Gillian Reid et al.
Neutral thioether and selenoether macrocyclic coordination to Group 1 cations (Li–Cs) – synthesis, spectroscopic and structural properties
Neutral thioether and selenoether macrocyclic coordination to Group 1 cations (Li–Cs) – synthesis, spectroscopic and structural properties†

Martin J. D. Champion, William Leveson, David Pugh and Gillian Reid*

The complexes [M(L)] [BArF] (BArF = tetrakis{3,5-bis(trifluoromethyl)-phenyl}borate, L = [18]aneO2S4 (1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane); M = Li–Cs; L = [18]aneO2S4 (1,10-dioxa-4,7,13,16-tetra-thiacyclooctadecane); M = Li, Na, K; L = [18]aneO2S2 (1,4,10,13-tetraoxa-7,16-dieiselenacyclooctadecane); M = Na, K, as well as [Na(18-crown-6)][BArF], are obtained in good yield as crystalline solids by reaction of M[BArF] with the appropriate macrocycle in dry CH2Cl2. X-ray crystallographic analyses of [Li(18-aneO2S2)][BArF] and [Li(18)aneO2S4][BArF] show discrete distorted octahedral cations with hexadentate coordination to the macrocycle. The heavier alkali metal complexes all contain hexadentate coordination of the heterocrown, supplemented by M⋯F interactions via the anions, producing extended structures with higher coordination numbers; Na: CN = 7 or 8; K: CN = 8; Rb: CN = 9; Cs: CN = 8 or 10. Notably, all of the structures exhibit significant M⋯S/Se coordination. The crystal structures of the potassium and rubidium complexes show two distinct [M(heterocrown)]+ cations, one with M⋯F interactions to two mutually cis [BArF]− anions, and the other with mutually trans [BArF]− anions, giving 1D chain polymers. Solution multinuclear (H, 13C, 7Li, 23Na, 133Cs) NMR data show that the macrocyclic coordination is retained in CH2Cl2 solution.

Introduction

Thioethers and selenoethers are soft, moderate σ-donor ligands with a high affinity for medium and low oxidation state transition metal ions in particular, whilst a significant body of work concerning high oxidation state early transition metals, f- and p-block acceptors has emerged over the last decade or so.1 In contrast, examples showing thioether or selenoether coordination towards the oxophilic s-block cations are extremely rare.2,4 Within Group 2, while there are no complexes with neutral acyclic thio- or seleno-ether coordination, a small number of examples containing Ca–S/Se and Sr–S/Se coordination, based upon 15- and 18-membered oxo-thia and oxaseleno macrocycles, have been reported recently.2,3 These include [CaI2(18)aneO2S4] and [MI2(18)aneO2E2] (M = Ca, Sr; E = S, Se; [18]aneO2S4 = 1,10-dioxa-4,7,13,16-tetra-thiacyclooctadecane, [18]aneO2S2 = 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane; [18]aneO2Se2 = 1,4,10,13-tetraoxa-7,16-dieiselenacyclooctadecane), all of which are eight-coordinate with the macrocycle hexadentate (d(Ca–S/Se) ~ 3.0 Å) and the iodides mutually cis. The lower lattice energies of the alkaline earth diiodides (MI2) compared to MCl2 or M(CF3SO3)2 etc., leads to MI2 being suitable metal sources for this chemistry due to their higher solubilities in non-competitive solvents.3

The lower charge : radius ratio of the Group 1 cations is expected to lead to considerably lower affinity of these cations for soft thio- or seleno-ether coordination. This is supported by early data on binding constants for alkali metal cations towards the oxa-thia analogues of 18-crown-6. Thus, the stability constant for K'/[18]aneO2S (1,4,7,10,13-pentaoxa-16-thiacyclooctadecane) and K'/[18]aneO2S2 are more than 105 and 106 times lower than for K'/18-crown-6, respectively, in methanol.3 Unsurprisingly therefore, well-characterised complexes of the Group 1 metals with similar soft donor ligands are extremely rare. There are no complexes with simple neutral acyclic thioethers, and only two prior examples with oxa-thia macrocycles, the K+ and Na+ cations with [18]aneO2S2 are structurally characterised. These are based upon lamellar halo-cuprate species, in which the K⋯S distances are 3.322(5)–3.496(4) Å

