

Trivalent scandium, yttrium and lanthanide complexes with thia-oxa and seleno-oxa macrocycles and crown ether coordination†

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Complexes of the oxa-thia macrocycles [18]aneO₄S₂, [15]aneO₃S₂ and the oxa-selena macrocycle [18]aneO₄Se₂ (L) of types [MCl₂(L)]FeCl₄ (M = Sc or Y) were prepared from [ScCl₃(thf)₃] or [YCl₂(THF)₅][YCl₄(THF)₂] and the ligand in anhydrous MeCN, using FeCl₃ as a chloride abstractor. The [MI₂(L)]I, [La₃(L)] and [Lu₂(L)]I have been prepared from the ligands and the appropriate anhydrous metal triiodide in MeCN. Complexes of type [La₃(crown)] and [Lu₂(crown)]I (crown = 18-crown-6, 15-crown-5) were made for comparison. Use of the metal iodide results in complexes with high solubility compared to the corresponding chlorides, although also with increased sensitivity to moisture. All complexes were characterised by microanalysis, IR, ¹H, ⁴⁵Sc and ⁷⁷Se NMR spectroscopy as appropriate. X-ray crystal structures are reported for [ScCl₂([18]aneO₄S₂)]FeCl₄, [ScCl₂([18]aneO₄S₂)]I, [YCl₂(18-crown-6)]₃[Y₂Cl₉], [YCl₂([18]aneO₄S₂)]FeCl₄, [La₃(15-crown-5)], [La₂(18-crown-6)(MeCN)]I, [Lu(18-crown-6)(MeCN)]₂I₂, [Lu(15-crown-5)(MeCN)₂(OH₂)]₃, [La₃([18]aneO₄S₂)], [La([18]aneO₄S₂)(OH₂)]₂I₂, [La₃([18]aneO₄Se₂)] and [Lu₂([18]aneO₄Se₂)]I. In each complex all the neutral donor atoms of the macrocycles are coordinated to the metal centre, showing very rare examples of these oxophilic metal centres coordinated to thioether groups, and the first examples of coordinated selenoether donors. In some cases MeCN or adventitious water displaces halide ligands, but *not* the S/Se donors from La or Lu complexes. A complex of the oxa-tellura macrocycle [18]aneO₄Te₂, [ScCl₂([18]aneO₄Te₂)]FeCl₄ was isolated, but is unstable in MeCN solution, depositing elemental Te. YCl₃ and 18-crown-6 produced [YCl₂(18-crown-6)]₃[Y₂Cl₉], the asymmetric unit of which contains two cations with a *trans*-YCl₂ arrangement and a third with a *cis*-YCl₂ group.

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Introduction

The coordination chemistry of the trivalent lanthanides is characterised by an affinity for small hard donor ligands – preferably charged anions such as F[−], O^{2−}, OH[−], OR[−] or NO₃[−], or polydentate nitrogen or oxygen donor ligands.¹ The bonding is usually described as predominantly ionic or highly polar ion-dipole in nature, the complexes often have high coordination numbers reflecting the large ion size (ionic radii in 6-coordination La³⁺ 1.22 Å–Lu³⁺ 0.85 Å) and are labile in solution. Yttrium(III) chemistry closely resembles that of the later

lanthanides, not least due to its similar ionic radius (1.04 Å). Scandium is also exclusively trivalent, but smaller (Sc³⁺ 0.74 Å), and thus often favours a lower coordination number. The structural chemistry of lanthanide†-crown ether complexes has been summarised in review articles.^{1,2} Typically the crown is coordinated to the lanthanide by all of the O-donors, with additional coordination of anions, water or donor solvent completing high (commonly eight- or nine-) coordination. Representative examples of crown ether complexes are Sc,^{3,4} Y,^{5–7} La–Lu.^{7–11} Examples with softer donors are rare, and although Ln–S or Ln–Se bonds are known, they are almost all of anionic thiolate (SR[−]) or selenolate (SeR[−]) groups.^{1,12,13} Neutral lanthanide-thioether links were reported in [Ln'I₃([9]aneS₃)(MeCN)₂][[9]aneS₃ = 1,4,7-trithiacyclonane, Ln' = La or Ce) obtained from anhydrous MeCN solution, which contain eight-coordinate metal centres,¹⁴ and [La([18]aneO₄S₂)(OH₂)(κ¹-ClO₄)(κ²-ClO₄)]ClO₄ ([18]aneO₄S₂ = 1,4,10,13-tetraoxa-7,16-dithia-cyclooctadecane) with contains ten-coordinate La with an O₈S₂

