64(5) | S(1)–K(1)–O(5) | 125.35(5) |
| N(1)–K(1)–O(4) | 101.03(7) | S(1)–C(1)–N(1) | 119.2(2) | S(1)–K(1)–O(6) | 116.08(5) | N(1)–K(1)–O(5) | 73.76(7) |
| S(1)–K(1)–O(1) | 85.99(5) | N(1)–K(1)–O(1) | 111.49(7) | N(1)–K(1)–O(6) | 92.29(7) | S(1)–K(1)–O(2) | 80.70(4) |
| Compound 4 | | | | | | | |
| Li(1)–S(1) | 2.604(4) | Li(1)–O(1) | 2.149(4) | Li(1)–O(3A) | 2.011(4) | N(1)–C(1) | 1.356(3) |
| Li(1)–N(1) | 2.057(4) | Li(1)–O(2A) | 2.026(4) | S(1)–C(1) | 1.737(2) | | |
| S(1)–Li(1)–N(1) | 67.78(1) | S(1)–Li(1)–O(1) | 166.3(2) | N(1)–Li(1)–O(1) | 99.0(2) | Li(1)–S(1)–C(1) | 73.51(1) |
| S(1)–Li(1)–O(2A) | 110.3(2) | N(1)–Li(1)–O(2A) | 123.7(2) | S(1)–C(1)–N(1) | 116.6(2) | S(1)–Li(1)–O(3A) | 101.9(2) |
| N(1)–Li(1)–O(3A) | 113.2(2) | | | | | | |
| C(1)–N(1)–Li(1) | 102.0(2) | | | | | | |
| Compound 5 | | | | | | | |
| Na(1)–S(1) | 2.764(1) | Na(1)–O(1) | 2.593(2) | Na(1)–O(3) | 2.451(2) | S(1)–C(1) | 1.736(3) |
| Na(1)–N(1) | 2.649(2) | Na(1)–O(2) | 2.513(2) | Na(1)–O(4) | 3.020(2) | N(1)–C(1) | 1.358(3) |
| S(1)–Na(1)–N(1) | 58.91(5) | S(1)–Na(1)–O(1) | 115.02(6) | N(1)–Na(1)–O(1) | 96.17(7) | Na(1)–S(1)–C(1) | 84.84(9) |
| S(1)–Na(1)–O(2) | 148.62(6) | N(1)–Na(1)–O(2) | 89.74(7) | S(1)–C(1)–N(1) | 118.4(9) | S(1)–Na(1)–O(3) | 107.49(6) |
| N(1)–Na(1)–O(3) | 87.66(8) | | | | | | |
| C(1)–N(1)–Na(1) | 97.4(2) | S(1)–Na(1)–O(4) | 82.34(5) | N(1)–Na(1)–O(4) | 120.12(7) | | |
| Compound 6 | | | | | | | |
| Na(1)–O(1) | 2.464(7) | Na(2)–O(10) | 2.511(6) | Na(3)–N(1) | 2.455(8) | Na(4)–S(4) | 2.907(4) |
| Na(1)–O(2) | 2.514(6) | Na(2)–O(11) | 2.487(6) | Na(3)–N(2) | 2.483(8) | Na(4)–S(4A) | 2.879(4) |
| Na(1)–O(3) | 2.477(7) | Na(2)–O(12) | 2.417(6) | Na(3)–O(17) | 2.385(8) | Na(4)–N(3) | 2.433(8) |
| Na(1)–O(4) | 2.441(7) | Na(2)–O(13) | 2.421(6) | S(1)–C(37) | 1.758(9) | Na(4)–N(4A) | 2.482(8) |
| Na(1)–O(5) | 2.472(6) | Na(2)–O(14) | 2.513(6) | N(1)–C(37) | 1.351(1) | S(3)–C(47) | 1.743(8) |
| Na(1)–O(6) | 2.448(7) | Na(2)–O(15) | 2.437(6) | S(2)–C(42) | 1.758(8) | N(3)–C(47) | 1.375(9) |
| Na(1)–O(7) | 2.546(7) | Na(2)–O(16) | 2.480(6) | N(2)–C(42) | 1.343(1) | S(4)–C(52) | 1.756(9) |
| Na(1)–O(8) | 2.437(7) | Na(3)–S(1) | 2.823(5) | Na(4)–S(3) | 2.933(4) | N(4)–C(52) | 1.323(9) |
| Na(2)–O(9) | 2.509(6) | Na(3)–S(2) | 2.812(4) | | | | |
| S(1)–Na(3)–N(1) | 60.9(2) | S(1)–Na(3)–S(2) | 151.2(2) | N(3)–Na(4)–S(4) | 102.3(2) | Na(3)–S(1)–C(37) | 78.4(3) |
| S(1)–Na(3)–N(2) | 113.2(2) | N(3)–Na(4)–S(4A) | 109.6(2) | S(1)–C(37)–N(1) | 119.6(7) | S(2)–Na(3)–N(1) | 114.6(2) |
| N(3)–Na(4)–N(4A) | 156.4(3) | | | | | | |
| C(37)–N(1)–Na(3) | 100.5(6) | N(1)–Na(3)–N(2) | 160.1(3) | S(4)–Na(4)–N(4A) | 100.0(2) | | |
| S(2)–Na(3)–N(2) | 60.2(2) | S(3)–Na(4)–N(3) | 58.7(2) | S(4)–Na(4A)–N(4) | 58.8(2) | Na(3)–S(2)–C(42) | 78.7(3) |
| Na(4)–S(3)–C(47) | 78.5(3) | S(4)–Na(4)–S(4A) | 98.64(1) | S(2)–C(42)–N(2) | 118.4(7) | S(3)–C(47)–N(3) | 117.1(6) |
| Na(4A)–S(4)–C(52) | 79.0(3) | C(42)–N(2)–Na(3) | 99.5(5) | C(47)–N(3)–Na(4) | 105.5(5) | S(4)–C(52)–N(4) | 118.5(7) |
| O(17)–Na(3)–S(1) | 101.8(2) | S(3)–Na(4)–S(4) | 123.73(1) | C(52)–N(4)–Na(4A) | 103.6(5) | O(17)–Na(3)–N(1) | 93.5(3) |
| S(3)–Na(4)–S(4A) | 137.09(1) | Na(4)–S(4)–Na(4A) | 81.36(1) | O(17)–Na(3)–S(2) | 106.9(2) | S(3)–Na(4)–N(4A) | 113.7(2) |
| C(52)–S(4)–Na(4) | 93.3(3) | O(17)–Na(3)–N(2) | 106.4(3) | | | | |

[Li(12C4)(NC₅H₄S-2)] (1): Li(1) is six-coordinate with interactions to the four 12C4 oxygen atoms and both N and S atoms of the chelating thiolate ligand (Figure 1). The O–Li(1)–O bond angles (77.8(2)–148.3(2)°) do not indicate a specific coordination geometry. This is further corroborated by the N(1)–Li(1)–O and S(1)–Li(1)–O angles (98.9(2)–162.0(3)° and 99.0(2)–163.4(2)°, respectively). Instead, the crown ether and

thiolate ligands each occupy one coordination hemisphere of the cation. The Li(1)–S(1) bonding interaction distance is exceptionally long at 2.894(5) Å, while the Li(1)–N(1) bond is correspondingly short at 2.002(5) Å. The Li(1)–O distances vary between 2.061(5) and 2.237(5) Å, a reflection of the cation displacement above the plane of oxygen atoms in the crown by 0.995 Å. The four-membered Li(1)–S(1)–N(1)–C(1)

Table 2. (Continued)