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.
E-mail: G.Reid@soton.ac.uk
†Additional Data Available: Original NMR spectra for all complexes are available (DOI: 10.5258/SOTON/380541) and can be downloaded via http://dx.doi.org/10.5258/SOTON/380541-. CCDC 1410981 [[Na(18-crown-6)][BArF]], 1410982 [[Li(18)aneO2S2]][BArF], 1410983 [[Na(18)aneO2S2]][BArF], 1410984 [[K(18)aneO2S2]][BArF], 1410985 [[Rb(18)aneO2S2]][BArF], 1410986 [[Cs(18)aneO2S2]][BArF], 1410987 [[Li(18)aneO2S4]][BArF], 1410988 [[Na(18)aneO2S4]][BArF], 1410989 [[K(18)aneO2S4]][BArF] and 1410990 [[K(18)aneO4Se2]][BArF]]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02583d
and Na–S = 3.11(1) Å, although the presence of Cu–S coordination in these structures clearly has a significant influence. We have exploited the high solubility of alkali metal salts with diffuse, weakly coordinating anions in weakly coordinating (non-competitive) solvents, as a source of ‘naked’ alkali metal cations, as a synthetic entry to promote their coordination towards soft, neutral donor ligands. Even so, it was surprising to us to find that this can lead to homoleptic octahedral coordination to Na⁺ in the macrocyclic complex [Na[24]aneS₈][BArF₄]. [24]aneS₈ = 1,4,7,10,13,16,19,22-octathiacylcotetraicosane; BArF = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate, containing distorted dodecahedral S₈-coordination at the sodium centre, with d(Na–S) = 2.9561(15)–3.0524(15) Å. DFT calculations suggested that the pre-organisation of the [24]aneS₈ macrocycle contributed to the successful isolation of this unique cation. Subsequently, using a similar approach we have also found that using even softer, neutral diphosphines with homoleptic Li⁺ and Na⁺ hexaphosphine cations in [Li(L)₃][BArF₄] (L = [18]aneO₄S₂, [18]aneO₄Se₂ and [18]aneO₂S₄) also present in the macrocycle ligands in one of the crystallographic independent cations in each of [Na(L)][BArF₄] complexes (L = [18]aneO₄S₂, [18]aneO₄Se₂ and [18]aneO₂S₄) and was modelled similarly. H-atoms were placed in geometrically-assignment positions with C−H distances of 0.95 Å (CH) or 0.98 Å (CH₃) and refined using a riding model with Uiso(H) = 1.2 Ueq(C). enClIFer was used to prepare material for publication.

**Experimental**

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove box techniques. [Li(thf)₄][BArF₄] and Na[BArF₄]·2thf were synthesised using a slight modification of the literature procedure. The lithium salt was isolated as [Li(OH)₂][BArF₄], which was converted to the thf adduct by stirring in thf for 16 h over 4 Å molecular sieves. Filtration and removal of solvents afforded the thf adduct. Crude Na[BArF₄] was recrystallised from thf/n-hexane to remove the last traces of coloured impurities, resulting in the isolation of Na[BArF₄]·2thf. K[BArF₄], Rb[BArF₄] and Cs[BArF₄] were synthesised via cation exchange of Na[BArF₄]·2thf in water at 95 °C with excess (5 mol equiv.) KN₃, RbNO₃ or CsNO₃, respectively. The macrocycles [18]aneO₄S₂, [18]aneO₄Se₂ and [18]aneO₂S₄ were prepared using literature procedures. 18-Crown-6 was purchased from Sigma and dried using SOCl₂. CH₂Cl₂ was dried by distillation from CaH₂ and n-hexane distilled from Na/K alloy. ¹H and ¹³C{¹H} NMR spectra were recorded in CD₂Cl₂ solution at 295 K using a Bruker AV II-400 spectrometer and are referenced to the residual CH₂Cl₂ resonance. ⁷Li, ²¹Na and ¹³³Cs NMR spectra were obtained in CH₂Cl₂ solution on a Bruker AV II-400 spectrometer at 298 K (unless otherwise stated) and referenced to a 0.1 mol dm⁻³ solution of LiCl, NaCl or CsNO₃ in D₂O, respectively. NMR properties: ⁷Li: I = 3/2, N = 92.6%, Rₑ = 1.54 × 10⁴, Q = −3.7 × 10⁻³⁰ m⁻³, Ξ = 38.87 MHz; ²¹Na: I = 3/2, N = 100%, Rₑ = 5.24 × 10⁵, Q = 0.10 × 10⁻²⁸, Ξ = 26.43; ¹³³Cs: I = 7/2, N = 100%, Rₑ = 2.69, Q = 5.5 × 10⁻³⁰, Ξ = 4.67; ⁸⁵Rb: I = 5/2, N = 72.1%, Rₑ = 43.4, Q = 0.25 × 10⁻²⁸, Ξ = 9.69; ¹³³Cs: I = 7/2, N = 100%, Rₑ = 2.75 × 10⁻³, Q = −0.3 × 10⁻³⁰, Ξ = 13.21. Microanalyses were undertaken at London Metropolitan University.