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†Electronic supplementary information (ESI) available: A table of crystallographic parameters. Synthesis and spectroscopic data for the (18-crown-6) and 15-crown-5 halide complexes of La, Lu, Ce or Nd discussed in the main text and for [La(O₃SCF₃)₂(18-crown-6)][O₃SCF₃]. Figure and selected bond length and angle data for the cation in [CeI₂(18-crown-6)(MeCN)]I·*n*MeCN, and for [Y₃Cl₉]^{3−} anion in [YCl₂(18-crown-6)]₃[Y₂Cl₉]. CCDC 940218–940229. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51405f

†“Lanthanide” also includes Y and Sc in this general discussion.



donor set.¹⁵ A few related complexes of [18]aneO₄S₂ and of [18]aneO₂S₄ (1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane) have been described but with little data and they lack X-ray crystallographic authentication.¹⁵ We have recently reported complexes of thia-oxa and seleno-oxa macrocycles with p-block metals and metalloids, including Pb(II),¹⁶ Sb(III),¹⁷ or Ge(II)¹⁸ and notably, some s-block complexes of Ca(II) and Sr(II).¹⁹ Under rigorously anhydrous conditions, reaction of MI₂ with the ligands [18]aneO₄S₂ or [18]aneO₄Se₂ (1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane) in MeCN produces [MI₂(ligand)] (M = Ca or Sr, ligand = [18]aneO₄S₂, [18]aneO₄Se₂) which contain eight-coordinate metal centres (O₄Se/S₂I₂). Most unexpectedly, exposure of these complexes to trace amounts of water, resulted in displacement of the iodide ligands rather than the soft donors, to give, for example, the structurally authenticated [Sr([18]aneO₄Se₂)(H₂O)₃]₂. These results suggested that thia-oxa and seleno-oxa macrocycles may support a range of coordination environments on other hard metal centres, and thus we have explored reactions of some lanthanide halides (and also yttrium and scandium halides), and report here the key results. Studies of selected crown ether analogues are also reported for comparison purposes.

In this work, anhydrous lanthanide iodides were generally used in preference to the corresponding chlorides due to their higher solubility in weakly coordinating solvents like MeCN, which mainly reflects the lower lattice energies of MI₃ compared to the lighter halides. In the scandium and yttrium systems, cationic chloride species generated using FeCl₃ as a chloride abstractor were also prepared.

Experimental

All reactions were carried out using standard Schlenk and vacuum line techniques. Samples were handled and stored in a glove-box and under a dry dinitrogen atmosphere. Dichloromethane and acetonitrile were distilled over CaH₂ and diethyl ether from sodium benzophenone ketyl. Anhydrous LaCl₃ was prepared by refluxing the heptahydrate in freshly distilled thionyl chloride, followed by removing the excess thionyl chloride *in vacuo*. La(OTf)₃ and ScI₃ were obtained from Aldrich and used as received. Anhydrous MCl₃ (M = Sc, Y) and M'I₃ (M' = Y, La, Lu) were obtained from Alfa, and NdI₃ from Strem, and used as received. [Sc(THF)₃Cl₃] and [YCl₂(THF)₅]-[YCl₄(THF)₂] were made by literature methods.^{20,21} 18-Crown-6 was dried by dissolution in anhydrous CH₂Cl₂ followed by addition of thionyl chloride and then stirred for 1 h. The solvent and excess thionyl chloride were removed under vacuum. 15-Crown-5 was dried by dissolving in dry CH₂Cl₂ and storing over 3 Å molecular sieves for 1 week. The solvent was removed under vacuum and the 15-crown-5 pumped on for several hours at 50 °C/0.5 mmHg. [18]aneO₄S₂, [18]aneO₄Se₂, [18]aneO₄Te₂ and [15]aneO₃S₂ were prepared according to literature procedures.^{16,22,23}

IR spectra were obtained as Nujol mulls on a Perkin Elmer Spectrum 100 spectrometer. ¹H and ¹⁹F{¹H} NMR spectra were

recorded on a Bruker AV 300 spectrometer and referenced to residual solvent (¹H) and external CFCl₃ (¹⁹F). ⁷⁷Se{¹H} NMR spectra were obtained on a Bruker DPX400 and referenced to neat external Me₂Se. ⁴⁵Sc, ⁸⁹Y and ¹³⁹La NMR spectra were recorded on a Bruker DPX400 and are referenced to external aqueous solutions of the corresponding aquo-cations at pH = 1 in water. Microanalysis were conducted by Medac Ltd or London Metropolitan University. Conductivity measurements were carried out under inert atmosphere, using a platinum electrode conductivity cell on a PYE & Co conductance bridge.

Preparations

All the complexes are very moisture sensitive and rigorously anhydrous conditions must be maintained throughout.