| | | | | Compound 7 | | | |
|-----------------|-----------|------------------|-----------|-----------------|-----------|-----------------|-----------|
| K(1)–S(1) | 3.387(2) | K(1)–O(3) | 2.822(3) | K(2)–S(2) | 3.266(2) | K(2)–O(3) | 3.263(3) |
| K(1)–S(1A) | 3.350(2) | K(1)–O(4) | 3.408(3) | K(2)–S(2A) | 3.399(2) | K(2)–O(4) | 2.864(3) |
| K(1)–N(1) | 2.984(4) | K(1)–O(5) | 2.910(3) | K(2)–N(2) | 2.922(4) | K(2)–O(5) | 3.255(4) |
| K(1)–N(1A) | 2.834(4) | S(1)–C(1) | 1.750(5) | K(2)–N(2A) | 2.896(4) | S(2)–C(6) | 1.735(5) |
| K(1)–O(1) | 2.774(3) | N(1)–C(1) | 1.350(6) | K(2)–O(2) | 2.772(3) | N(2)–C(6) | 1.374(5) |
| K(1)–O(2) | 3.000(3) | | | | | | |
| S(1)–K(1)–N(1) | 48.87(8) | N(1)–K(1)–O(3) | 158.21(1) | K(2)–N(2)–K(2A) | 82.98(1) | K(1)–S(1)–C(1) | 71.1(2) |
| N(1)–K(1)–O(4) | 120.79(9) | S(2)–K(2)–S(2A) | 109.37(4) | S(1)–C(1)–N(1) | 117.7(3) | N(1)–K(1)–O(5) | 90.62(1) |
| S(2)–K(2)–N(2A) | 84.17(8) | C(1)–N(1)–K(1) | 89.7(3) | S(1A)–K(1)–O(1) | 95.94(7) | N(2)–K(2)–S(A) | 81.43(7) |
| C(1)–S(1)–K(1A) | 80.0(2) | S(1A)–K(1)–O(2) | 86.89(6) | N(2)–K(2)–N(2A) | 97.02(1) | K(1)–S(1)–K(1A) | 70.61(3) |
| S(1A)–K(1)–O(3) | 101.65(7) | S(2A)–K(2)–N(2A) | 49.50(8) | C(1)–N(1)–C(5) | 119.0(4) | S(1A)–K(1)–O(4) | 152.31(6) |
| S(2)–K(2)–O(2) | 174.62(7) | C(1)–N(1)–K(1A) | 108.2(3) | S(1A)–K(1)–O(5) | 151.64(7) | S(2)–K(2)–O(3) | 133.28(6) |
| C(5)–N(1)–K(1) | 117.5(3) | N(1A)–K(1)–O(1) | 142.40(1) | S(2)–K(2)–O(4) | 87.12(7) | C(5)–N(1)–K(1A) | 126.8(3) |
| N(1A)–K(1)–O(2) | 99.41(1) | S(2)–K(2)–O(5) | 94.02(6) | K(1)–N(1)–K(1A) | 83.98(1) | N(1A)–K(1)–O(3) | 71.51(1) |
| N(2)–K(2)–O(2) | 124.40(1) | S(1)–K(1)–S(1A) | 109.39(3) | N(1A)–K(1)–O(4) | 107.99(1) | N(2)–K(2)–O(3) | 166.58(1) |
| S(1)–K(1)–N(1A) | 83.68(8) | N(1A)–K(1)–O(5) | 158.23(1) | N(2)–K(2)–O(4) | 120.91(9) | N(1)–K(1)–S(1A) | 82.13(8) |
| S(2)–K(2)–N(2) | 50.86(8) | N(2)–K(2)–O(5) | 86.02(9) | N(1)–K(1)–N(1A) | 96.02(1) | K(2)–S(2)–C(6) | 80.4(2) |
| S(2A)–K(2)–O(2) | 70.71(7) | N(1A)–K(1)–S(1A) | 50.12(8) | S(2)–C(6)–N(2) | 118.2(3) | S(2A)–K(2)–O(3) | 105.63(6) |
| S(1)–K(1)–O(1) | 128.54(8) | C(6)–N(2)–K(2) | 99.8(3) | S(2A)–K(2)–O(4) | 157.66(7) | S(1)–K(1)–O(2) | 160.22(7) |
| C(6)–S(2)–K(2A) | 74.30(1) | S(2A)–K(2)–O(5) | 136.11(7) | S(1)–K(1)–O(3) | 110.66(7) | K(2)–S(2)–K(2A) | 70.63(4) |
| N(2A)–K(2)–O(2) | 99.49(1) | S(1)–K(1)–O(4) | 80.42(6) | C(6)–N(2)–C(10) | 118.1(4) | N(2A)–K(2)–O(3) | 96.20(9) |
| S(1)–K(1)–O(5) | 85.19(7) | C(6)–N(2)–K(2A) | 97.9(3) | N(2A)–K(2)–O(4) | 120.70(1) | N(1)–K(1)–O(1) | 94.07(1) |
| C(10)–N(2)–K(2) | 128.3(3) | N(2A)–K(2)–O(5) | 174.21(1) | | | | |
| N(1)–K(1)–O(2) | 148.42(1) | C(10)–N(2)–K(2A) | 121.4(3) | | | | |

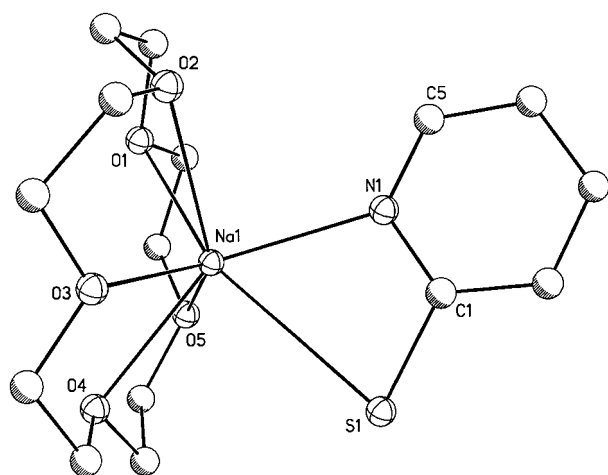


Figure 1. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

chelate ring has interior angles of $62.41(1)^\circ$ about Li(1), $69.15(1)^\circ$ about S(1), $117.0(2)^\circ$ about C(1), and $111.2(2)^\circ$ about N(1). Within the pyridine-2-thiolate ligand, the C(1)–S(1) and C(1)–N(1) distances are 1.741(3) and 1.358(3) Å, respectively, while the C–C bond lengths fall in the range 1.376(3)–1.414(3) Å.

[Na(15C5)(NC₅H₄S-2)] (2): Na(1) is seven-coordinate with five crown ether oxygen contacts and an S/N-chelating pyridine-2-thiolate ligand (Figure 1). The broad ranges observed in the O–Na(1)–O, N(1)–Na(1)–O, and S(1)–Na(1)–O angles ($65.31(7)–133.32(9)^\circ$, $84.47(8)–145.14(9)^\circ$, and $88.38(6)–149.98(6)^\circ$, respectively) preclude assignment of the coordination environment about the cation to any clear geometry. Rather, the crown ether molecule occupies one coordination hemisphere of the cation, while the thiolate

ligand occupies the other hemisphere. The Na(1)–S(1) and Na(1)–N(1) bond lengths are 3.038(1) and 2.429(3) Å, respectively, and the Na(1)–O interactions range over 2.433(2)–2.621(2) Å. The cation is displaced 1.021 Å above the plane of the oxygen atoms in the macrocycle. Angles within the Na(1)–S(1)–C(1)–N(1) four-membered chelate ring are $56.98(7)^\circ$ about Na(1), $76.41(1)^\circ$ about S(1), $118.3(2)^\circ$ about C(1), and $107.9(2)^\circ$ about N(1). Bond lengths and angles within the thiolate ligand are unremarkable, with an S(1)–C(1) bond length of 1.735(3) Å and a C(1)–N(1) distance of 1.358(4) Å. The C–C bond lengths in the aromatic ring are in the range 1.375(4)–1.413(4) Å.

[K(18C6)(NC₅H₄S-2)] (3): K(1) is eight-coordinate with six crown ether oxygen contacts and the S/N-chelating pyridine-2-thiolate ligand. The O–K(1)–O, S(1)–K(1)–O, and N(1)–K(1)–O bond angles occur over a broad range of $57.65(6)–153.85(6)^\circ$, $80.70(4)–27.53(5)^\circ$, and $73.76(7)–132.35(7)^\circ$, respectively. The coordination geometry is composed of two hemispheres with the crown ether occupying one site and the thiolate ligand the other. The K(1)–S(1) and K(1)–N(1) bond lengths are 3.2558(1) and 2.854(3) Å, respectively, and K(1)–O contacts range over 2.878(2)–2.956(2) Å. K(1) is displaced 0.773 Å above the oxygen atoms in the crown ether. Angles within the K(1)–S(1)–C(1)–N(1) four-membered chelate ring are $51.64(5)^\circ$ about K(1), $82.72(1)^\circ$ about S(1), $119.2(2)^\circ$ about C(1), and $106.4(2)^\circ$ about N(1). Geometrical data within the thiolate ligand are as expected, with an S(1)–C(1) bond of 1.744(3) Å and an N(1)–C(1) interaction of 1.363(4) Å. The C–C bond lengths in the aromatic ring are in the range 1.375(4)–1.415(4) Å.

[Li(NC₅H₄S-2)]₂[18C6] (4): The crown ether resides over a crystallographic inversion center so that one [Li(NC₅H₄S-2)] unit is associated with one-half of the crown. The complete symmetry-generated structure therefore has two [Li(NC₅H₄S-

2)} units per crown ether. The cation Li(1) is five-coordinate with three crown ether oxygen interactions and the S/N-chelating thiolate ligand (Figure 2). The coordination geometry about Li(1) can be described as a distorted trigonal bipyramid, where N(1), O(3), and O(2a) occupy equatorial

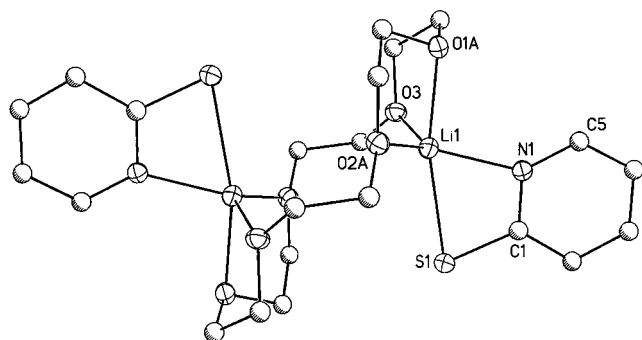


Figure 2. Computer-generated plot of **4** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

positions and S(1) and O(1a) the axial sites. Equatorial bond angles fall in the range $113.2(2)–123.7(2)^\circ$, while the axial–equatorial angles lie between $67.78(1)^\circ$ and $110.3(2)^\circ$, and the axial–axial S(1)–Li(1)–O(1a) angle is $166.3(2)^\circ$. Distortions from an ideal trigonal-bipyramidal geometry are mainly associated with the S(1)–equatorial bond angles. In order for the thiolato S atom to move into the axial coordination position of Li(1), the pyridine-2-thiolate ligand must pivot about N(1). This can be observed in the very wide C(5)–N(1)–Li(1) angle of $138.7(2)^\circ$ and the compression of the S(1)–C(1)–N(1) angle to $116.6(2)^\circ$. The Li(1)–S(1) and Li(1)–N(1) bond lengths are $2.606(4)$ and $2.057(4)$ Å, respectively, and the lithium–crown interactions range between $2.011(4)$ and $2.149(4)$ Å. The cation is displaced 1.157 Å above the plane of the three crown oxygen atoms ligated to Li(1). Angles within the four-membered Li(1)–S(1)–C(1)–N(1) chelate ring are $67.78(1)^\circ$ about Li(1), $73.51(1)^\circ$ about S(1), $116.6(2)^\circ$ about C(1), and $102.0(2)^\circ$ about N(1). The S(1)–C(1) and N(1)–C(1) bond lengths are $1.737(2)$ and $1.356(3)$ Å, respectively, as expected, and C–C bond lengths in the aromatic ligand are observed to be between $1.371(3)$ and $1.409(3)$ Å.