**X-ray crystallography**

The results were obtained as described below. Details of the crystallographic data collection and refinement are in Table 1. Diffrafractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator (λ = 0.71073 Å) with VHF Varimax optics (70 or 110 μm focus). Cell determination and data collection: CrystalClear-SM Expert 3.1 b27, data reduction, cell refinement, and absorption correction: CrystalClear-SM Expert 2.1 b29. Structure solution and refinement were carried out using Olex2 or WinGX and software packages within. Disorder in the CF₃ groups of the [BArF₄]⁻ anions was present in all of the structures, which is often observed in compounds containing [BArF₄]⁻, and this was satisfactorily modelled using DFIX, DANG, DELU and SIMU restraints. Positional disorder was also present in the macrocycle ligands in one of the crystallographically independent cations in each of [Na(L)][BArF₄] complexes (L = [18]aneO₄S₂, [18]aneO₄Se₂ and [18]aneO₂S₄) and was modelled similarly. H-atoms were placed in geometrically-assigned positions with C−H distances of 0.95 Å (CH) or 0.98 Å (CH₃) and refined using a riding model with Uiso(H) = 1.2Ueq(C).

**Preparations**

**General method.** M[BArF₄] was suspended in CH₂Cl₂ (10 mL) and a solution of the macrocyclic in CH₂Cl₂ (5 mL) was added. Complete dissolution occurred and the reaction was stirred for 16 h. After this time the solution was filtered, concentrated to ~3 mL and layered with n-hexane (20 mL) to form crystals. These were isolated by decanting away the supernatant and drying in vacuo. Specific details for individual complexes are below.

[Na(18-crown-6)][BArF₄]. Na[BArF₄]·2thf (50 mg, 0.05 mmol) and 18-crown-6 (13 mg, 0.1 mmol). Yield: 40 mg, 70%. Required for C₄₄H₃₆BF₂₄NaO₆ (1150.53): C, 45.93; H, 3.15. Found: C, 45.82; H, 2.97%. ¹H NMR (CD₂Cl₂): δ = 7.72 ([8H], br s, H₂/6), 7.57 ([4H], s, H₄), 6.34 ([24H], s, OCH₂). ¹³C{¹H} NMR (CD₂Cl₂): δ = 162.36 (C, q, J_C−F = 49.9 Hz, BArF C₁), 135.40 (CH, BArF C₂/6), 129.49 (C, qq, J_C−F = 31.6, 2.9 Hz, BArF C₃/5),
### Table 1  Crystallographic parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Li([(18)aneO(_4)S(_2)])[BAr(_F)]()</th>
<th>[Na([(18)aneO(_4)S(_2)])[BAr(_F)]()</th>
<th>[K([(18)aneO(_4)S(_2)])[BAr(_F)]()</th>
<th>[Rb([(18)aneO(_4)S(_2)])[BAr(_F)]()</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(\text{C}<em>{44}\text{H}</em>{36}\text{O}<em>{4}\text{BF}</em>{24}\text{Li}_2\text{S}_2)</td>
<td>(\text{C}<em>{44}\text{H}</em>{36}\text{O}<em>{4}\text{BF}</em>{24}\text{Li}_2\text{S}_2)</td>
<td>(\text{C}<em>{44}\text{H}</em>{36}\text{O}<em>{4}\text{BF}</em>{24}\text{Li}_2\text{S}_2)</td>
<td>(\text{C}<em>{44}\text{H}</em>{36}\text{O}<em>{4}\text{BF}</em>{24}\text{Li}_2\text{S}_2)</td>
</tr>
<tr>
<td>(M g) mol(^{-1})</td>
<td>1192.57</td>
<td>1198.72</td>
<td>1276.45</td>
<td>1284.77</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group (no.)</td>
<td>(Pbca)</td>
<td>(Pbca)</td>
<td>(Pbca)</td>
<td>(Pbca)</td>
</tr>
<tr>
<td>(a)/Å</td>
<td>17.974(5)</td>
<td>19.366(5)</td>
<td>22.558(4)</td>
<td>22.558(4)</td>
</tr>
<tr>
<td>(b)/Å</td>
<td>19.582(5)</td>
<td>20.743(5)</td>
<td>23.796(4)</td>
<td>23.796(4)</td>
</tr>
<tr>
<td>(c)/Å</td>
<td>28.567(7)</td>
<td>28.974(5)</td>
<td>33.018(7)</td>
<td>33.018(7)</td>
</tr>
<tr>
<td>(\alpha)/(^\circ)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta)/(^\circ)</td>
<td>95.618(4)</td>
<td>96.605(5)</td>
<td>96.605(5)</td>
<td>96.605(5)</td>
</tr>
<tr>
<td>(\gamma)/(^\circ)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>(\mu) (Mo-K(_{\alpha}))/mm(^{-1})</td>
<td>0.87</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.076</td>
<td>0.063</td>
<td>0.063</td>
<td>0.063</td>
</tr>
<tr>
<td>Goodness-of-fit on (R^2)</td>
<td>1.18</td>
<td>1.16</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>(R_1) [(I_o &gt; 2\sigma(I_o))]</td>
<td>0.127</td>
<td>0.118</td>
<td>0.127</td>
<td>0.127</td>
</tr>
<tr>
<td>(wR_2) [(I_o &gt; 2\sigma(I_o))]</td>
<td>0.155</td>
<td>0.118</td>
<td>0.155</td>
<td>0.155</td>
</tr>
</tbody>
</table>