[ScCl₂([15]aneO₃S₂)] [FeCl₄]. [ScCl₃(THF)₃] (0.060 g, 0.16 mmol) and FeCl₃ (0.027 g, 0.16 mmol) were dissolved together in MeCN (15 mL) and left to stir for 1 h. [15]aneO₃S₂ (0.042 g, 0.16 mmol) was then added, and the yellow solution was allowed to stir overnight at room temperature. The volatiles were removed and the remaining yellow solid washed with CH₂Cl₂, filtered off and dried *in vacuo*. Yield: 0.038 g, 41%. Required for C₁₀H₂₀Cl₆FeO₃S₂Sc (565.9): C, 21.2; H, 3.6. Found: C, 21.6; H, 4.1%. ¹H NMR (CD₃CN, 293 K): δ = 3.55 (v.br, SCH₂), 3.77 (v.br, SCH₂), 4.34 (v.br, OCH₂), 4.48 (v.br, OCH₂). ⁴⁵Sc NMR (MeCN, 298 K): δ = 201. IR (Nujol/cm⁻¹): 380 (FeCl₄), 362, 293 (ScCl).

[ScCl₂([18]aneO₄S₂)] [FeCl₄]. This was made similarly from [ScCl₃(THF)₃] (0.060 g, 0.16 mmol), FeCl₃ (0.027 g, 0.16 mol) and [18]aneO₄S₂ (0.049 g, 0.16 mmol). 0.065 g, 65%. X-ray quality crystals were grown by dissolving the solid in MeCN-CH₂Cl₂ and leaving in a fridge at 5 °C. Required for C₁₂H₂₄Cl₆FeO₄S₂Sc (610.0): C, 23.6; H, 4.0. Found: C, 24.1; H, 4.8%. ¹H NMR (CD₃CN, 293 K): δ = 2.88–3.34 (vbr m, [8H], SCH₂), 3.82 (vbr, [8H], SCH₂CH₂O), 4.41 (vbr, [8H], OCH₂); (230 K): δ = 2.77 (vbr, SCH₂), 3.55 (v.br, SCH₂CH₂O), 4.34 (v.br, OCH₂); (d₆-acetone, 263 K): δ = 2.71 (br, [8H], SCH₂), 3.55, 3.63 (br m, [16H], OCH₂). ⁴⁵Sc NMR (MeCN, 293 K): δ = 204. IR (Nujol/cm⁻¹): 381 (FeCl₄), 316, 288(sh) (ScCl).

[ScCl₂([18]aneO₄Se₂)] [FeCl₄]. This was made similarly to the [18]aneO₄S₂ complex from [ScCl₃(THF)₃] (0.060 g, 0.16 mmol), FeCl₃ (0.027 g, 0.16 mmol), [18]aneO₄Se₂ (0.064 g, 0.16 mmol) producing a dark ochre solid. Yield: 61%. Required for C₁₂H₂₄Cl₆FeO₄ScSe₂ (703.8): C, 20.5; H, 3.4. Found: C, 20.6; H, 3.5%. ¹H NMR (CD₃CN, 298 K): δ = 2.83 (br, [8H], SeCH₂), 3.59 (br, [8H], SeCH₂CH₂O), 3.75 (br, [8H], OCH₂); (230 K): δ = 2.81 (br, [8H], SeCH₂), 3.54 and 3.70 (br m, [16H], OCH₂). ⁴⁵Sc NMR (MeCN, 298 K): δ = 205. ⁷⁷Se NMR (MeCN, 298 K): δ = 150; (233 K): δ = 153. IR (Nujol, cm⁻¹): 388 (FeCl₄) 317, 307(sh) (ScCl).

[ScCl₂([18]aneO₄Te₂)] [FeCl₄]. [ScCl₃(THF)₃] (0.060 g, 0.16 mmol) and FeCl₃ (0.027 g, 0.16 mmol) were dissolved together in MeCN (15 mL) and left to stir for 1 h. To the yellow solution [18]aneO₄Te₂ (0.049 g, 0.16 mmol) was then added and the solution was allowed to stir overnight at room temperature. The solution darkened to orange. The volatiles were removed and the remaining brown solid washed with CH₂Cl₂, filtered



and dried *in vacuo*. Yield: 0.070 g, 53%. Required for $C_{12}H_{24}Cl_6FeO_4ScTe_2$ (801.0): C, 18.0; H, 3.0. Found: C, 17.8; H, 2.9%. 1H NMR (CD_3CN , 295 K): $\delta = 3.74$ (vbr m, [16H]), 4.19 (vbr, [8H]); (230 K): $\delta = 3.72$ (vbr m), 4.15 (v br.), see text. ^{45}Sc NMR (MeCN, 298 K): see text. IR (Nujol/ cm^{-1}): 381 (FeCl₄), 324 vbr (ScCl).