[Na(18C6)(NC₅H₄S-2)] (5): Na(1) is six-coordinate with four crown ether interactions and an S/N-chelating thiolate ligand (Figure 3). Bond angles about Na(1) are in the range $58.91(5)–148.62(6)^\circ$, and the Na(1)–S(1) and Na(1)–N(1) bond lengths are $2.764(1)$ and $2.649(2)$ Å, respectively. Na(1) resides in the crown so that four Na(1)–O contacts can be considered significant ($2.451(2)–3.020(2)$ Å), while O(5) and O(6) are considerably further away (>3.4 Å). Na(1) is displaced above the plane of O(1)–O(4) by 0.810 Å. S(1)–Na(1)–O angles are observed to be in the broad range of $82.34(5)–148.62(6)^\circ$, while the N(1)–Na(1)–O

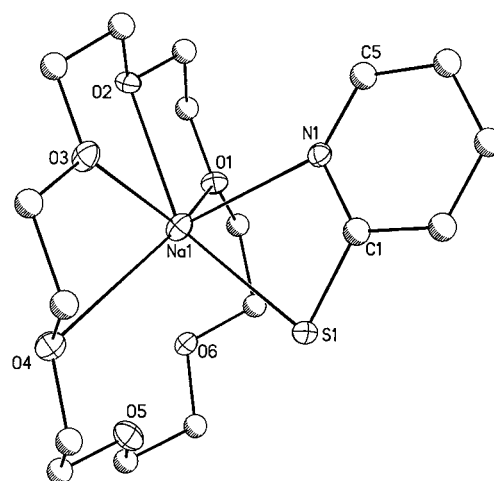


Figure 3. Computer-generated plot of **5** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

angles lie in a narrower range of $87.66(8)–120.12(7)^\circ$. Bond angles within the four-membered Na(1)–S(1)–C(1)–N(1) chelate ring are $58.91(5)^\circ$ about Na(1), $84.84(9)^\circ$ about S(1), $118.4(2)^\circ$ about C(1), and $97.4(2)^\circ$ about N(1). The S(1)–C(1) and N(1)–C(1) bond lengths are $1.736(3)$ and $1.358(3)$ Å, respectively, and the C–C bond lengths in the aromatic ring are observed to be between $1.363(4)$ and $1.419(4)$ Å.

[[Na(12C4)₂]₂{Na(NC₅H₄S-2)₂(thf)}]{Na(NC₅H₄-μ-S-2)-(NC₅H₄S-2)}₂ (6): Compound **6** resides over a crystallographic inversion center, which is located in the center of the Na₂S₂ four-membered ring [Na(4)–S(4)–Na(4A)–S(4A)]. The two sodium-centered anions are shown in Figure 4. With respect to the cations in the asymmetric unit, Na(1) and Na(2) are each eight-coordinate; two 12C4 molecules complex each metal in a sandwich fashion. Na(1)–O(crown) and Na(2)–O(crown) contacts range over $2.441(7)–2.546(7)$ and $2.417(6)–2.513(6)$ Å, respectively. The first of the two distinctive sodium anions is Na(3), which is five-coordinate with two S/N-chelating thiolate ligands and one THF molecule. The overall geometry can be described as a distorted square

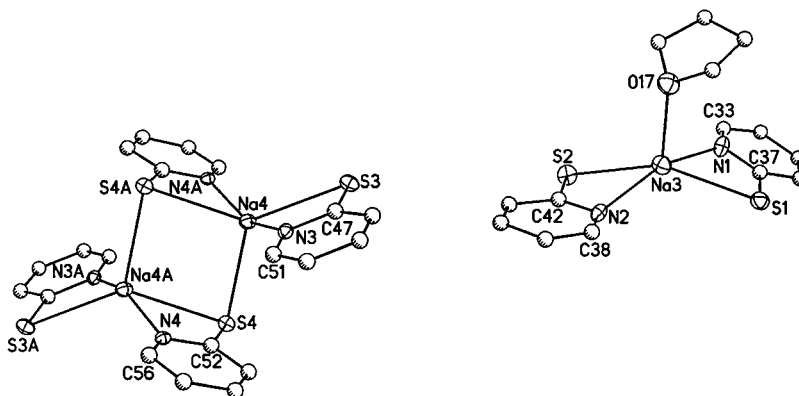


Figure 4. Computer-generated plot showing the sodium-centered anions in **6** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

pyramid, where the pyridine-2-thiolates comprise the base and THF is located in the axial position. Distortion from an ideal square pyramid can be seen in the O(17)-Na(3)-S(1), O(17)-Na(3)-S(2), O(17)-Na(3)-N(1), and O(17)-Na(3)-N(2) bond angles of 101.8(2)°, 106.9(2)°, 93.5(3)°, and 106.4(3)°, respectively. Within the S₂N₂ basal plane, angles about sodium vary between 60.2(2)° and 160.1(3)°. The acute values are attributable to the internal angles of the chelating ligands, and the obtuse values are between the thiolate ligands. Bond lengths about Na(3) are 2.823(5) Å to S(1), 2.812(4) Å to S(2), 2.455(8) Å to N(1), 2.483(8) Å to N(2), and 2.385(8) Å to O(17). Angles within the four-membered Na(3)S(1)C(37)N(1) chelate ring are 60.9(2)° about Na(3), 78.4(3)° about S(1), 119.6(7)° about C(37), and 100.5(6)° about N(1). S(1)-C(37) and N(1)-C(37) bond lengths are 1.758(9) and 1.351(1) Å, as expected. The overall structural parameters of the second pyridine-2-thiolate ligand in this anion are similar. Angles within the four-membered chelate ring are 60.2(2)° about Na(3), 78.7(3)° about S(2), 118.4(7)° about C(42), and 99.5(5)° about N(2). The S(2)-C(42) and N(2)-C(42) bond lengths are again as expected, being 1.758(8) and 1.343(1) Å, respectively.

The second sodate ion in the asymmetric unit is Na(4), which is part of the pyridine-2-thiolate-bridged dimeric unit shown in Figure 4. Within this symmetry-generated dimer, one thiolate ligand bridges two symmetry-related metal centers, while a second thiolate ligand occupies a terminal coordination site. The dimer can be described as a rhombus with internal angles of 98.64(1)° about Na(4) and 81.36(1)° about S(4). Similarly to the first sodium anion, Na(3), Na(4) is also five-coordinate, with three sulfur and two nitrogen contacts; the coordination geometry about Na(4) likewise can be described as a distorted square pyramid. Two thiolate ligands, S(3)/N(3) and S(4a)/N(4a), occupy the basal plane, while in place of a THf molecule in the axial position, a bridging thiolate atom, S(4), coordinates at this site. Distortion from square-pyramidal geometry is evident in the axial-equatorial angles as well as in the intrabasal angles. S(4)-Na(4)-S(3), S(4)-Na(4)-S(4a), S(4)-Na(4)-N(3), and S(4)-Na(4)-N(4a) angles are in the range 98.64(1)–123.73(1)°, while the intrabasal angles range between 58.7(2)° and 156.4(3)°. With respect to the ligands about Na(4), one thiolate is terminally coordinating, with Na(4)-S(3) and Na(4)-N(3) bond lengths of 2.933(4) and 2.433(8) Å, respectively. S(4) is the bridging thiolate atom with a contact of 2.907(4) Å to Na(4) and 2.879(4) Å to the symmetry-generated Na(4a). N(4a), from the symmetry-related bridging pyridine-2-thiolate, coordinates to Na(4) at 2.482(8) Å. Interestingly, the bridging Na-S interactions are shorter than the terminal Na-S contact: the bridging Na(4)-S(4) and Na(4)-S(4a) bond lengths are observed to be 2.907(4) and 2.879(4) Å, in comparison with the terminal Na(4)-S(3) interaction of 2.933(4) Å.