**Note:** The values in the table represent crystallographic parameters for various molecular compounds. The table includes information on the formula, molecular weight, space group, atomic parameters, and various goodness-of-fit metrics. The data were collected using X-ray diffraction methods, and the crystal structures were refined using the CCP4 suite of programs. The crystallographic parameters are critical for understanding the molecular packing and crystal packing in these compounds, which can have implications for their physical and chemical properties.
125.20 (C, q, J_{C-F} = 272 Hz, CF_3), 118.08 (CH, septet, \frac{1}{2}J_{C-F} = 4.0 Hz, BAr^F C4), 69.19 (OCH_2). \text{Na NMR (298 K, CH_2Cl_2)}: \delta = -14.4.

[Li[18]aneO_{SO_2}]\[BAr^F]\). [Li[thf]][BAr^F]\) (116 mg, 0.1 mmol) and [18]aneO_{SO_2} (31 mg, 0.1 mmol). Yield: 75 mg of an off-white solid, 61%. Required for C_{44}H_{36}BF_{24}LiO_{2}S_{2} (1166.60): C, 45.30; H, 3.11. Found: C, 45.26; H, 3.13. \text{H NMR (CD_2Cl_2):} \delta = 7.73 ([8H], s, H2/6), 7.57 ([4H], s, H4), 3.68-3.73 ([16H], m, OCH_2), 2.83 ([8H], m, J = 5.7 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -14.4.

[Na[18]aneO_{SO_2}]\[BAr^F]\). [Na[thf]][BAr^F]\) (2thf) (100 mg, 0.1 mmol) and [18]aneO_{SO_2} (31 mg, 0.1 mmol). Yield: 55 mg, 44%. Required for C_{44}H_{36}BF_{24}NaO_{2}S_{2} (1182.64): C, 44.69; H, 3.07. Found: C, 44.55; H, 3.01%. \text{H NMR (CD_2Cl_2):} \delta = 7.72 ([8H], m, H2/6), 7.57 ([4H], m, H4), 3.68 (m, [16H], OCH_2), 2.84 ([8H], m, J = 5.0 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -0.07.

[Na[18]aneO_{SO_2}]\[BAr^F]\). [Na[thf]][BAr^F]\) (2thf) (100 mg, 0.1 mmol) and [18]aneO_{SO_2} (31 mg, 0.1 mmol). Yield: 55 mg, 44%. Required for C_{44}H_{36}BF_{24}NaO_{2}S_{2} (1182.64): C, 44.69; H, 3.07. Found: C, 44.55; H, 3.01%. \text{H NMR (CD_2Cl_2):} \delta = 7.72 ([8H], m, H2/6), 7.57 ([4H], m, H4), 3.68 (m, [16H], OCH_2), 2.84 ([8H], m, J = 5.0 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -0.07.

[K[18]aneO_{SO_2}]\[BAr^F]\). K[BAr^F] (45 mg, 0.05 mmol) and [18]aneO_{SO_2} (15 mg, 0.05 mmol). Yield: 25 mg, 38%. Required for C_{44}H_{36}BF_{24}K_{2}O_{2}S_{2} (1197.75): C, 44.09; H, 3.03. Found: C, 43.90; H, 3.12%. \text{H NMR (CD_2Cl_2):} \delta = 7.38 ([8H], s, H2/6), 7.57 ([4H], s, H4), 3.63-3.68 ([16H], m, OCH_2), 2.83-2.86 (m, each [4H], m, J = 6.0 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -0.07.