[ScI₂([15]aneO₃S₂)]I. ScI₃ (0.040 g, 0.094 mmol) was suspended in MeCN (15 mL) and [15]aneO₃S₂ (0.024 g, 0.094 mmol) added. The ligand dissolved and a pale yellow solution formed. After 24 h, the yellow solution was pumped to dryness and the remaining light yellow powder was washed with CH₂Cl₂ and dried *in vacuo*. Yield: 0.040 g, 63%. Required for $C_{10}H_{20}I_3O_3S_2Sc$ (678.1): C, 17.7; H, 3.0. Found: C, 17.6; H, 2.9%. 1H NMR (CD_3CN , 293 K): $\delta = 3.83$ (br), 4.38 (br), 4.48 (br), 4.62 (br). ^{45}Sc NMR (MeCN, 298 K): $\delta = 297$.

[ScI₂([18]aneO₄S₂)]I. This was made similarly from ScI₃ (0.040 g, 0.094 mmol) and [18]aneO₄S₂ (0.028 g, 0.094 mmol). X-ray quality crystals were obtained by re-dissolving in MeCN and slow evaporation of the solvent. Yield: 0.043 g, 63%. Required for $C_{12}H_{24}I_3O_4S_2Sc$ (721.8): C, 14.8; H, 2.5. Found: C, 14.5; H, 2.6%. 1H NMR (CD_3CN , 293 K): $\delta = 2.75$ – 2.98 (br m, [8H], SCH₂), 3.56 (br s, [8H], SCH₂CH₂O), 4.24 (br, [8H], OCH₂). ^{45}Sc NMR (MeCN, 298 K): $\delta = 206$ (CH₂Cl₂, 295 K) $\delta = 220$.

[ScI₂([18]aneO₄Se₂)]I. ScI₃ (0.023 g, 0.054 mmol) was suspended in MeCN (15 mL) and heated to reflux. The mixture was maintained at reflux until a yellow solution remained then allowed to cool and [18]aneO₄Se₂ (0.021 g, 0.054 mmol) added. The reaction was left at room temperature to stir for 45 min, some darkening of the solution was observed. The volatiles were removed *in vacuo* and the oily solid left behind washed with CH₂Cl₂. The ochre solid produced was separated and dried *in vacuo*. Yield 0.026 g, 59%. Required for $C_{12}H_{24}I_3O_4ScSe_2$ (815.8): C, 17.7; H, 3.0. Found: C, 17.5; H, 3.1%. 1H NMR (CD_3CN , 298 K): $\delta = 2.78$ – 3.16 (br, [8H], SeCH₂), 3.64 (s, [8H], SeCH₂CH₂O), 4.19–4.38 (br, [8H], OCH₂). ^{45}Sc NMR (MeCN, 295 K): not observed. $^{77}Se\{^1H\}$ NMR (MeCN, 298 K): not observed.

[YCl₂([15]aneO₃S₂)]FeCl₄. [YCl₂(THF)₅][YCl₄(THF)₂]²¹ (0.107 g, 0.12 mmol) and FeCl₃ (0.039 g, 0.24 mmol) were dissolved together in MeCN (15 mL) and left to stir for 1 h. [15]aneO₃S₂ (0.060 g, 0.24 mmol) was then added and the yellow solution was allowed to stir overnight at room temperature. The volatiles were removed and the remaining yellow solid washed with CH₂Cl₂, filtered off and dried *in vacuo*. Yield: 0.090 g, 62%. Required for $C_{10}H_{20}Cl_6FeO_3S_2Y$ (609.9): C, 19.7; H, 3.3. Found: C, 20.0; H, 3.7%. 1H NMR (CD_3CN , 293 K): $\delta = 3.20$ (vbr, [8H], SCH₂), 4.17 (vbr, [12H], OCH₂). IR (Nujol/ cm^{-1}): 380 (FeCl₄), 268 (sh), 262 (YCl).

[YCl₂([18]aneO₄S₂)]FeCl₄. This was made similarly from [YCl₂(THF)₅][YcCl₄(THF)₂]²¹ (0.060 g, 0.067 mmol), FeCl₃ (0.022 g, 0.13 mmol) and [18]aneO₄S₂ (0.040 g, 0.13 mmol). X-ray quality crystals were grown by dissolving in MeCN and slow evaporation of the solvent. Yield: 0.034 g, 37%. Required for $C_{12}H_{24}Cl_6FeO_4S_2Y$ (653.9): C, 22.0; H, 3.7. Found: C, 21.9; H, 3.7%. 1H NMR (CD_3CN , 293 K): $\delta = 2.94$ (br, [4H], SCH₂),

3.29 (br, [4H], SCH₂), 4.29 and 4.36 (br m, [16H], OCH₂). IR (Nujol/ cm^{-1}): 375 (FeCl₄), 268 (sh), 265 (YCl).