Geometrical data for the two distinctive pyridine-2-thiolates in this anion are quite similar, regardless of their bridging or terminal orientation. Bond angles within the four-membered chelate ring of the terminal thiolate ligand are 58.7(2)° about Na(4), 78.5(3)° about S(3), 117.1(6)° about C(47), and 105.5(5)° about N(3), and for the four-membered chelate ring

of the bridging thiolate the bond angles are 58.8(2)° about Na(4a), 79.0(3)° about S(4), 118.5(7)° about C(52), and 103.6(5)° about N(4). The S-C_{ipso} and N-C_{ipso} distances are as expected and fall in the range 1.743(8)–1.756(9) and 1.323(9)–1.375(9) Å, respectively. The coordination geometry about the bridging thiolate sulfur, S(4), can be described as a compressed pyramid with an angle sum of 253.7°.

[[K(μ-NC₅H₄-μ-S-2)]₂{15C5}]_∞ (7): The crown ether 15C5 serves as a template upon which two distinctive {K(NC₅H₄S-2)} units interact, one on each face of the crown. An inversion center relates K(1) to K(1a) and K(2) to K(2a). Likewise, the two bridging μ-S/μ-N pyridine-2-thiolates doubly bridge the symmetry-related potassium pairs and are also repeated by the crystallographic inversion center. The overall result is two distinct K₂/N₂/S₂ motifs, which are linked through a 15C5 molecule (Figure 5). K(1) is nine-coordinate with five crown

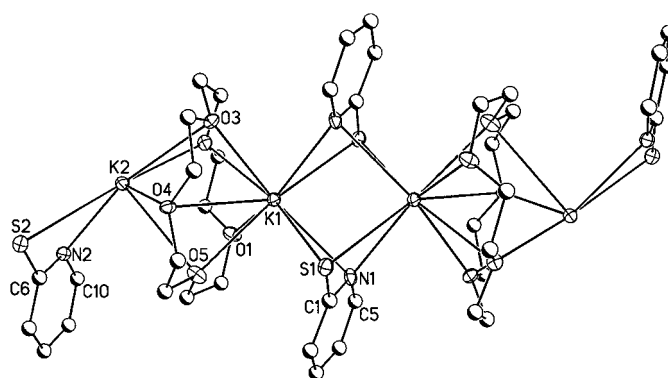


Figure 5. Computer-generated plot of part of the polymeric chain displayed in **7** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

contacts ranging from 2.774(3) to 3.408(3) Å and two S/N-chelating pyridine-2-thiolate molecules, one of which is generated by the inversion center. The K(1)-S(1) and K(1)-S(1a) bond lengths are 3.387(2) and 3.350(2) Å, respectively, while the K(1)-N(1) and K(1)-N(1a) bond lengths are 2.984(4) and 2.834(4) Å. Geometrical data for K(2) are similar to those for K(1), except that the former cation is eight-coordinate with only four significant contacts to the crown ether and two S/N-chelating pyridine-2-thiolate molecules. K(2)-O interactions range between 2.772(3) and 3.263(3) Å, with O(1) more than 3.9 Å from K(2). The K(2)-S(2) and K(2)-S(2a) interactions are 3.266(2) and 3.399(2) Å, respectively, while K(2)-N(2) and K(2)-N(2a) bond lengths are 2.922(4) and 2.896(4) Å.

Each pyridine-2-thiolate ligand bridges two symmetry-related potassium cations with both sulfur and nitrogen atoms, resulting in four-membered KSCN, K₂S₂, and K₂N₂ rings. The S(1)/N(1)-K(1)-S(1a)/N(1a) angles range between 82.13(8) and 109.39(3)°, while the S(1)/N(1)-K(1)-O and S(1a)/N(1a)-K(1)-O angles are found to lie between 71.51(1)° and 160.22(7)°. Angles within the four-membered K(1)-S(1)-C(1)-N(1) chelate ring are 48.87(8)° about K(1), 71.1(2)° about S(1), 117.7(3)° about C(1), and 89.7(3)° about N(1). The second four-membered K(1a)-S(1)-C(1)-N(1) chelate ring has

internal bond angles of $50.12(8)^\circ$ about K(1a), $80.0(2)^\circ$ about S(1), $117.7(3)^\circ$ about C(1), and $108.2(3)^\circ$ about N(1). The S(1)–C(1) and N(1)–C(1) bond lengths are 1.750(5) and 1.350(6) Å, respectively. The sum (221.9°) of angles about S(1) indicates a compressed pyramidal geometry, while the range of angles about N(1), $83.98(1)–126.8(3)^\circ$, indicates a distorted tetrahedral geometry.

In the second thiolate molecule, S(2)/N(2)–K(2)–S(2a)/N(2a) angles range between $81.43(7)^\circ$ and $109.37(4)^\circ$, while S(2)/N(2)–K(2)–O and S(2a)/N(2a)–K(2)–O angles are in the range $86.02(9)–174.62(7)^\circ$. Angles within the four-membered chelate rings are: for K(2)–S(2)–C(6)–N(2), $50.86(8)^\circ$ about K(2), $80.4(2)^\circ$ about S(2), $118.2(3)^\circ$ about C(6), and $99.8(3)^\circ$ about N(2); and for K(2a)–S(2)–C(6)–N(2), $49.50(8)^\circ$ about K(2a), $74.30(1)^\circ$ about S(2), $118.2(3)^\circ$ about C(6), and $97.9(3)^\circ$ about N(2). The S(2)–C(6) and N(2)–C(6) bond lengths are 1.735(5) and 1.374(5) Å, respectively. The sum of the angles about S(2) is 225.33° , indicating a very compressed pyramidal geometry, while the range of angles about N(2) ($99.8(3)–128.3(3)^\circ$) suggests a distorted tetrahedral geometry.

Discussion

The initial observation which launched this investigation into alkali metal pyridine-2-thiolate structural chemistry was the exceptional length of the Li(1)–S(1) bond in **1** (2.894(5) Å), and the corresponding relative shortness of the Li(1)–N(1) distance (2.002(5) Å). The question was then raised of whether the strong Li(1)–N(1) contact was a manifestation of the hard-acid/hard-base pairing between lithium and the nitrogen center of the resonance-delocalized anion, and if so, how the geometrical interactions between cation and anion would change with an increase in the metal radius. With the goal of answering these seemingly straightforward questions, the synthesis of a family of crown-ether-coordinated alkali metal pyridine-2-thiolates was initiated. As expected, pairing of the appropriately sized crown ether according to the radius of the cations led to the monomers **1–3**. Indeed, the geometrical relationship between cation and anion is influenced by the metal ionic radius (vide infra); however, two reaction parameters have been changed simultaneously in the syntheses of **1–3**: the metal center and the crown ether. In an attempt to change just one reaction parameter at a time and allow for the most meaningful structural comparisons, the syntheses of all the Li/Na/K- and 12C4/15C5/18C6-containing permutations were explored. The subsequently identified group of crown ether-coordinated alkali metal pyridine-2-thiolates **4–7** display a fascinating range of structural diversity, highlighting the role that a mismatched crown ether can play in the solid state, and by inference, in solution.

The anomalously long Li(1)–S(1) bond length in **1** can be compared with several analogous lithium–sulfur interactions in related S–C–N resonance-delocalized systems. For example, in the dimeric lithio-2-mercaptobenzimidazole $[\text{Li}(\text{hmpa})_2(\text{C}_6\text{H}_4\text{NC}(\text{S})\text{N})\text{Li}(\mu\text{-hmpa})]_2$ (hmpa = hexamethylphosphoramide), one weak Li–S interaction of 2.842(1) Å and one strong Li–S contact of 2.525(1) Å are observed. In the related lithio-2-mercaptopyrimidine $[\text{Li}(\text{hmpa})(\text{C}_3\text{H}_3\text{NC}$

(S)N)] $_\infty$, only a weak Li–S interaction of 2.804(5) Å has been identified.^[6] In both of these structures the coordination environment about the cation is completed by strong interactions between Li and the O and N of hmpa, resulting in a coordination number of four. The dimeric formulation of lithio-2-mercaptobenzoxazole, $[\text{Li}(\mu\text{-hmpa})\text{C}_6\text{H}_4\text{NC}(\text{S})\text{O}]_2 \cdot \text{H}_2\text{O}$, features a marginally stronger Li–S bond of 2.757(1) Å, with amide, H₂O, and bridging hmpa donor molecules completing the coordination environment about the four-coordinate cations.^[7]

The weak Li(1)–S(1) interaction of 2.894(5) Å in **1** can be attributed, in part, to the six-coordinate cation; however, the presence of a strong Li–N_{amido} bond (2.002(5) Å) indicates preferential hard-acid/hard-base pairing. The sole example of a six-coordinate lithium cation in thiolate-related structural chemistry is the pyrazine thiolate $[\text{Li}(\text{tmeda})\text{S}_2\text{CCH}_2(\text{C}_4\text{H}_2\text{N}_2\text{Me}_2)]_\infty$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine). The thiolato S atoms coordinate lithium at 2.554(4) and 2.688(5) Å, respectively. Also chelating the cation is one TMEDA molecule, and the nascent monomeric units are linked into an infinite chain through Li–N interactions of 2.129(5) Å.^[8] In comparison with **1**, the six-coordinate cation in the pyrazine thiolate forms significantly shorter Li–S bonds. Indeed, the common upper limit for Li–S_{thiolato} interactions is approximately 2.6 Å, as in a large family of structurally identified compounds.^[9] The Li–S_{thiolato} values above can be contrasted with those for neutral sulfur donor ligation of lithium in $[\text{Li}(\text{tmeda})(\text{C}_6\text{H}_5\text{S}(t\text{Bu})_2)]_2$ and $[\text{Li}(\text{tmeda})(\text{C}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{S})]_2$.^[10, 11] The former exhibits a Li–S interaction of 2.712(5) Å, while the latter has a Li–S contact of 2.516 Å.