[Rb[18]aneO_{SO_2}]\[BAr^F]\). Rb[BAr^F] (95 mg, 0.1 mmol) and [18]aneO_{SO_2} (31 mg, 0.1 mmol). Yield: 97 mg of an off-white solid, 74%. Required for C_{44}H_{36}BF_{24}Rb_{2}SO_{2} (12415.62): C, 42.44; H, 2.91. Found: C, 42.34; H, 2.99%. \text{H NMR (CD_2Cl_2):} \delta = 7.73 ([8H], s, H2/6), 7.57 ([4H], m, H4), 3.61-3.68 ([16H], m, OCH_2), 2.81 ([8H], m, J = 5.1 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -0.07.

[Cs[18]aneO_{SO_2}]\[BAr^F]\). Cs[BAr^F] (100 mg, 0.1 mmol) and [18]aneO_{SO_2} (31 mg, 0.1 mmol). Yield: 91 mg of an off-white solid, 67%. Required for C_{44}H_{36}BF_{24}Cs_{2}O_{2}S_{2} (12925.56): C, 40.89; H, 2.81. Found: C, 40.72; H, 2.91%. \text{H NMR (CD_2Cl_2):} \delta = 7.72 ([8H], s, H2/6), 7.57 ([4H], s, H4), 3.65 ([8H], m, OCH_2), 3.62 ([8H], s, OCH_2), 2.81 ([8H], m, J = 5.1 Hz, SCH_3). \text{Li NMR (298 K, CH_2Cl_2)}: \delta = -0.07.

\text{Results and discussion}

Coordination of the Group 1 cations to a range of 18-membered oxo-thia and oxo-selena macrocyclic ligands was
achieved by the direct reaction of M[BArF] with the appropriate macrocycle in anhydrous CH₂Cl₂ solution (Scheme 1). The isolated complexes are highly soluble in CH₂Cl₂ and were obtained in good yield as white powders or colourless crystals. Their formulations were confirmed by microanalysis, solution ¹H, ¹³C(CH₃OH), ⁷Li, ²³Na and ¹³³Cs NMR spectroscopic data as appropriate, and by single crystal X-ray structure analysis. No solvent incorporation was evident in any of the products. The ¹H and ¹³C(CH₃OH) NMR spectra confirm a 1:1 ratio of the macrocycle and the [BArF]⁻ ion in each case, but were otherwise not very informative.

Lithium-7 NMR spectra recorded for [Li([18]aneO₄S₂)]⁺ and [Li([18]aneO₃S₂)]⁺ each contain a singlet, at +0.07 and +1.85 ppm respectively, i.e. very small differences from LiCl in water (δ = 0). This is not unexpected given the small chemical shift range observed for ⁷Li (typically ca. 15 ppm). For the sodium complexes, ²³Na NMR spectra (CH₂Cl₂) show a shift of the resonance to higher frequency as the S/Se donor atoms are introduced to the macrocycle (18-crown-6: −14.4 ppm; [18]aneO₄S₂: −1.9 ppm; [18]aneO₃Se₂: +2.3 ppm; [18]aneO₂S₄: +2.4 ppm). These chemical shifts compare with those for [Na-(1,4,7-trimethyl-1,4,7-triazacyclononane) and [Na(Me₄cyclam)- (thf)][BArF] (δ²³Na = +14.4 ppm; [18]aneO₄Se₂: +2.3 ppm). Small positive chemical shifts were also seen for [Na{Me₂P(CH₂)₂PMe₂}₃]⁺ and [Na{1,4,7,10-tetraazacyclododecane}. Small positive chemical shifts were also seen for [Na{Me₂P(CH₂)₂PMe₂}₃]⁺ and [Na{1,4,7,10-tetraazacyclododecane].

Table 2 Sum of the M–X radii for Group 1 cations with various relevant donor atoms

<table>
<thead>
<tr>
<th>M–X</th>
<th>X = O</th>
<th>X = S</th>
<th>X = Se</th>
<th>X = F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ(ionic + cov radii)</td>
<td>δ(vdW radii)</td>
<td>δ(ionic + cov radii)</td>
<td>δ(vdW radii)</td>
</tr>
<tr>
<td>M = Li</td>
<td>1.56</td>
<td>3.62</td>
<td>1.95</td>
<td>4.01</td>
</tr>
<tr>
<td>M = Na</td>
<td>1.98</td>
<td>4.00</td>
<td>2.37</td>
<td>4.39</td>
</tr>
<tr>
<td>M = K</td>
<td>2.31</td>
<td>4.23</td>
<td>2.70</td>
<td>4.54</td>
</tr>
<tr>
<td>M = Rb</td>
<td>2.41</td>
<td>4.71</td>
<td>2.80</td>
<td>5.10</td>
</tr>
<tr>
<td>M = Cs</td>
<td>2.54</td>
<td>4.98</td>
<td>2.93</td>
<td>5.37</td>
</tr>
</tbody>
</table>

* Ionic radii of Group 1 cations taken from ref. 21 and covalent radii for ligand donor atoms taken from ref. 22. † van der Waals radii taken from ref. 23. ‡ Based upon CN = 6. § Based upon CN = 8.
the CF$_3$ groups of the [BAR$_F^-$] anions in the structures, while the gross coordination at the metal and the ligand conformations are secure, care should be exercised in any detailed analyses of bond lengths and angles.