[YI₂([18]aneO₄Se₂)]I. A suspension of YI₃ (0.075 g, 0.160 mmol) in MeCN (10 mL) was added a solution of [18]aneO₄Se₂ (0.062 g, 0.160 mmol) in MeCN (10 mL). This was stirred for one hour and a small amount of solid was filtered off. Diethyl ether (25 mL) was layered on top of the solution and clear crystals formed overnight. The crystals were filtered off, washed with diethyl ether (5 mL) and dried under vacuum. Yield: 0.08 g, 51%. Required for $C_{12}H_{24}I_3O_4Se_2Y$ (859.9): C, 16.7; H, 2.8. Found: C, 16.9; H, 3.0%. 1H NMR (CD_3CN , 300 K): $\delta = 2.90$ (m, [4H], SeCH₂), 3.28 (m, [4H], SeCH₂), 4.25 (br m, [8H], SeCH₂CH₂O), 4.35 (m, [4H], OCH₂), 4.56 (m, [4H], OCH₂). $^{77}Se\{^1H\}$ NMR (CH₃CN, 300 K): $\delta = 125$.

[YCl₂([18]aneO₄Se₂)]FeCl₄. To a Schlenk flask containing [YCl₂(THF)₅][YCl₄(THF)₂]²¹ (0.050 g, 0.056 mmol) and FeCl₃ (0.018 g, 0.11 mmol) was added acetonitrile (15 mL) which gave a clear yellow solution. To this was added a solution of [18]aneO₄Se₂ (0.044 g, 0.11 mmol) in acetonitrile (5 mL) and stirred for 1 h. The solvent was removed under vacuum and the resulting yellow solid washed with dichloromethane (10 mL). Yield: 0.07 g, 63%. Required for $C_{12}H_{24}Cl_6FeO_4Se_2Y$ (747.7): C, 19.3; H, 3.2. Found: C, 19.1; H, 3.1%. 1H NMR (CD_3CN , 300 K): $\delta = 2.85$ (br m, [4H], SeCH₂), 3.15 (br m, [4H], SeCH₂), 4.21 (br s, [8H], SeCH₂CH₂O), 4.32 (br m, [4H], OCH₂), 4.48 (br m, [4H], OCH₂). $^{77}Se\{^1H\}$ NMR (MeCN, 300 K): $\delta = 103$. IR (Nujol mull/ cm^{-1}): 387 (FeCl₄), 279 (YCl).

[YCl₂(18-crown-6)]₃[Y₂Cl₉]. YCl₃ (0.153 g, 0.80 mmol) was suspended in acetonitrile (20 mL) and stirred for 1 h. This solution was filtered to remove residual YCl₃ and added to a solution of 18-crown-6 (0.103 g, 0.40 mmol) in acetonitrile (10 mL) and left to stand for 15 h upon which an off-white polycrystalline material precipitated. Yield: 0.065 g, 28%. Required for $C_{36}H_{72}Cl_{15}O_{18}Y_3 \cdot 2MeCN$ (1845.3): C, 26.0; H, 4.3; N, 1.5. Found: C, 26.0; H, 4.1; N, 1.9%. 1H NMR (CD_3CN , 298 K): $\delta = 4.15$ (s). IR (Nujol mull/ cm^{-1}): 279 (YCl).

[LaI₃([18]aneO₄S₂)]I. To a Schlenk flask containing a suspension of LaI₃ (0.150 g, 0.29 mmol) in MeCN (10 mL) was added a solution of [18]aneO₄S₂ (0.086 g, 0.29 mmol) in MeCN (10 mL). This was stirred for 1 h and a small amount of precipitate was filtered off and discarded. Diethyl ether (20 mL) was layered onto the solution and the system precipitated a white solid overnight. Yield: 0.110 g, 46%. Required for $C_{12}H_{24}I_3LaO_4S_2 \cdot 0.3MeCN$ (828.3): C, 18.3; H, 3.0; N, 0.5. Found: C, 18.0; H, 3.4; N, 0.5%. 1H NMR (CD_3CN , 295 K): $\delta = 3.04$ (br, [4H], SCH₂), 3.21 (br, [4H], SCH₂), 4.07–4.44 (m, [16H], OCH₂).

