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 Levason, David Pugh and Gillian Reid*

The complexes [M(L)][BArF] (BArF = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate), L = [18]aneO4S2 (1,4,10,13-tetraoxa-7,16-dithiacyclododecane): M = Li–Cs; L = [18]aneO2S4 (1,10-dioxao-4,7,13,16-tetra-thiacyclododecane); M = Na, K; L = [18]aneO4Se2 (1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane): 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]aneO2Se2)][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 much rarer.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 oxathia and oxaseleno macrocycles, have been reported recently.2,3 These include [CaL([18]aneO2S2)] and [MlL([18]aneO2E2)] (M = Ca, Sr; E = S, Se; [18]aneO2S4 = 1,10-dioxao-4,7,13,16-tetraphenyl-2,5-thiacyclododecane; [18]aneO2Se2 = 1,4,10,13-tetraoxa-7,16-thiacyclopentadecane; [18]aneO4Se2 = 1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane), 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 (ML2) compared to MCl2 or M(CF3SO3)2, etc., leads to ML2 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]aneO2Se are more than 105 and 106 times lower than for K′/18-crown-6, respectively, in methanol.5 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 oxathia 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.
and Na–S = 3.11(1) Å, although the presence of Cu–S coordination in these structures clearly has a significant influence.4 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 octahedra coordination to Na+ in the macrocyclic complex [Na([24]aneS8)][BARF] ([24]aneS8 = 1,4,7,10,13,16,19,22-octacteylcyclocotracosane; BARF = tetakis(3,5-bis(trifluoromethyl)-phenyl)borate), containing distorted dodecahedral S-coordinate at the sodium centre, with d(Na–S) = 2.9561(15)–3.0524(15) Å.6 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 leads to coordination of neutral thioether functions to alkali metal cations, which demonstrate that coordination to Al{OC(CF3)3}4 and Na[BARF]·2thf were synthesised using a general method.8 The key role in the cyclisation reaction of thioether macrocycles via high dilution cyclisation reactions in dmf solution.8 The key role in the cyclisation reaction is the formation of a Cs+–thiolate ion pair, however, despite the widespread application of this procedure for thioether macrocycle formation, evidence of caesium–thioether coordination, i.e. following ring-closure, has remained elusive.

We report here the results of a systematic study of the preparation, spectroscopic and structural features of a series of complexes of the Group 1 cations with hexadentate, 18-membered ring macrocycles containing both hard (O) and soft (S, Se) donor functions, which demonstrate that coordination of neutral thioether functions to alkali metal cations is not limited to just sodium and potassium, but extends to examples with all five cations from Li+ to Cs+. We also report the first examples of neutral selenoether coordination to a Group 1 cation, including structural authentication for [M([18]-aneO4Se2)][BARF], M = Na and K.

**Experimental**

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove box techniques. [Li(thf)4][BARF] and Na[BARF]·2thf were synthesised using a slight modification of the literature procedure.9 The lithium salt was isolated as [Li(OH2)4][BARF], 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[BARF] was recrystallised from thf/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.

**Preparations**

**General method.** M[BARF] was suspended in CH2Cl2 (10 mL) and a solution of the macrocyle 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)][BARF].** Na[BARF]·2thf (50 mg, 0.05 mmol) and 18-crown-6 (13 mg, 0.1 mmol). Yield: 40 mg, 70%. Required for C44H44BF2NaO6 (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), 6.45 ([24H], s, OCH2). 13C{1H} NMR (CD2Cl2): δ = 162.36 (C, q, JCF = 49.9 Hz, BARF C1), 135.40 (CH, BARF C2/6), 129.49 (C, q, JCF = 31.6, 2.9 Hz, BARF C3/5), 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%, R = 1.54 × 104, Q = 3.7 × 10−30 m3, ξ = 38.87 MHz; 21Na: I = 3/2, N = 100%, R = 5.24 × 104, Q = 0.10 × 10−28, ξ = 26.43; 133Cs: I = 7/2, N = 100%, R = 2.69, Q = 5.5 × 10−30, ξ = 4.67; 85Rb: I = 5/2, N = 72.1%, R = 43.4, Q = 0.25 × 10−28, ξ = 9.69; 133Cs: I = 7/2, N = 100%, R = 2.75 × 107, Q = 0.3 × 10−30, ξ = 13.21.12 Microanalyses were undertaken at London Metropolitan University.