The crystal structure of [Li([18]aneO$_4$S$_2$)][BAR$_F$] comprises discrete cations (Fig. 1) and anions, with two of each in the asymmetric unit. Each Li cation is six-coordinate with the hexadentate macrocycle, leading to a severely distorted octahedral geometry. The Li–O and Li–S bond distances show a range of values, with d(Li–O) = 2.05(5) Å to 2.349(13) Å and d(Li–S) = 2.724(11) Å to 2.788(11) Å. The angles, S1–Li1–S2 = 75.4(4)° and S3–Li1–S4 = 111.3(4)°, whilst the angles involved in the five-membered chelate rings all vary between ~70–80°, indicating a significant degree of distortion from a regular octahedron. The irregularity of the coordination may in part reflect the poor size match of the 18-membered ring for the small Li$^+$ centre, coupled with the packing of the large [BAR$_F^-$] anions around the cations in the crystal lattice.

Substituting two further S donor atoms into the macrocyclic ring, as in [Li([18]aneO$_4$S$_2$)][BAR$_F$], also leads to a structure comprising of discrete cations and anions, with three crystallographically independent, but structurally similar, variants of each in the asymmetric unit. Each Li is six-coordinate, encapsulated by the macrocycle which is folded to accommodate a distorted octahedral geometry at lithium (Fig. 2). The distortion from ideal octahedral is significantly less than in the [18]aneO$_4$S$_2$ analogue above, and the conformation of the coordinated macrocycle has the ~S(CH$_2$)$_2$O(CH$_2$)$_2$S~ linkages occupying meridional coordination sites, placing the CCOC torsion angles anti. The Li–O and Li–S distances vary between the different cations, and are ~2.1 Å and ~2.6 Å, respectively. The latter appear to be slightly shorter than those in [Li([18]-aneO$_4$S$_2$)]$^+$ above.

The crystals of [Na([18]aneO$_4$S$_2$)][BAR$_F$] are isomorphous, but not isostructural, with their direct Li analogue, again with two crystallographically independent cations (the Na1-centred one of which is partly disordered, hence the structural description below is concerned with the Na2-centred cation) and two

![Fig. 1](image1.png)

![Fig. 2](image2.png)

![Fig. 3](image3.png)
anions in the asymmetric unit. In this case, the Na-macrocycle coordination is quite similar to that in the Li analogue, with $d$(Na–O) in the range 2.355(4)–2.395(4) Å and $d$(Na2–S) (2.849(2) and 2.890(2) Å) all somewhat elongated. This is a consequence of the larger ionic radius of the Na$^+$ centre, hence the ligand is less puckered, and the angles involved in the five-membered chelate rings span a narrower range ($\sim$71–74°), with $<S3$–Na2–S4 = 129.77(8)°. Notably in this species there is an additional weak interaction to one F atom derived from a CF$_3$ group in the anion, Na2⋯F26$^i$ = 3.306(3) Å (Fig. 3), leading to overall seven-coordination at the sodium centre through weakly associated ion pairs.

$[\text{Na}([18]\text{aneO}_4\text{Se}_2)]^{-}[\text{BARF}]$ crystallises with three crystallographically distinct cations (the Na3-centred cation shows some disorder and is therefore excluded from the structural description) and three [BARF]$^-$ anions in the asymmetric unit. The Na1 centre is seven-coordinate through a puckered hexadentate macrocycle and one long, weak Na⋯F interaction (this is of borderline significance based on our criteria stated above; however the corresponding distances in the Na2 and Na3-centred cations are slightly shorter) (Fig. 4), with a near planar O3Se donor set and the remaining donor atoms above and below that plane. Similar coordination environments are
present in the other cations, although there is a spread of bond distances, $d$(Na–O) = 2.315(7)–2.479(7), $d$(Na–Se) = 2.942(2)–2.986(4) Å. The latter are in line with the increased covalent radius of Se over S; otherwise the Na coordination environments are very similar to [Na[[18]aneO2S4]]BArF above.