Bond lengths that are similar to that of the Li(1)–N(1) bond (2.002(5) Å) in **1** have been observed in donor-free and donor-coordinated lithium bis(trimethylsilyl)amides. For example, in trimeric $[\text{LiN}(\text{SiMe}_3)_2]_3$ the metal–N_{amido} contact distance is 2.000(1) Å, and in the ether-coordinated dimer $[\text{Li}(\text{Et}_2\text{O})\text{N}(\text{SiMe}_3)_2]_2$ the metal–N_{amido} distance is greater (2.055(1) Å).^[12] Clearly, then, the coordination about Li(1) in **1** is composed of a significant amide contribution and a relatively weak thiolate interaction.

Compounds **2** (Figure 1) and **3** are the first monomeric, heavier alkali metal pyridine-2-thiolates to be structurally characterized. Few structural studies have been published on sodium thiolates or potassium thiolates in general,^[13] and only one sodium pyridine-2-thiolate structure has been described in the literature to date—that of the bis(*tert*-butyldimethylsilyl)-substituted $[\text{Na}(\text{NC}_5\text{H}_2\text{S}-2-(\text{SiMe}_2t\text{Bu})_2-3,6)]_6$.^[14] This compound displays a hexagonal-prismatic structure based on an Na₆S₆ core framework. Each sodium cation interacts with three thiolato sulfur atoms and one intramolecularly coordinating nitrogen atom, resulting in a coordination number of four. Na–S distances range from 2.792(5) to 2.831(5) Å, while the Na–N distance is 2.481(9) Å. Of relevance to **3** is the structure of a K₁₂S₁₂ cluster species, $[\text{K}_2\text{S}_2\text{C}(\text{CNC}_2\text{N}-i\text{Pr}_2-2,5-\text{Me}_2-3,4)]_6$, which is based on a K₆S₆ hexagonal prism surrounded by a K₆S₆ 12-membered ring.^[15] The K–S_{thiolato} interactions range between 3.023(3) and 3.308(5) Å for cations in four- and five-coordinate environments. In contrast with these heavier alkali metal pyridine-2-

thiolate derivatives, the seven-coordinate sodium cation in **2** displays an interaction of 3.038(1) Å with S(1), while eight-coordinate K(1) in **3** bonds to S(1) at 3.2558(1) Å. The large discrepancy in Na–S bond lengths between [Na(NC₅H₂S-2-(SiMe₂tBu)₂-3,6)]₆ and **2** does not rest solely in the different coordination numbers about the cation. The matching of the relative sizes of the alkali metal cation and the chelating pyridine-2-thiolate must play an important role in the structural geometry (vide infra).

The series of monomeric alkali metal trityl derivatives [Li(OEt)₂C(N-2-C₅H₄)Ph₂], [Na(thf)₃C(N-2-C₅H₄)Ph₂], and [K(pmdta)(thf)C(N-2-C₅H₄)Ph₂] (pmdta = pentamethyldiethylenetriamine) feature intramolecular M–N bonding of 1.972(5), 2.414(7), and 2.809(5) Å, respectively.^[16] Furthermore, in the sodium and potassium bis(trimethylsilyl)amides [Na(N(SiMe₃)₂)_∞ and [KN(SiMe₃)₂]₂, metal–N_{amido} bonding is exhibited at 2.355(4) Å and 2.750(3) and 2.803(3) Å, respectively.^[12] Comparison of these values with the metal–N_{amido} bond lengths of 2.002(5) Å in **1**, 2.429(3) Å in **2**, and 2.854(3) Å in **3** suggests relatively strong M–N interactions in the monomeric complexes.

Compounds **1–3** display a smooth increase in metal–S_{thiolato} and metal–N_{amido} bond lengths, in accord with an increasing ionic radii and coordination numbers (Table 3). M–S and M–N bond lengths in [Li(12C4)(NC₃H₄S-2)] are 2.894(5) and

2.429(3) Å compared with 2.81 Å in **2**, and 2.854(3) Å compared with 3.45 Å in **3**. These values suggest a strong amide contribution to the metal environment throughout the series. Indeed, similar M–N distances have been observed in alkali metal amides (vide supra). The sums of the ionic M⁺ and sulfur van der Waals radii, however, point to a significant increase in the M–S bonding interaction as the cation radius increases. In **1** the Li(1)–S(1) bond length (2.894(5) Å) is 0.194 Å longer than the sum of the ionic Li⁺ (CN=6) and sulfur van der Waals radii. Furthermore, although several examples of resonance-delocalized lithium thiolates with long Li–S interactions are known, the vast majority of structures have an Li–S interaction under 2.60 Å, suggesting the thiolato interaction with lithium in **1** is very weak. Compound **2** displays a slightly stronger Na–S interaction than was observed for Li(1)–S(1) in **1**. The bond length of 3.038(1) Å for Na(1)–S(1) is just less than the sum (93.06 Å) of the ionic Na⁺ (CN=7) and sulfur van der Waals radii. This should still be considered a weak interaction, however, as typical Na–S bond lengths fall below 2.80 Å.^[9a, 13, 14] The larger potassium cation allows for significant K–S_{thiolato} and K–N_{amido} interactions to occur simultaneously. In **3** the K(1)–S(1) bond length of 3.2558(1) Å is shorter than the sum (3.45 Å) of the ionic K⁺ (CN=8) and sulfur van der Waals radii, and the K(1)–S(1) distance correlates well with data from other structural investigations on potassium thiolate complexes.^[9a, 13, 15] The increase in the alkali metal–S_{thiolato} interaction in the above series is also evident in the C(1)–N(1)–M(1) bond angle. From **1** to **3** this angle steadily decreases as the M(1)–S(1) interaction becomes more significant: it is 112.2(2)^o in **1**, 107.9(2)^o in **2**, and 106.4(2)^o in **3**.

An increase in ionic radius may not be the sole reason for the variance in M–S and M–N bonding in **1–3**. According to the hard/soft acid/base concept, the larger cation (acid) should demonstrate a preference for interacting with the larger anion (base).^[18] In the potassium pyridine-2-thiolate **3**, this preference is modestly exhibited by a strong K(1)–S(1) contact and a K(1)–N(1) bond length that is marginally longer

than typical K–N_{amido} interactions. Further up the alkali metal family, the sodium pyridine-2-thiolate **2** displays intermediate values: the Na(1)–S(1) and Na(1)–N(1) bond lengths are long in comparison with reference data; in the lithium pyridine-2-thiolate **1** there is clearly a predominance of an amide contribution from the resonance-delocalized S–C–N anion.

In the absence of an intramolecularly coordinating functionality, the resulting structure of lithium aryl thiolates is very sensitive to the steric nature of the aromatic moiety. For example, in the series [Li(py)(SCH₂Ph)]_∞, [Li(py)₂(SPh)]_∞, and [Li(py)₃(SC₆H₄Me-2)] (py = pyridine), small changes in the aryl ligand lead to distinct structural modifications: a ladder-like polymer, an infinite one-dimensional chain, and a monomer, respectively.^[9k] Each cation is four-coordinate, and the ranges of Li–S and Li–N bond lengths are

2.002(5) Å, in [Na(15C5)(NC₃H₄S-2)] 3.038(1) and 2.429(3) Å, and in [K(18C6)(NC₃H₄S-2)] 3.2558(1) and 2.854(3) Å. This constitutes an increase in the series from **1** to **3** for the M–S and M–N distances of 0.362 and 0.852 Å. With a change in ionic radius of 0.75 Å from Li⁺ (CN=6) to K⁺ (CN=8), the 0.852 Å difference between Li–N and K–N bonding reflects the increasing radius of the cation.^[17] The 0.362 Å difference in M–S bonding accounts for the exceptionally long Li(1)–S(1) interaction in **1**, and also reflects the increase in ionic radius of the metal down the series.

Table 3. Comparison of M–S, M–N, and M–O bond lengths for compounds **1–3** and **4–7**.

| Compound | M CN ^[a] | M–S [Å] | M–N [Å] | M–O [Å] ^[b] |
|-------------------------------------------------------------------------------------------|---------------------|--------------------|----------|-------------------------|
| [Li(12C4)(NC ₃ H ₄ S-2)], 1 | 6 | 2.894(5) | 2.002(5) | 2.061(5)–2.237(5) |
| [Na(15C5)(NC ₃ H ₄ S-2)], 2 | 7 | 3.038(1) | 2.429(3) | 2.433(2)–2.621(2) |
| [K(18C6)(NC ₃ H ₄ S-2)], 3 | 8 | 3.2558(1) | 2.854(3) | 2.878(2)–2.956(2) |
| [Na(18C6)(NC ₃ H ₄ S-2)], 5 | 6 | 2.764(1) | 2.649(2) | 2.451(2)–3.020(2) |
| 6 | Na(1) 8 | | | 2.441(7)–2.546(7) |
| | Na(2) 8 | | | 2.417(6)–2.513(6) |
| | Na(3) 5 | 2.823(5), 2.812(4) | 2.455(8) | 2.385(8) ^[c] |
| | | | 2.483(8) | |
| | Na(4) 5 | 2.879(4), 2.907(4) | 2.482(8) | |
| | | | 2.933(4) | |
| | | | 2.433(8) | |
| [[K(μ-NC ₃ H ₄ μ-S-2)] ₂ {15C5}] _∞ , 7 | K(1) 9 | 3.350(2) | 2.834(4) | 2.774(3)–3.408(3) |
| | | 3.387(2) | 2.984(4) | |
| | K(2) 8 | 3.266(2) | 2.922(4) | 2.772(3)–3.263(3) |
| | | 3.399(2) | 2.896(4) | |

[a] CN = coordination number. [b] oxygen = crown ether. [c] = THF.