**X-ray crystallography**

We report here the results of a systematic study of the preparation, spectroscopic and structural features of a series of complexes of the Group 1 cations with hexadentate, 18-membered ring macrocycles containing both hard (O) and soft (S, Se) donor functions, which demonstrate that coordination of neutral thioether functions to alkali metal cations is not limited to just sodium and potassium, but extends to examples with all five cations from Li+ to Cs+. We also report the first examples of neutral selenoether coordination to a Group 1 cation, including structural authentication for [M([18]-aneO4Se2)][BARF], M = Na and K.
### Table 1 Crystallographic parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Li([18]aneO₂S₂)][Bar²]</th>
<th>[Na([18]aneO₂S₂)][Bar²]</th>
<th>[K([18]aneO₂S₂)][Bar²]</th>
<th>[Rub([18]aneO₂S₂)][Bar²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
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<td>C₄₄H₁₈B₂F₂NaO₂S₂</td>
<td>C₄₄H₁₈B₂R₁₂F₁₄K₂O₂S₂</td>
<td>C₄₄H₁₈B₂F₂RubO₂S₂</td>
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<tr>
<td>M/γ mol⁻¹</td>
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<td>11.685</td>
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<td>10.481(2)</td>
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<td>10.481(2)</td>
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</tr>
<tr>
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<tr>
<td>f(000)</td>
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<td>3624</td>
<td>3624</td>
<td>3624</td>
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<td>27 127</td>
<td>27 127</td>
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<tr>
<td>Rint</td>
<td>0.079</td>
<td>0.079</td>
<td>0.079</td>
<td>0.079</td>
</tr>
<tr>
<td>Goodness-of-fit on R²</td>
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<td>0.672 (all data)</td>
<td>0.672 (all data)</td>
<td>0.672 (all data)</td>
</tr>
<tr>
<td>wR² [I &gt; 2σ(I)]</td>
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<td>0.155</td>
<td>0.155</td>
<td>0.155</td>
</tr>
<tr>
<td>wR² (all data)</td>
<td>0.234</td>
<td>0.234</td>
<td>0.234</td>
<td>0.234</td>
</tr>
</tbody>
</table>

a Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ (max) = 27.5°. R = ∑|Fo| - |Fc|)/∑|Fo|; wR² = (∑w(Fo² - Fc²)²)1/2. |  | View Article Online  |  |  |
white solid, 63%. Required for C_{44}H_{36}BF_{24}LiO_{4}S_{2} (1198.72): C, 44.09; H, 3.03. Found: C, 44.00; H, 2.98%. \(^{1}H\) NMR (CDCl\(_{3}\)): \(\delta = 7.72\) ([8H], s, H2/6), 5.75 ([4H], s, H4), 3.70 ([8H], t, \(J = 5.5\) Hz, OCH2), 2.90 ([8H], s, SCH2), 2.82 ([8H], t, \(J = 5.5\) Hz, SCH2). \(^{13}C\) (H) NMR (CDCl\(_{3}\)): \(\delta = 162.35\) (C, q, J_{C-B} = 49.9 Hz, Barf\(^{\text{B}}\) C1), 135.39 (CH, Barf\(^{\text{B}}\) C2/6), 129.47 (C, qq, J_{C-F} = 31.6, 2.9 Hz, Barf\(^{\text{B}}\) C3/5), 125.20 (C, q, J_{C-F} = 272 Hz, C\(_{F}\)), 118.07 (CH, septr, J_{C-F} = 4.0 Hz, Barf\(^{\text{B}}\) C4), 69.06 (OCH2), 31.54, 31.03 (SCH2). \(^{7}Li\) NMR (298 K, CH\(_{3}\)Cl\(_{2}\)): \(\delta = +1.85\).