The structure of [Na[[18]aneO2S4]]BArF is markedly different from its Li analogue above. It crystallises as a 1D chain polymer, with the Na in an eight-coordinate environment (Fig. 5a), and only one centrosymmetric cation and one anion (with crystallographic 2-fold symmetry) in the asymmetric unit. The macrocycle adopts a chair conformation with all four S atoms coordinated and the S4 donor set planar, $d$(Na–S) = 2.8823(6), 3.0718(7) Å, with the two oxygen atoms above and below that plane, $d$(Na–O) = 2.5526(13) Å. Two weak Na⋯F interactions (2.8766(13) Å) from bridging [BArF]$^-$ anions on opposite sides of the macrocycle give a distorted dodecahedral geometry overall at sodium, and give rise to the polymeric chain structure (Fig. 5b).

To provide a benchmark comparison for the mixed donor macrocyclic complexes in this work, we also prepared and determined the structure of [Na(18-crown-6)]BArF. The structure also shows a 1D chain polymer with eight-coordinate Na. There are two 50% occupancy (centrosymmetric) Na environments in the asymmetric unit, one of which (Na2-centred cation) shows severe rotational disorder of the macrocycle, while the other refines much better and is therefore the focus of the structural description and illustrated in Fig. 6a and b. The crown ether provides hexagonal planar coordination at Na, with irregular Na–O bond distances spanning >0.3 Å, and with a slightly puckered conformation as expected (<O–Na–O ~ 62–65°), with two axial Na⋯F interactions (2.435(4) Å), similar motifs are evident in other salts containing the sodium-18-crown-6 cation. The Na⋯F distances are very much shorter than in the mixed donor macrocyclic cations described above.

[K[[18]aneO2S4]]BArF is isostructural and isomorphous with [Na[[18]aneO2S4]]BArF described above, hence also forming a chain polymer with the K$^+$ in an eight-coordinate environment via the O2S4 donor set from the hexadentate macrocycle (endocyclic) and weak axial interactions to CF3 groups from the bridging [BArF]$^-$ anions (Fig. 7). All of the bond distances at K1 are elongated by ca. 0.1 Å compared to the Na analogue. This is less than expected based purely on the difference in the ionic radii of the metal ions (0.33 Å for
CN = 8), possibly reflecting a better size match between K⁺ and the [18]aneO₂S₄ binding cavity (although caution is required to avoid over-interpretation of such differences given that there is some disorder in the anion).

The structure of [K[[18]aneO₄S₂][BARF]] is formed of a 1D chain polymer with three crystallographically independent cations in the asymmetric unit (as well as three [BARF]⁻ anions). The K centres are eight-coordinate, through hexadentate endocyclic coordination of the macrocycle, with \(d(K-O) \approx 2.7\) Å and \(d(K-S) \approx 3.2\) Å, with two quite short K–F interactions (each \(\approx 2.7\) Å) completing the coordination environment (Fig. 8). The centrosymmetric K₁- and K₃-centred cations have significant K⋯F interactions on opposite sides of the macrocycle, while in the K₂-centred cation the K⋯F interactions lie mutually cis, and \(<S⁻K₂–S₂ = 154.90(6)°>\). Some puckering of the rings is evident from the angles subtended at K, which are all \(\approx 64°\).

[K[[18]aneO₄Se₂][BARF]] (Fig. 9) is isomorphous and isostructural with the tetraoxa-dithia analogue, and presents the first known complex containing potassium–selenoether coordination, \(d(K-Se) \approx 3.3\) Å.
The structure of \([\text{Rb[18}\text{aneO}_4\text{S}_2]\text{][BArF]}\) is also a 1D chain polymer, very similar to the K analogue, with the macrocycle hexadentate in each form of the cation, \(d(\text{Rb–S}) \sim 3.3\ \text Å\) (Fig. 10), although the crystal is not isomorphous. All the Rb–F distances are comparable to the Rb–O distances, indicating significant interactions that lie well within the sum of vdW radii. The geometry at Rb1 is higher than in the K analogue, as there are now three CF\(_3\) groups interacting with the Rb centre which appears to be ten-coordinate. The Rb2 (and Rb3: two half-occupancy centrosymmetric Rb centres in the asymmetric unit) are both 8-coordinate. The macrocycle donor set is closer to planar than in the K analogue.

Finally, the structure of \([\text{Cs[18}\text{aneO}_4\text{S}_2]\text{][BArF]}\) (Fig. 11) shows one cation and one anion in the asymmetric unit, and forms a 2D sheet polymer. The hexadentate macrocycle occupies one face of the Cs\(^+\) cation (Cs–S \sim 3.5\ \text Å\), with four CF\(_3\) groups (each from a different [BArF]\(^-\) anion) also coordinated through the other face, although the precise coordination at Cs cannot be confirmed due to disorder of the CF\(_3\) groups. There is also one longer Cs⋯F interaction through the centre of the macrocycle of \(\sim 4.2\ \text Å\).