The overall bonding trends in **1–3** can be understood in light of related M–S and M–N distances and comparison with the sum of the ionic and van der Waals radii. Each of compounds **1–3** displays an M–N interaction which is significantly less than the sum of the ionic M⁺ and nitrogen van der Waals radii: 2.002(5) Å compared with 2.45 Å in **1**,

2.002(5) Å, in [Na(15C5)(NC₃H₄S-2)] 3.038(1) and 2.429(3) Å, and in [K(18C6)(NC₃H₄S-2)] 3.2558(1) and 2.854(3) Å. This constitutes an increase in the series from **1** to **3** for the M–S and M–N distances of 0.362 and 0.852 Å. With a change in ionic radius of 0.75 Å from Li⁺ (CN=6) to K⁺ (CN=8), the 0.852 Å difference between Li–N and K–N bonding reflects the increasing radius of the cation.^[17] The 0.362 Å difference in M–S bonding accounts for the exceptionally long Li(1)–S(1) interaction in **1**, and also reflects the increase in ionic radius of the metal down the series.

2.412(6)–2.513(6) Å and 2.045(5)–2.05(6) Å, respectively. It is also informative to compare the monomeric formulations of compounds **1–3** with the structures of alkali metal phenoxides without crown ethers. In the absence of the coordination-satiating effects of a crown ether, the sterically unencumbered phenoxide ligand leads to polymeric species for the alkali metal family.^[19] In another example, a polymer has also been observed in $[\text{Na}(\text{OC}_6\text{H}_4\text{-4-Me})]_\infty$, where the methyl substituent had little effect on the ionic association.^[20] In contrast, an intramolecularly coordinating functionality on the aryl ligand or Lewis-base donor makes it possible to isolate oligomeric alkali metal aryloxide species, for example, trimeric $[\text{Li}(\text{OC}_6\text{H}_2\text{-2,6-(CH}_2\text{NMe}_2)_2\text{-4-Me})]_3$ and tetrameric $[\text{Na}(\text{OC}_6\text{H}_2\text{-2,6-(CH}_2\text{NMe}_2)_2\text{-4-Me})]_4$, and the tetrameric and hexameric phenoxides $[\text{Na}(\text{tmu})(\text{OPh})]_4$ (tmu = *N,N,N',N'*-tetramethylurea) and $[\text{Na}(\text{thf})(\text{OPh})]_6$.^[21] It is expected, then, that the family of alkali metal pyridine-2-thiolates would exhibit oligomeric or polymeric structures in the absence of macrocyclic Lewis-donor coordination.

The synthesis of mismatched crown ether/alkali metal pairs was undertaken to address the effect on the solid-state structural chemistry if one reaction parameter at a time is changed (for example, if 12C4 coordination of lithium pyridine-2-thiolate is changed to 18C6). In the permutations that were examined subsequently, a diverse group of crown ether-coordinated alkali metal pyridine-2-thiolates could be identified in which seemingly innocuous changes in the crown ether had led to vastly different structural formulations.

The solid-state structure of **4** can be viewed as an 18C6-bridged lithium pyridine-2-thiolate dimer, in which one $\{\text{Li}(\text{NC}_5\text{H}_4\text{S-2})\}$ unit interacts with three crown oxygen atoms through the cation and the second unit is generated by an inversion center in the crown ether ring (Figure 2). A related structural motif has been observed in the lithium phenoxide $[\{\text{Li}(\text{OPh})\}_2\{18\text{C6}\}]$, where the cation is five-coordinate with three crown ether oxygen interactions and has contacts with both phenoxide units.^[22] An important distinction between the two structures, however, is the location of the cations relative to the mean plane of the crown ether. In the phenoxide, the lithium cations are essentially in the crown ether plane; however, in **4** the cations are displaced above or below the crown ether. This displacement is probably a manifestation of the steric presence and chelating nature of the pyridine-2-thiolate ligand.

In marked contrast with **1**, which has a Li(1)–S(1) bond length of 2.894(5) Å, **4** displays a shorter Li(1)–S(1) interaction of 2.604(4) Å and a comparatively long Li(1)–N(1) bond of 2.057(4) Å. This is further corroborated by the tighter C(1)–N(1)–Li(1) bond angle of 102.0(2)° in the dimer, compared with 111.2(2)° in **1**. A lower coordination environment about a cation will result in a decrease in relevant bond lengths; however, the Li(1)–S(1) distance in **4** is 0.290 Å shorter than in the 12C4-coordinated monomer **1**, a difference too significant to attribute solely to a reduced coordination number. The discrepancy in Li–S_{thiolato} bonding may well reside in the steric interaction between the crown ether and pyridine-2-thiolate, which is manifested in the S(1)–Li(1)–O bond angles. The narrow S(1)–Li(1)–O(1) and S(1)–Li(1)–O(4) angles of 99.0(2) and 101.4(2)° in **1** (Figure 1) may be

contrasted with the more open values of 101.9(2) and 110.3(2)° for S(1)–Li(1)–O(3) and S(1)–Li(1)–O(2a) in **4** (Figure 4). Further, the axial–axial bond angle for S(1)–Li(1)–O(1a) of 166.3(2)° in **4** is 2.9° larger than the corresponding angle in **1**. These data suggest a crown ether conformation in the dimer **4** which facilitates a closer Li(1)–S(1) interaction by way of a reduced steric presence when compared with 12C4-ligated **1**.

In contrast with the monomer **3** and the dimer **4**, asymmetric crown-ether ligation of the sodium cation is observed in **5**, where four of six crown ether oxygen atoms interact with the cation (Figure 3). Several examples exist of unusual coordination modes of crown ethers with sodium cations, although no examples involving sodium thiolates and 18C6 have been reported in the literature. For example, a remarkable triple-decker ion triple, $[(18\text{C6})\text{Na}(18\text{C6})\text{Na}(18\text{C6})][\text{C}_5\text{H-2,3,4,5-Ph}_4]_2$, features eight-coordinate sodium cations, where each metal interacts with six oxygen atoms of an 18C6 molecule and two oxygen atoms of a shared 18C6 ligand.^[23] In the dimeric sodium phenoxide $[\text{Na}(\mu\text{-dicyclohexo}18\text{C6})(\mu\text{-OPh})\text{Na}(\mu\text{-OPh})]_2$, the crown ether sequesters one cation with all six of its oxygen atoms while interacting with the second cation with just two oxygen atoms.^[24] In another example, two 15C5 molecules surround the sodium cation in $[\{\text{Na}(15\text{C5})\}_2\{\text{NbOCl}_4(\text{CH}_3\text{CN})\}]$.^[25] The alkali metal resides essentially in the plane of one crown, while the second crown is oriented orthogonally with respect to the first and interacts with just two of its oxygen atoms. In **5**, four Na(1)–O interactions are in the range from 2.451(2) to 3.020(2) Å, while the remaining two Na–O contacts are longer than 3.4 Å. When it is borne in mind that the sum of ionic Na⁺ (CN = 6) and oxygen van der Waals radii is 2.66 Å, the Na(1)–O(4) bond length of 3.020(2) Å can be considered very weak; thus there is some uncertainty in the cation coordination number (five or six).^[17] Indeed, the geometrical data for **5** suggest a lower coordination environment about Na(1). Specifically, the Na(1)–S(1) bond length of 2.764(1) Å in **5** is decidedly shorter than the corresponding distance of 3.038(1) Å in the 15C5-coordinated monomer **2**. This value is actually quite similar to the average Na–S interaction (four-coordinate sodium) in $[\text{Na}(\text{tmeda})(\text{SC}_6\text{H}_2\text{-2,4,6-}i\text{Pr}_3)]$ (2.772(1) Å).^[13a] If the Na_{cation}–N_{amido} bonding is considered, the Na(1)–N(1) distance of 2.649(2) Å in **5** is longer than Na(1)–N(1) interaction in **2** (2.429(3) Å). As with $[\{\text{Li}(\text{NC}_5\text{H}_4\text{S-2})\}_2\{18\text{C6}\}]$, the stronger Na_{cation}–S_{thiolato} bonding in **5** may be the result of a lower cation coordination number in conjunction with a reduced steric presence from the orientation and asymmetric ligation of 18C6.