**[Na[18]aneO\(_{3}\)S\(_{2}][BF_{4}]]**. \(^{11}B\) (298 K, 0.1 mmol). Yield: 86 mg, 65%. Required for C_{44}H_{36}BF_{24}NaO_{4}S_{2} (1214.76): C, 43.51; H, 2.99. Found: C, 43.57; H, 2.87%. \(^{1}H\) NMR (CDCl\(_{3}\)): \(\delta = 7.72\) ([8H], br s, H2/6), 7.57 ([4H], s, H4), 3.74 ([8H], t, \(J = 6.0\) Hz, OCH2), 2.89 ([8H], s, SCH2), 2.80 ([8H], t, \(J = 6.0\) Hz, SCH2). \(^{13}C\) (H) NMR (CDCl\(_{3}\)): \(\delta = 162.34\) (C, q, J_{C-B} = 49.9 Hz, Barf\(^{\text{B}}\) C1), 135.40 (CH, Barf\(^{\text{B}}\) C2/6), 129.46 (C, qq, J_{C-F} = 31.6, 2.9 Hz, Barf\(^{\text{B}}\) C3/5), 125.21 (C, q, J_{C-F} = 272 Hz, C\(_{F}\)), 118.07 (CH, septr, J_{C-F} = 4.0 Hz, Barf\(^{\text{B}}\) C4), 68.87 (OCH2), 31.58, 30.61 (SCH2). \(^{23}Na\) NMR (298 K, CH\(_{3}\)Cl\(_{2}\)): \(\delta = +2.4\).

**[K[18]aneO\(_{3}\)S\(_{2}][BF_{4}]]**. \(^{11}B\) (45 mg, 0.05 mmol) and [18]aneO\(_{3}\)S\(_{2}\\(\text{16 mg, 0.05 mmol}) ) Yield: 41 mg of an off-white solid, 67%. Required for C_{44}H_{36}BF_{24}K\(_{2}\)O\(_{4}\)S\(_{2}\) (1230.87): C, 42.94; H, 2.95. Found: C, 42.86; H, 2.89%. \(^{1}H\) NMR (CDCl\(_{3}\)): \(\delta = 7.72\) ([8H], s, H2/6), 7.57 ([4H], s, H4), 3.72 ([8H], t, \(J = 5.1\) Hz, OCH2), 2.89 ([8H], s, SCH2), 2.84 ([8H], t, \(J = 5.1\) Hz, SCH2). \(^{13}C\) (H) NMR (CDCl\(_{3}\)): \(\delta = 162.34\) (C, q, J_{C-B} = 49.9 Hz, Barf\(^{\text{B}}\) C1), 135.41 (CH, Barf\(^{\text{B}}\) C2/6), 129.46 (C, qq, J_{C-F} = 31.6, 2.9 Hz, Barf\(^{\text{B}}\) C3/5), 125.20 (C, q, J_{C-F} = 272 Hz, C\(_{F}\)), 118.08 (CH, septr, J_{C-F} = 4.0 Hz, Barf\(^{\text{B}}\) C4), 68.94 (OCH2), 31.75 (SCH2). \(^{23}Na\) NMR (298 K, CH\(_{3}\)Cl\(_{2}\)): \(\delta = +2.3\).

**[K[18]aneO\(_{3}\)Se\(_{2}][BF_{4}]]**. \(^{11}B\) (45 mg, 0.05 mmol) and [18]aneO\(_{3}\)Se\(_{2}\\(\text{16 mg, 0.05 mmol}) ) Yield: 71 mg, 56%. Required for C_{44}H_{36}BF_{24}NaO\(_{4}\)Se\(_{2}\) (1276.64): C, 41.40; H, 2.84. Found: C, 41.29; H, 2.74%. \(^{1}H\) NMR (CDCl\(_{3}\)): \(\delta = 7.72\) ([8H], br s, H2/6), 7.57 ([4H], s, H4), 3.70 ([16H], m, OCH2), 2.86 ([8H], t, \(J = 6.0\) Hz, SeCH2). \(^{13}C\) (H) NMR (CDCl\(_{3}\)): \(\delta = 162.35\) (C, q, J_{C-B} = 49.9 Hz, Barf\(^{\text{B}}\) C1), 135.41 (CH, Barf\(^{\text{B}}\) C2/6), 129.49 (C, qq, J_{C-F} = 31.6, 2.9 Hz, Barf\(^{\text{B}}\) C3/5), 125.20 (C, q, J_{C-F} = 272 Hz, C\(_{F}\)), 118.08 (CH, septr, J_{C-F} = 4.0 Hz, Barf\(^{\text{B}}\) C4), 68.94, 68.54 (OCH2), 34.45 (SeCH2). \(^{23}Na\) NMR (298 K, CH\(_{3}\)Cl\(_{2}\)): \(\delta = +2.0\).