[LaI₃([15]aneO₃S₂)]I. To a Schlenk flask containing a suspension of LaI₃ (0.150 mg, 0.29 mmol) in MeCN (15 mL) was added a solution of [15]aneO₃S₂ (0.073 g, 0.29 mmol) in MeCN (10 mL). This was stirred for 1 h and a small amount of precipitate was filtered off. The solvent volume was reduced to approximately 5 mL and upon standing for several hours a white microcrystalline product precipitated. This was collected by filtration and dried under vacuum. Yield 0.044 g, 18%. Required for $C_{10}H_{20}I_3LaO_3S_2$ (772.0): C, 15.6; H, 2.6. Found:



C, 15.5; H, 2.6%. ^1H NMR (CD_3CN , 295 K): $\delta = 2.96$ and 3.10 (vbr m, [8H], SCH_2), 4.00 (br [12H], OCH_2).

[LaI₃([18]aneO₄Se₂)]. To a Schlenk flask containing a suspension of anhydrous LaI₃ (0.075 g, 0.144 mmol) in MeCN (10 mL) was added a solution of [18]aneO₄Se₂ (0.056 g, 0.144 mmol) in MeCN (10 mL). This was stirred for 1 h and a small amount of fine precipitate was filtered off. The solution was left to stand for five days upon which clear crystalline plates formed. The solvent was removed *via* filtration and the crystals dried under vacuum. Yield: 0.045 g, 34%. Required for C₁₂H₂₄I₃LaO₄Se₂ (909.9): C, 15.8; H, 2.7. Found: C, 15.9; H, 2.8%. ^1H NMR (CD_3CN , 295 K): $\delta = 2.99$ (br, [4H], SeCH_2), 3.20 (br, [4H], SeCH_2), 4.29 and 4.36 (m, [16H], OCH_2). $^{77}\text{Se}\{^1\text{H}\}$ NMR (MeCN, 295 K): $\delta = +137.5$; with added ligand: $\delta = +140.0$, $+137.1$.

[LuI₂([18]aneO₄S₂)]I. To a Schlenk flask containing a suspension of LuI₃ (0.075 g, 0.135 mmol) in MeCN (10 mL) was added a solution of [18]aneO₄S₂ (0.040 g, 0.135 mmol) in MeCN (10 mL). This was stirred for 1 h and the solution filtered. Diethyl ether (20 mL) was layered on top and on mixing the system precipitated fine colourless needle crystals. The resulting crystals were filtered off, washed with diethyl ether (5 mL) and dried under vacuum. Yield: 0.047 g, 41%. Required for C₁₂H₂₄I₃LuO₄S₂·0.5MeCN (872.6): C, 17.9; H, 3.0; N, 0.8. Found: C, 17.7; H, 3.1; N, 1.6%. ^1H NMR (CD_3CN , 295 K): $\delta = 2.95$ (m, [4H], SCH_2), 3.45 (m, [4H], SCH_2), 4.22 (s, [8H], $\text{SCH}_2\text{CH}_2\text{O}$), 4.30 – 4.80 (m, [8H], OCH_2).

[LuI₂([18]aneO₄Se₂)]I. This was made similarly to the [18]aneO₄S₂ from LuI₃ (0.075 g, 0.135 mmol) and [18]aneO₄Se₂ (0.055 g, 0.135 mmol). Yield: 0.076 g, 57%. Required for C₁₂H₂₄I₃LuO₄Se₂: C, 15.2; H, 2.6. Found: C, 15.2; H, 2.6%. ^1H NMR (CD_3CN , 295 K): $\delta = 2.87$ (m, [4H], SeCH_2), 3.25 (m, [4H], SeCH_2), 4.24 (m, [8H], $\text{SeCH}_2\text{CH}_2\text{O}$), 4.38 (m, [4H], OCH_2), 4.60 (m, [4H], OCH_2). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CH_3CN , 295 K): $\delta = +108$; with added ligand: $\delta = +140$, 108 .

[NdI₃([18]aneO₄Se₂)]. This was made similarly as a mint green microcrystalline solid. Yield: 0.050 g, 38%. Required for C₁₂H₂₄I₃NdO₄Se₂: C, 15.75; H, 2.6. Found: C, 15.7; H, 2.7%. ^1H NMR (CD_3CN , 295 K): $\delta = 9.4$, 7.2 , 4.6 , 4.0 (all vbr).

X-ray crystallography

Summary details of the crystallographic data collection and refinement are given in the ESI.† Crystals were obtained as described above. Data collection used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (100 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinement were straightforward,^{24,25} except as detailed below, with H atoms being placed in calculated positions using the default C–H distance.