Changing just one reaction parameter by using 12C4 instead of 18C6 leads to a remarkable solid-state product. Compound **6** is the first solvent-separated, sodium-centered, anionic pyridine-2-thiolate ion quadruple (Figure 4; only the anions are shown). The only other related complexes known are the contact-ion complex $[\text{Rb}_2\{\text{Na}(\text{hfac})_3\}]$ (hfac = hexafluoroacetylacetonate) and the solvent-separated contact ion quadruple $[\text{Na}(18\text{C6})(\text{thf})_2][\text{Na}(18\text{C6})\{\text{C}(\text{NO}_2)_3\}_2]$.^[26, 27] Geometrical data for **6** may be compared with the 15C5- and 18C6-coordinated sodium pyridine-2-thiolates **2** and **5**, respectively (Table 3). The Na(1) and Na(2)–O(crown) dis-

tances in **6** are comparable with the values for **2** and those in the lower range for **5**. The Na–S_{thiolato} and Na–N_{amido} bonds in the metallate **6** exhibit intermediate values in comparison with the other two crown ether-complexed pyridine-2-thiolates, although cations Na(3) and Na(4) are both only five-coordinate in **6**. For example, the range of Na–S bonding in **6** is 2.812(4)–2.933(4) Å, while the seven-coordinate cation in **2** has an Na(1)–S(1) interaction of 3.038(1) Å, and the six-coordinate cation in **5** displays an Na(1)–S(1) distance of 2.764(1) Å. The longer Na–S distances in the metallate compared with the Na–S distance in the higher coordinate cation in **2** can be attributed to anionic repulsion of the two pyridine-2-thiolate ligands about Na(3) and Na(4).

The intermediate Na–S bond lengths in **6** can also be correlated with median Na–N values. The Na–N_{amido} interactions in the metallate range from 2.433(8) to 2.483(8) Å, which lies between the comparable values of 2.429(3) Å in **2** and 2.649(2) Å in **5**. Clearly, the Na–S and Na–N interactions are coupled so that an increase in the Na_{cation}–S_{thiolato} bond length results in a stronger Na_{cation}–N_{amido} interaction and, conversely, a decrease in the Na_{cation}–S_{thiolato} bond length results in a weaker Na_{cation}–N_{amido} bond. It is also noteworthy that the product stoichiometry in **6** reflects the reactant stoichiometry: there is one 12C4 molecule per cation and per pyridine-2-thiolate.

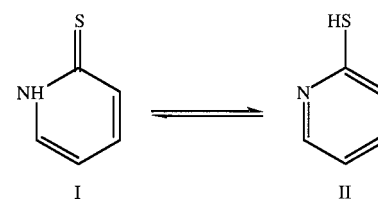
15C5 coordination of sodium allowed the isolation of monomeric [Na(15C5)(NC₅H₄S-2)]; however, in the presence of potassium the same crown ether results in the one-dimensional polymer, **7** (Figure 5). Compound **7** does not reflect the initial thiol:crown ether:metal hydride reaction stoichiometry of 1:1:1; instead, only one-half of the available macrocycle was utilized in the formation of this one-dimensional polymer. The crown ether serves to bridge the unusual {K(NC₅H₄S-2)}₂ dimeric units, structural motifs resembling the hypothetical structure of dimeric [K₂(OPh)₂(15C5)₂].^[28]

Geometrical data for **3** and **7** are very similar, reflecting high cation coordination numbers. The bridging nature of the two pyridine-2-thiolates in polymeric **7** results in slightly longer K–S and K–N distances than those in monomeric **3** (Table 3). For example, K–S bond lengths in **7** range from 3.266(2) to 3.399(2) Å, and the K(1)–S(1) distance in **3** is 3.2258(1) Å. A similar effect is observed in the K–N distances in **7** as compared with that in monomeric **3**. The bridging K–N interactions cover the range 2.834(4) to 2.984(4) Å in the polymer, and K–N is 2.854(3) Å in the monomer. The K_{cation}–O_{crown ether} bond lengths in **7** are observed over a broader range than in **3**, and different values are exhibited for K(1) and K(2) in the polymer. K(1) interacts with all five oxygen atoms of 15C5 between 2.774(3) and 3.408(3) Å, while K(2) has four crown ether oxygen contacts between 2.772(3) and 3.262(3) Å, with the remaining oxygen significantly further away (> 3.9 Å) than the sum (3.15 Å) of the ionic K⁺ (CN = 8) and oxygen van der Waals radii.^[17]

The polymeric formulation of **7** may be contrasted with dimeric **4**. In the latter complex, the small lithium cation is adequately coordinated by three crown ether oxygen atoms and the chelating pyridine-2-thiolate, resulting in a distorted trigonal-bipyramidal ligand arrangement. With a larger potassium ion, however, the more spacious coordination envi-

ronment allows for numerous cation–anion and cation–crown ether interactions, thereby leading to polymerization.

The S–C_{ipso} bonding in **1–7** can be compared with early crystallographic work on the structure of pyridine-2-thiol.^[29] Solid-state structural investigations supported the α -thiopyridone assignment I in Scheme 1. Evidence for this thione



Scheme 1. Tautomeric forms of pyridine-2-thiol.

tautomer (rather than the thiol form II) comes from an analysis of pertinent bond angles and also by analogy with the oxygen congener α -pyridone, which has been shown to exist as the ketone tautomer in the solid state.^[30] In contrast, an analysis of the S–C_{ipso} bond lengths in **1–7** suggests that the bond order decreases uniformly upon metalation. Specifically, in the structure of α -thiopyridone the S–C_{ipso} bond length was found to be 1.68(2) Å, a value associated with partial double-bond character; however, in the alkali metal pyridine-2-thiolate complexes **1–7** S–C_{ipso} bonds are observed to be in the range 1.735(3)–1.758(9) Å, suggesting a decrease in the bond order.

Conclusion

Through the synthesis and solid-state structural identification of **1–7**, an unexpected structural diversity has emerged with respect to both specific geometrical comparisons and overall molecular topology. We had anticipated the gross structural chemistry of established crown ether/cation pairings, as observed in a series of monomeric alkali metal pyridine-2-thiolates; however, the connective relationships between cation and anion turned out to be more complex than we expected. In contrast, when pyridine-2-thiol is metalated in the presence of a crown ether that is either too small or too large relative to the cationic radius, an asymmetrically coordinated monomer, a crown-ether-templated dimer or polymer, or a very unusual separated metalloanionic ion quadruple can be isolated.

The monomeric formulations of **1**, **2**, and **3** can be attributed to the pairing of an alkali metal with a crown ether which is capable of sequestering the cation, while simultaneously, and in conjunction with chelating pyridine-2-thiolate, satiating many of the cation's coordinative requirements. Significant geometrical differences were observed, however, in the relationship between the cation and anion in this series. The small lithium center was shown to interact primarily with the hard nitrogeno center of the resonance-delocalized S–C–N anion, with little contribution from the thiolato S atom. Further down the alkali metal family, sodium exhibited a moderately stronger Na–S contact (albeit longer than

expected) and potassium displayed an anticipated K–S bond length, while the metal–N_{amido} contacts for both compounds were reminiscent of weak alkali metal–N_{amido} interactions. The cation–anion bonding in this series, therefore, appears to be governed not only by hard/soft acid/base pairing but also by a size effect: the large potassium cation can accommodate both strong amido and thiolato contributions, whereas the much smaller lithium center interacts preferentially with amido groups, and sodium exhibits intermediate interactions.

When a crown ether that was either too small or too large relative to the alkali metal cation was employed in the metalation of pyridine-2-thiol, a structurally diverse family of complexes was obtained. 15C5 and 18C6 both served as bridging units in **7** and **4**: the larger potassium cation paired with a crown ether too small to bind the metal in-plane leads to polymerization, while the coordination environment about lithium when paired with a crown ether larger than the metal is satiated by three oxygen atoms and the anion, leading to a dimeric product. A simple change of ligand, from 18C6 to 12C4, leads to vastly different solid-state products in **5** and **6**. 18C6 can accommodate sodium in-plane, but in the presence of chelating pyridine-2-thiolate only four out of six crown oxygen atoms can interact with the cation. In contrast, two molecules of 12C4 (which are far too small to coordinate sodium in-plane) form a coordination sandwich with the metal, thereby allowing the assembly of an unprecedented solvent-separated, sodium-centered pyridine-2-thiolate ion quadruple with two distinctive sodium metalates.

Experimental Section

General procedures: All reactions were performed under a purified nitrogen atmosphere using modified Schlenk techniques and a Braun Labmaster 100 dry-box. Toluene and THF were distilled just before use from Na/K alloys, then subjected to two freeze–pump–thaw cycles. Commercially available [12]crown-4 (12C4) and [15]crown-5 (15C5) were dried over 3 Å molecular sieves; [18]crown-6 (18C6) was dissolved in freshly distilled diethyl ether and stirred with finely cut sodium metal for one day. After filtration from the metal, the crown ether was recrystallized at –20 °C and used as isolated. Readily available *n*BuLi was used as a 1.6 M solution in hexanes. Mineral oil suspensions of NaH and of KH were each washed repeatedly with freshly distilled hexane and dried under vacuum. Pyridine-2-thiol was purified by sublimation inside a nitrogen-purged cold-finger apparatus. 300 MHz ¹H NMR and 100 MHz ¹³C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer PE 1600 FTIR spectrometer.