**[K[18]aneO\(_{3}\)Se\(_{2}][BF_{4}]]**. \(^{11}B\) (45 mg, 0.05 mmol) and [18]aneO\(_{3}\)Se\(_{2}\\(\text{19 mg, 0.05 mmol}) ) Yield: 47 mg, 79%. Required for C_{44}H_{36}BF_{24}K\(_{2}\)O\(_{4}\)Se\(_{2}\) (1292.55): C, 40.89; H, 2.81. Found: C, 40.93; H, 2.69%. \(^{1}H\) NMR (CDCl\(_{3}\)): \(\delta = 7.72\) ([8H], br s, H2/6), 7.57 ([4H], s, H4), 3.74 ([8H], t, \(J = 6.0\) Hz, OCH2), 2.89 ([8H], s, SCH2), 2.80 ([8H], t, \(J = 6.0\) Hz, SCH2). \(^{13}C\) (H) NMR (CDCl\(_{3}\)): \(\delta = 162.32\) (C, q, J_{C-B} = 49.9 Hz, Barf\(^{\text{B}}\) C1), 135.41 (CH, Barf\(^{\text{B}}\) C2/6), 129.46 (C, qq, J_{C-F} = 31.6, 2.9 Hz, Barf\(^{\text{B}}\) C3/5), 125.20 (C, q, J_{C-F} = 272 Hz, C\(_{F}\)), 118.07 (CH, septr, J_{C-F} = 4.0 Hz, Barf\(^{\text{B}}\) C4), 70.80, 69.89 (OCH2), 24.76 (SeCH2).

**Results and discussion**

Coordination of the Group 1 cations to a range of 18-membered oxa-thia and oxa-selena macrocyclic ligands was...
achieved by the direct reaction of M[BArF] with the appropriate macrocycle in anhydrous CH\textsubscript{2}Cl\textsubscript{2} solution (Scheme 1). The isolated complexes are highly soluble in CH\textsubscript{2}Cl\textsubscript{2} and were obtained in good yield as white powders or colourless crystals. Their formulations were confirmed by microanalysis, solution 1\textsuperscript{H}, 1\textsuperscript{3}C\textsuperscript{(1}H), 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 1\textsuperscript{H} and 1\textsuperscript{3}C\textsuperscript{(1}H) NMR spectra confirm a 1:1 ratio of the macrocycle and the [BArF]\textsuperscript{–} anion in each case, but were otherwise not very informative.

Lithium-7 NMR spectra recorded for [Li[[18]aneO\textsubscript{2}S\textsubscript{2}]]\textsuperscript{+} and [Li[[18]aneO\textsubscript{2}S\textsubscript{2}]]\textsuperscript{+} 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).\textsuperscript{12} For the sodium complexes, 23Na NMR spectra (CH\textsubscript{2}Cl\textsubscript{2}) 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]aneO\textsubscript{2}S\textsubscript{2}: −1.9 ppm; [18]aneO\textsubscript{2}Se\textsubscript{2}: +2.3 ppm; [18]aneO\textsubscript{3}S\textsubscript{2}: +2.4 ppm). These chemical shifts compare with those for [Na-

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>
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<tbody>
<tr>
<td></td>
<td>∑(ionic + cov radii)\textsuperscript{a}</td>
<td>∑(vdW radii)\textsuperscript{b}</td>
<td>∑(ionic + cov radii)\textsuperscript{a}</td>
<td>∑(vdW radii)\textsuperscript{b}</td>
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<td>M = Li\textsuperscript{c}</td>
<td>1.56</td>
<td>3.62</td>
<td>1.95</td>
<td>4.01</td>
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<td>4.00</td>
<td>2.37</td>
<td>4.39</td>
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<td>M = K\textsuperscript{d}</td>
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<td>2.70</td>
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</tr>
<tr>
<td>M = Rb\textsuperscript{d}</td>
<td>2.41</td>
<td>4.71</td>
<td>2.80</td>
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<tr>
<td>M = Cs\textsuperscript{d}</td>
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<td>4.98</td>
<td>2.93</td>
<td>5.37</td>
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</table>