For [LaI([18]aneO₄S₂)(OH₂)₂]₂·H₂O the crystal quality was modest and H-atoms on the water oxygens were not found. [LaI₃([18]aneO₄S₂)] – Disorder was evident in the crown backbone at C(3) and C(4), which was satisfactorily modelled as

two sites C3A,C3B and C4A,C4B, with refined occupancies of 60%:40%. In [LaI₃(15-crown-5)]·MeCN the molecule has mirror symmetry and carbon atoms C1, C4 and C5 are disordered over two sites (A/B) which was satisfactorily modelled. [Lu(MeCN)₂(18-crown-6)]I₂ – The crystal quality was rather poor with large Q peaks near to Lu and I, hence while the structure confirms the connectivities, detailed comparisons of bond distances *etc.* should be treated with caution. In [LuI₂([18]aneO₄Se₂)]I·2MeCN disorder at C2 and C5 was modelled as two sites (A/B) and it was necessary to ‘split’ C1 and C6, which were refined as C1/C1B and C6/C6B (both pairs with the same coordinates and same U_{ij}) to add H atoms. Some slight disorder of the carbon backbone was apparent in the structure of [ScI₂([18]aneO₄S₂)]I·MeCN, and two C atoms were modelled as disorder over two sites.

CCDC reference numbers 940218–940229 contain crystallographic data in cif format.

Results and discussion

Scandium

Previous studies of the reaction of [ScCl₃(THF)₃] with 15-crown-5 and either SbCl₅, CuCl₂ or FeCl₃ as chloride abstractors in MeCN solution^{3,4,26} led to seven-coordinate pentagonal bipyramidal cationic scandium complexes, [ScCl₂(15-crown-5)]Y (Y = SbCl₆, FeCl₄, 1/2CuCl₄) and [ScCl(MeCN)(15-crown-5)]-[SbCl₆]₂.

The 15-membered ring thia-oxa macrocycle [15]aneO₃S₂ ([15]aneO₃S₂ = 1,4-dithia-7,10,13-trioxacyclopentadecane) reacted with [ScCl₃(THF)₃] in the presence of one molar equivalent of FeCl₃ to form [ScCl₂([15]aneO₃S₂)]-[FeCl₄], and with anhydrous ScI₃ to form yellow [ScI₂([15]aneO₃S₂)]I. Attempts to use SbCl₅ as a chloride abstractor for the thia-oxa macrocycle complexes resulted in intensely coloured solutions due to redox chemistry at sulfur leading to Sb(III) complexes,¹⁷ and even FeCl₃ cannot be used in the iodide systems due to instability of FeI₃.²⁷ The complexes are extremely sensitive to moisture and attempts to obtain crystals suitable for an X-ray study have been unsuccessful. The IR spectrum of [ScCl₂([15]aneO₃S₂)]-[FeCl₄] confirms the absence of MeCN and shows strong bands at 380 cm^{-1} assigned to [FeCl₄]^{−28} and 363 and 293 cm^{-1} $\nu(\text{ScCl})$. The ^1H NMR spectra of both complexes in CD₃CN show broad resonances with no resolved couplings to high frequency of those in [15]aneO₃S₂, whilst they show broad singlets in the ^{45}Sc NMR spectra (Table 1).§ The high frequency ^{45}Sc chemical shifts (compared to the 15-crown-5 complex) are consistent with coordination of the sulfur in the [15]aneO₃S₂ complexes. The high frequency shift $I > \text{Cl}$ is also consistent with data on scandium halide-phosphine oxide systems.²⁹

The reaction of [ScCl₃(THF)₃] with the 18-membered ring thia-oxa macrocycle, [18]aneO₄S₂ in the presence of FeCl₃ produced yellow [ScCl₂([18]aneO₄S₂)]-[FeCl₄], for which yellow

§ ^{45}Sc has $I = 7/2$, 100%, $E = 29.24$ MHz, $Q = -0.22 \times 10^{-28}$ m², $R_c = 1710$.



Table 1 ^{45}Sc NMR data^a

Complex	$\delta(^{45}\text{Sc})$	Ref.
$[\text{ScCl}_2([\text{15}] \text{aneO}_3\text{S}_2)][\text{FeCl}_4]$	201	This work
$[\text{ScI}_2([\text{15}] \text{aneO}_3\text{S}_2)]\text{I}$	297	This work
$[\text{ScCl}_2(\text{15-crown-5})][\text{FeCl}_4]$	130	3, 4
$[\text{ScCl}(\text{MeCN})(\text{15-crown-5})][\text{FeCl}_4]_2$	99.5	3
$[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{S}_2)][\text{FeCl}_4]$	202	This work
$[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{Se}_2)][\text{FeCl}_4]$	205	This work
$[\text{ScCl}_2(\text{18-crown-6})][\text{FeCl}_4]$	132	3
$[\text{ScI}_2([\text{18}] \text{aneO}_4\text{S}_2)]\text{I}$	See text	This work
$[\text{ScI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I}$	n.o.	This work

^a 295 K in MeCN solution. n.o. not observed.