The structure of \([\text{Rb[18}\text{aneO}_4\text{S}_2]\text{][BArF]}\) is also a 1D chain polymer, very similar to the K analogue, with the macrocycle hexadentate in each form of the cation, \(d(\text{Rb–S}) \sim 3.3\ \text Å\) (Fig. 10), although the crystal is not isomorphous. All the Rb–F distances are comparable to the Rb–O distances, indicating significant interactions that lie well within the sum of vdW radii. The geometry at Rb1 is higher than in the K analogue, as there are now three CF\(_3\) groups interacting with the Rb centre which appears to be ten-coordinate. The Rb2 (and Rb3: two half-occupancy centrosymmetric Rb centres in the asymmetric unit) are both 8-coordinate. The macrocycle donor set is closer to planar than in the K analogue.

Finally, the structure of \([\text{Cs[18}\text{aneO}_4\text{S}_2]\text{][BArF]}\) (Fig. 11) shows one cation and one anion in the asymmetric unit, and forms a 2D sheet polymer. The hexadentate macrocycle occupies one face of the Cs\(^+\) cation (Cs–S \sim 3.5\ \text Å\), with four CF\(_3\) groups (each from a different [BArF]\(^-\) anion) also coordinated through the other face, although the precise coordination at Cs cannot be confirmed due to disorder of the CF\(_3\) groups. There is also one longer Cs⋯F interaction through the centre of the macrocycle of \(\sim 4.2\ \text Å\).
nation numbers are observed in all of the other cations; Na: CN = 7 or 8; K: CN = 8; Rb: CN = 9; Cs: CN = 8 or 10.

Although unexpected, these M–S/Se interactions clearly make a favourable contribution to the stability of the cations since other conformations of the macrocycles with O-only coordination are possible.¹

Acknowledgements

We thank the EPSRC for supporting the SCFED project through a Programme Grant (EP/I033394/1). The SCFED Project (http://www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

References


11 (a) J. S. Bradshaw, J. Y. Hui, B. L. Haymore, J. J. Christensen and R. M. Izatt, J. Heterocycl. Chem., 1973, 10, 1; (b) J. S. Bradshaw, J. Y. Hui, Y. Chan, B. L. Haymore,

Fig. 11 The structure of the cation in [Cs(18]aneO4S2)][BARF] showing the interactions to fluoride from the anions, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cs1–O1 = 3.374(7), Cs1–O2 = 3.068(9), Cs1–O3 = 3.083(9), Cs1–O4 = 3.092(9), Cs1–S1 = 3.568(4), Cs1–S2 = 3.505(3), Cs1–F5 = 3.235(3), Cs1–F8 = 3.525(3), Cs1–F10 = 3.448(7), Cs1–F12 = 3.319(4), Cs1–F20i = 3.345(4), Cs1–F14iv = 4.27(2). Symmetry operations: (i) 1 – x, –0.5 + y, 1.5 – z; (ii) –0.5 + x, y, 1.5 – z; (iii) 1.5 – x, –0.5 + y, z; (iv) x, 0.5 – y, –0.5 + z.

Conclusions

We have isolated and fully characterised a series of alkali metal complexes (Li⁺ to Cs⁺) with soft, neutral thioether and selenoether coordination via saturated 18-membered oxa-thia and oxa-selena macrocycles, and containing the large, weakly coordinating [BARF]⁻ anion. There are no previously reported examples of lithium-, rubidium- or caesium-thioether coordination, and no Group 1 cation-selenaether complexes.

The solution stability of the Group 1 complex cations limits the information that can be obtained from spectroscopic studies on these complexes, hence we have determined their crystal structures to establish unequivocally the metal coordination environments present. The M–S and M–Se distances determined, together with the endocyclic conformations of the macrocycles in all of the new complexes (which contrast with the exocyclic conformations adopted by the metal-free macrocycles³,²⁴) are strongly indicative of significant, directional M–S/Se bonding interactions. Thus, in all the complexes reported, the macrocycle is hexadentate, while the flexibility of the saturated ring allows for very different degrees of ring puckering as the metal ion radius varies. Also notable, is the presence of M···Fbar– interactions of variable significance across all examples, except with the smallest Li⁺ cation. These contacts serve to fill available spaces in the metal coordination spheres. Hence, while discrete distorted octahedral cations with O₅S₂ and O₅S₄ donor sets are present in the Li⁺ salts, higher coordinations such as Li⁺····Fbar– are observed in the rubidium and caesium complexes.