\textsuperscript{a} Ionic radii of Group 1 cations taken from ref. 21 and covalent radii for ligand donor atoms taken from ref. 22. \textsuperscript{b} van der Waals radii taken from ref. 23. \textsuperscript{c} Based upon CN = 6. \textsuperscript{d} Based upon CN = 8.
the CF₃ groups of the [BARF]⁻ 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]aneO₄S₂)][BARF] 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) = 2.055(12) to 2.349(13) Å and d(Li–S) = 2.724(11) to 2.788(11) Å. The angles, S₁–Li₁–S₂ = 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 [BARF]⁻ anions around the cations in the crystal lattice.

Substituting two further S donor atoms into the macrocyclic ring, as in [Li([18]aneO₄S₃)][BARF], 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 of the ideal octahedron is significantly less than in the [Li([18]aneO₂S₂)][BARF] analogue above, and the conformation of the coordinated macrocycle has the −S(CH₂)₂O(CH₂)₂S− 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]aneO₄S₂)]⁺ above.

The crystals of [Na([18]aneO₄S₂)][BARF] 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 The structure of the Li₁-centred cation in [Li([18]aneO₄S₂)][BARF] with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The Li₂ cation adopts a similar geometry, with some variation in the bond distances and angles. Selected bond lengths (Å) and angles (°): Li₁–O4 = 2.055(12), Li₁–O2 = 2.094(12), Li₁–O3 = 2.150(13), Li₁–O1 = 2.349(13), Li₁–S1 = 2.745(12), Li₁–S2 = 2.761(11), O4–Li₁–O3 = 78.5(5), O2–Li₁–O1 = 75.4(4), O4–Li₁–S1 = 81.2(4), O2–Li₁–S1 = 71.7(3), O2–Li₁–S2 = 77.7(4), O3–Li₁–S2 = 75.2(4), S1–Li₁–S2 = 106.2(4).

![Fig. 2 The structure of the Li₁-centred cation in [Li([18]aneO₄S₂)][BARF] with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Li₁–O2 = 2.082(18), Li₁–O1 = 2.118(18), Li₁–S3 = 2.539(16), Li₁–S1 = 2.573(16), Li₁–S2 = 2.593(16), Li₁–S4 = 2.604(15), O2–Li₁–S3 = 80.9(6), O1–Li₁–S1 = 82.1(6), O2–Li₁–S2 = 84.2(6), S1–Li₁–S2 = 81.5(4), O1–Li₁–S4 = 79.9(5), S3–Li₁–S4 = 85.6(5).

![Fig. 3 The structure of the Na₂-centred cation in [Na([18]aneO₄S₂)][BARF] showing the interaction to a fluoride from the anion, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Na₂–O5 = 2.389(4), Na₂–O6 = 2.355(4), Na₂–O7 = 2.394(4), Na₂–O8 = 2.395(4), Na₂–F26 = 3.306(3), Na₂–S3 = 2.849(2), Na₂–S4 = 2.890(2), O6–Na₂–O5 = 71.64(12), O7–Na₂–O8 = 71.55(12), O5–Na₂–S3 = 72.14(10), O8–Na₂–S3 = 73.73(10), O6–Na₂–S4 = 73.64(10), O7–Na₂–S4 = 70.74(9), S3–Na₂–S4 = 129.77(8). Symmetry operation: (i) −1 + x, −1 + y, z.
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$71–74$^\circ$), with $<S3$–Na2–S4 = 129.77(8)$^\circ$. Notably in this species there is an additional weak interaction to one F atom derived from a CF$_3$ group in the anion, Na2⋯F26i = 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

**Fig. 4** The structure of the Na1-centred cation in $[\text{Na}([18]\text{aneO}_4\text{Se}_2)]^{-} [\text{BArF}^{-}]$ showing the interaction to fluoride from the anion, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Na1–O3 = 2.332(7), Na1–O1 = 2.380(7), Na1–O4 = 2.393(6), Na1–O2 = 2.396(7), Na1–S1 = 2.942(3), Na1–S2 = 2.967(3), Na1⋯F5 = 3.50(1), O3–Na1–O1 = 2.967(3), O1–Na1⋯S1 = 71.9(2), O1–Na1⋯S2 = 74.90(18), O4–Na1⋯Se1 = 73.16(17), O3–Na1⋯Se2 = 74.54(17), O2–Na1⋯Se2 = 71.74(16), Se1–Na1⋯Se(2) = 121.13(13).