Compounds **1–7** were synthesized by a straightforward metathesis reaction of the appropriate alkali metal reagent (*n*BuLi, NaH, or KH) with NC₅H₄S(H)-2 in an aromatic or ethereal solvent and with the addition of an appropriate crown ether. Importantly, all reaction stoichiometries involved an equimolar ratio of reactants, and after the initial metalation each reaction was filtered hot through a Celite-padded filter frit. Crystallization was performed in the reaction solvents mentioned below. A representative synthesis is described in detail for **1**, and physical data are provided for all the compounds reported. The moisture- and oxygen-sensitive nature of **1–7** has precluded the acquisition of reliable elemental microanalysis results.

[Li(12C4)(NC₅H₄S-2)] (1): A Schlenk flask (100 mL) was charged with pyridine-2-thiol (0.11 g, 1.0 mmol) and 12C4 (0.18 g, 1.0 mmol). Toluene (25 mL) was added, then *n*BuLi (0.63 mL, 1.0 mmol) was added dropwise, and the mixture was stirred at room temperature for 30 min. A light-tan

gum formed quickly but was dissolved subsequently with brief heating. After the solution had been filtered hot through a Celite-padded frit and cooled to room temperature, a pale cloudiness developed and required the addition of THF (approximately 5 mL). Storage at –20 °C for several days led to the isolation of a small crop of clear needles in 18% yield (0.06 g). M.p.: irreversible melt to a yellow oil, 114–117 °C; ¹H NMR ([D₈]THF): δ = 7.71 (m, 1H), 7.12 (m, 1H), 6.94 (m, 1H), 6.37 (m, 1H), 3.62 (s, 16H); ¹³C{¹H} NMR ([D₈]THF): δ = 146.84, 134.29, 130.01, 113.12, 71.41; IR (Nujol): $\tilde{\nu}$ = 3034 (w), 2903 (s), 1580 (s), 1533 (m), 1461 (s), 1406 (m), 1377 (m), 1286 (w), 1270 (m), 1257 (m), 1130 (s), 1103 (m), 1079 (m), 1056 (m), 1025 (m), 984 (m), 924 (m), 852 (m), 735 (s), 728 (m), 640 (m), 533 (m), 439 (m) cm⁻¹.

[Na(15C5)(NC₅H₄S-2)] (2): Long colorless needles formed on storage of the THF-solvated reaction at 0 °C over several days in 19.1% yield (0.14 g). M.p.: decomposition to a brown oil above 185 °C; ¹H NMR ([D₅]pyridine): δ = 8.11 (m, 1H), 7.95 (m, 1H), 7.11 (m, 1H), 6.58 (m, 1H), 3.62 (s, 20H); ¹³C{¹H} NMR ([D₅]pyridine): δ = 148.40, 134.11, 130.35, 113.30, 70.14; IR (Nujol): $\tilde{\nu}$ = 2928 (s), 1572 (m), 1528 (w), 1463 (s), 1377 (s), 1352 (m), 1298 (w), 1124 (m), 1086 (m), 974 (m), 938 (w), 756 (m), 725 (m), 408 (w) cm⁻¹.

[K(18C6)(NC₅H₄S-2)] (3): Colorless plates formed in 36% yield (0.15 g) from the toluene-solvated reaction mixture after it had been cooled gradually to room temperature. M.p.: irreversible melt to a yellow oil, 80–84 °C; ¹H NMR ([D₈]THF): δ = 7.86 (bd, 1H), 7.27 (d, 1H), 7.09 (t, 1H), 6.47 (t, 1H), 3.57 (s, 24H); ¹³C{¹H} NMR ([D₈]THF): δ = 139.92, 135.69, 134.31, 111.56, 71.38; IR (Nujol): $\tilde{\nu}$ = 2920 (s), 1570 (m), 1531 (w), 1465 (s), 1404 (w), 1377 (m), 1350 (m), 1246 (m), 1103 (s), 961 (m), 836 (m), 752 (m), 732 (m), 485 (w), 442 (w) cm⁻¹.

[[Li(NC₅H₄S-2)]₂(18C6)] (4): Colorless needles formed in 32% yield (0.16 g) from the toluene-solvated reaction mixture when it was cooled to –20 °C for several days. M.p.: irreversible melt to a light-yellow oil, 128–132 °C; ¹H NMR ([D₈]THF): δ = 7.68 (d, 2H), 7.13 (d, 2H), 6.94 (t, 2H), 6.37 (t, 2H); ¹³C NMR ([D₈]THF, [D₅]pyridine) was precluded because of marginal solubility; IR (Nujol): $\tilde{\nu}$ = 3030 (w), 2918 (s), 1634 (w), 1578 (s), 1538 (s), 1458 (s), 1408 (s), 1377 (s), 1295 (m), 1132 (s), 1092 (s), 1076 (s), 1054 (m), 943 (s), 844 (m), 824 (m), 768 (s), 727 (s), 640 (w), 499 (w), 409 (m) cm⁻¹.

[Na(18C6)(NC₅H₄S-2)] (5): The pale-yellow toluene/THF-solvated reaction mixture produced colorless plates in 76% yield (0.30 g) after it was cooled to –20 °C for several days. M.p.: reversible melt to a tan oil, 115–120 °C; ¹H NMR ([D₈]THF): δ = 7.80 (d, 1H), 7.16 (d, 1H), 6.81 (t, 1H), 6.27 (t, 1H), 3.59 (s, 24H); ¹³C{¹H} ([D₈]THF) δ = 183.65, 147.92, 132.91, 129.85, 112.21, 71.07; IR (Nujol): $\tilde{\nu}$ = 2922 (s), 1573 (s), 1532 (s), 1465 (s), 1400 (s), 1377 (m), 1347 (s), 1282 (m), 1245 (m), 1104 (s), 964 (s), 839 (s), 752 (s), 727 (s), 622 (w), 528 (w), 492 (w), 444 (m), 410 (w) cm⁻¹.

[[Na(12C4)]₂][Na(NC₅H₄S-2)(thf)][Na(NC₅H₄μ-S-2)(NC₅H₄S-2)]₂ (6): Colorless plates formed in 55% yield (0.18 g) from a toluene/THF-solvated reaction mixture cooled to room temperature. M.p.: irreversible melt to a clear oil, 148–153 °C; ¹H NMR ([D₈]THF): δ = 7.73 (d, 8H), 7.16 (d, 8H), 6.83 (t, 8H), 6.28 (t, 8H), 3.61 (s, 128H); ¹³C{¹H} NMR ([D₈]THF): δ = 147.23, 132.83, 129.68, 112.08, 70.18; IR (Nujol): $\tilde{\nu}$ = 2921 (s), 1573 (m), 1553 (m), 1489 (m), 1465 (s), 1399 (m), 1377 (m), 1303 (w), 1287 (m), 1250 (m), 1167 (w), 1136 (m), 1121 (m), 1089 (s), 1021 (s), 975 (m), 921 (m), 850 (m), 771 (m), 724 (m), 626 (w), 557 (m), 442 (w), 416 (m) cm⁻¹.

[[K(μ-NC₅H₄μ-S-2)]₂][15C5]]_∞ (7): Colorless plates formed gradually in 39% isolated yield (0.10 g) from a THF-solvated reaction mixture over several days at room temperature. M.p.: shrinking above 160 °C, irreversible melt at 228–235 °C; ¹H NMR ([D₅]THF): δ = 7.75 d, 7.13 d, 6.73 t, 6.20 t, 3.62 s (integration was unreliable because of low solubility); ¹³C NMR ([D₅]THF, [D₅]pyridine) was precluded because of poor solubility; IR (Nujol): $\tilde{\nu}$ = 2920 (s), 1575 (s), 1530 (m), 1464 (m), 1436 (s), 1396 (s), 1377 (m), 1258 (m), 1122 (s), 1039 (w), 973 (m), 947 (m), 836 (w), 768 (s), 722 (m), 622 (w), 494 (m), 440 (m) cm⁻¹.

X-ray crystallographic studies: Crystals of X-ray quality were grown for all compounds as described above. They were removed from the Schlenk tube under a stream of N₂ and covered immediately with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope; it was attached to a glass fiber, and placed immediately in the low-temperature N₂ stream of the diffractometer.^[31] The intensity data sets for all compounds were collected utilizing a Siemens

SMART system, complete with three-circle goniometer and CCD detector operating at -54°C . Each data set was collected at -123°C using a Cryojet low-temperature device (Oxford Instruments) and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data collections nominally covered a hemisphere of reciprocal space by utilizing a combination of three groups of exposures, each with a different ϕ angle and each exposure covering 0.3° in ω . Crystal decay was monitored by repeating a set of initial frames at the end of the data collection and comparing the duplicate reflections; no decay was observed for any of the compounds reported. An absorption correction was applied by utilizing the program SADABS.^[32] The crystal structures of all the compounds were solved by direct methods (as included in the SHELXL program package). Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all the compounds were refined by full-matrix least-squares refinement on F^2 .^[33] Hydrogen atoms were placed geometrically and refined using a riding model and with U_{iso} constrained at 1.2 (for non-methyl groups) times U_{eq} of the carrier C atom. The crystallographic program used for structural refinement was installed on a Silicon Graphics Indigo² R10000 Solid Impact. Scattering factors were those provided by the SHELXL program.^[33] All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disordered thf positions in **6** were refined using split positions. Because of this disorder, high-angle data were very weak and were therefore suppressed.

Crystallographic parameters for compounds **1–7** are summarized in Table 1, and selected bond lengths and angles can be found in Table 2. Additional crystallographic data have been deposited with the CCDC.^[5]

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