**Fig. 5** (a) The structure of the centrosymmetric Na1-centred cation in $[\text{Na}([18]\text{aneO}_2\text{S}_4)]^{-} [\text{BArF}^{-}]$ showing the interactions to fluorides from the anions, with ellipsoids drawn at the 50% probability level. The other crystallographically independent cation adopts a similar structure. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Na1⋯F1 = 2.8766(13), Na1–O1 = 2.5526(13), Na1–S1 = 2.8766(13), Na1–S2 = 3.0718(7), O1–Na1⋯S1 = 67.26(3), O1–Na1⋯S2 = 66.22(3), S1–Na1⋯S2 = 69.427(14), O1–Na1⋯Se1 = 74.90(18), O4–Na1⋯Se1 = 73.16(17), O3–Na1⋯Se2 = 74.54(17), O2–Na1⋯Se2 = 71.74(16), Se1–Na1⋯Se(2) = 121.13(13). (b) View of a portion of the polymeric chain with the [BArF]$^{-}$ anions greyed out for clarity. Colour key: gold = Na, yellow = S, red = O, green = F, black = C.
present in the other cations, although there is a spread of bond distances, $d(\text{Na–O}) = 2.315(7)$–$2.479(7)$, $d(\text{Na–Se}) = 2.942(2)$–$2.986(4)$ Å. The latter are in line with the increased covalent radius of Se over S; otherwise the Na coordination environments are very similar to $[\text{Na}([18]\text{aneO}_2\text{S}_4)][\text{BAR}^\text{F}]$ above.

The structure of $[\text{Na}([18]\text{aneO}_2\text{S}_4)][\text{BAR}^\text{F}]$ 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 $S_4$ donor set planar, $d(\text{Na–S}) = 2.8823(6)$, 3.0718(7) Å, with the two oxygen atoms above and below that plane, $d(\text{Na–O}) = 2.5526(13)$ Å. Two weak Na···F interactions (2.8766(13) Å) from bridging $[\text{BAR}^\text{F}]^-$ 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 $[\text{Na}(18\text{-crown-6})][\text{BAR}^\text{F}]$. 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.

$[\text{K}([18]\text{aneO}_2\text{S}_4)][\text{BAR}^\text{F}]$ is isostructural and isomorphous with $[\text{Na}([18]\text{aneO}_2\text{S}_4)][\text{BAR}^\text{F}]$ described above, hence also forming a chain polymer with the K$^+$ in an eight-coordinate environment via the $O_2S_4$ donor set from the hexadentate macrocycle (endocyclic) and weak axial interactions to CF$_3$ groups from the bridging $[\text{BAR}^\text{F}]^-$ 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 \(d(K-O) \approx 2.7\ \text{Å}\) and \(d(K-S) \approx 3.2\ \text{Å}\), with two quite short K–F interactions (each \(\approx 2.7\ \text{Å}\)) 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 \(\angle S3-K2-S2 = 154.90(6)°\). 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, \(d(K-\text{Se}) \approx 3.3\ \text{Å}\).

![Fig. 7](image7.png)

**Fig. 7** View of the structure of the K1-centred cation in [K[[18]aneO₂S₂][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 (°): K1–O1 = 2.6253(18), K1⋯F7 = 2.9589(19), K1–S1 = 3.0445(8), K1–S2 = 3.1399(8), O1–K1–S1 = 65.74(4), O1–K1–S2 = 65.98(4), S1’–K1–S2 = 68.880(19). Symmetry operation: (i) −0.5 − x, 0.5 − y, −z.

![Fig. 8](image8.png)

**Fig. 8** The structures of (a) the K1-centred cation and (b) the K2-centred cation in the asymmetric unit of [K[[18]aneO₂S₂][BARF]], showing the interaction to fluoride from the anions, with ellipsoids drawn at the 50% probability level. The K3-centred cation is very similar to the K1-centred cation. Hydrogen atoms are omitted for clarity. The macrocycle around K1 is disordered positionally (up/down) around O2 with an occupancy split of roughly 3:2; the major component is shown. Selected bond lengths (Å) and angles (°): K1⋯F1 = 2.744(3), K1⋯S1 = 3.2163(12), K1⋯O1 = 2.703(3), K1⋯O2A = 2.7067(7), K2⋯F7 = 2.690(6), K2⋯F5 = 2.733(3), K2⋯S2 = 3.2119(15), K2⋯S3 = 3.2075(16), K2⋯O5 = 2.709(5), K2⋯O3 = 2.731(5), K2⋯O4 = 2.744(3), K2⋯O6 = 2.750(3), S3⋯K2⋯S2 = 154.90(6). Symmetry operation: (i) 1 − x, 1 − y, −z. (c) View of a portion of the polymer chain with the [BARF]⁻ anions greyed out for clarity. Colour key: blue = K, yellow = S, red = O, green = F, black = C.
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, \(d(\text{Rb}–\text{S}) \sim \) 3.3 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 CF3 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 Å), with four CF3 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 CF3 groups. There is also one longer Cs⋯F interaction through the centre of the macrocycle of \sim 4.2 Å.

The structure of \([\text{K}[18\text{aneO}_4\text{Se}_2]][\text{BARF}^+]\) is also a 1D chain polymer, very similar to the K analogue, with the macrocycle hexadentate in each form of the cation, \(d(\text{K}–\text{Se}) \sim \) 3.3 Å (Fig. 9), although the crystal is not isomorphous. All the K–O distances are comparable to the K–S distances, indicating significant interactions that lie well within the sum of vdw radii. The geometry at K1 is higher than in the K analogue, as there are now two CF3 groups interacting with the K centre which appears to be nine-coordinate. The K2 (and K3: two half-occupancy centrosymmetric K centres in the asymmetric unit) are both 8-coordinate. The macrocycle donor set is closer to planar than in the K analogue.

### Figures

**Fig. 9** The structures of the K1- and K2-centred cations in the asymmetric unit for \([\text{K}[18\text{aneO}_4\text{Se}_2]][\text{BARF}^+]\) showing the interactions to fluoride from the anions, with ellipsoids drawn at the 50% probability level. The K3-centred cation is very similar to the former. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): K1–O1 = 2.663(4), K1–O2 = 2.686(4), K1–F1 = 2.714(4), K1–Se1 = 3.3123(7), K2–O3 = 2.712(5), K2–O4 = 2.734(4), K2–O5 = 2.642(17), K2–O6 = 2.757(5), K2–F7 = 3.040(9), K2–F25 = 2.674(8), K2–Se2 = 3.3065(13), K2–Se3 = 3.307(4). Symmetry code: (i) \text{−}x, \text{−}y, 1\text{−}z.

**Fig. 10** The structures of the two independent cations in \([\text{Rb}[18\text{aneO}_4\text{S}_2]][\text{BARF}^+]\) 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 (°): Rb1–O1 = 2.944(3), Rb1–O2 = 3.026(3), Rb1–O3 = 2.981(3), Rb1–O4 = 3.030(7), Rb1–S1 = 3.35564(12), Rb1–S2 = 3.2897(13), Rb1–F7 = 2.965(3), Rb1–F8 = 3.269(2), Rb1–F37 = 3.249(2), Rb1–F44 = 3.269(2), Rb2–O5 = 2.901(3), Rb2–O6 = 2.907(2), Rb2–O7 = 3.2690(12), Rb1–F7 = 2.965(3), Rb1–F8 = 3.269(2), Rb1–F37 = 3.249(2), Rb1–F44 = 3.269(2), Rb2–O5 = 2.901(3), Rb2–O6 = 2.907(2), Rb2–O7 = 3.2690(12), Rb2–F23 = 2.818(7); O1–Rb1–O2 = 56.427, S2–Rb1–S1 = 146.623, O2–Rb1–S2 = 58.987, O3–Rb1–O4 = 57.341, O4–Rb1–S1 = 58.251, O1–Rb1–S1 = 57.997, O3–Rb1–S2 = 58.106, O5–Rb2–O6 = 59.109, O5–Rb2–S3 = 62.336, O6–Rb2–S3 = 61.726. Symmetry operation: (i) \text{−}x, \text{−}y, \text{−}z.
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.

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