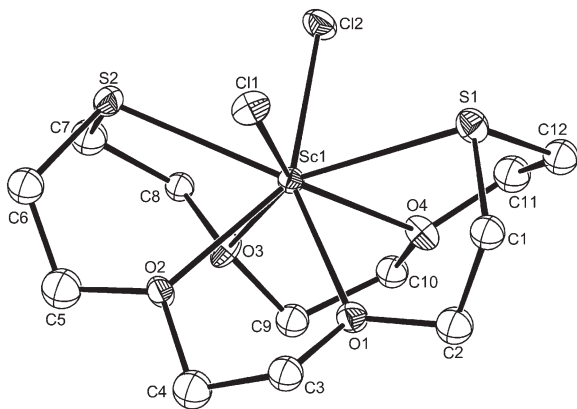


Fig. 1 The structure of the Sc1 centred cation in $[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{S}_2)][\text{FeCl}_4]$ showing the atom labelling scheme. The other two independent scandium cations are similar. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–O1 = 2.247(8), Sc1–O3 = 2.256(8), Sc1–O4 = 2.390(8), Sc1–O2 = 2.435(8), Sc1–S2 = 2.734(3), Sc1–S1 = 2.753(3), Sc1–Cl1 = 2.422(3), Sc1–Cl2 = 2.466(3), O1–Sc1–O2 = 67.9(3), O3–Sc1–O4 = 70.6(3), O3–Sc1–S2 = 70.3(2), O2–Sc1–S2 = 69.29(19), O4–Sc1–S1 = 69.16(19), O1–Sc1–S1 = 74.5(2), Cl2–Sc1–S1 = 79.36(10), Cl1–Sc1–Cl2 = 97.67(11), S2–Sc1–S1 = 139.97(11).

crystals were grown from MeCN–CH₂Cl₂ solution. The structure (Fig. 1) shows the scandium cation coordinated to all six donors of the ring and two *cis* disposed chlorines (Cl–Sc–Cl 97.7(1)°). The structure contrasts with those of $[\text{ScCl}_2(\text{18-crown-6})]\text{Y}^{3+}$ which have a *trans* arrangement of the chlorides and with only *five* of the six available oxygen donor atoms coordinated to the scandium. The Sc–O distances in the present complex, 2.247(8)–2.435(8) Å, are more disparate than in $[\text{ScCl}_2(\text{18-crown-6})][\text{FeCl}_4]$ (2.195(2)–2.264(2) Å). We note that in *exo*-coordinated crown and thia-oxacrown complexes of CrCl₃ and VCl₃, coordination of sequential donor groups produced very acute O–M–O angles, whereas the S–M–S angles did not show similar effects, due to the longer M–S bonds,³⁰ and this resulted in preferential sulfur coordination to the hard metal centres. In the present case, the longer Sc–S bonds of 2.74 Å (av) allows the ring to coordinate all six donors to the small scandium centre, with some small amount of folding of the macrocycle. In CD₃CN or d⁶-acetone solutions the ¹H NMR spectra contain several broad resonances shifted to high frequency from those in the ligand; these sharpen on cooling the

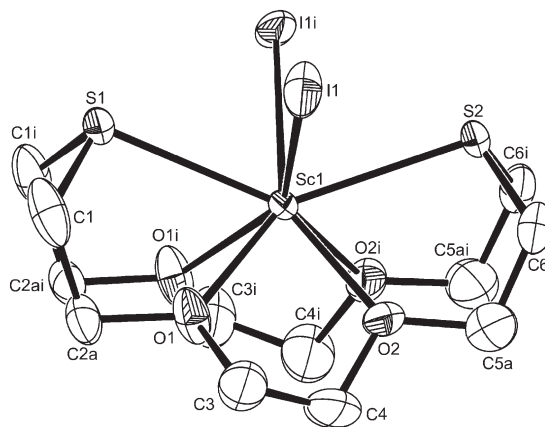


Fig. 2 The structure of the cation in $[\text{ScI}_2([\text{18}] \text{aneO}_4\text{S}_2)]\text{I} \cdot \text{MeCN}$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. The cation has mirror symmetry. C2 and C5 were modelled as two disordered sites and only the major A site is shown. Symmetry operation: $i = x, 1/2 - y, z$. Selected bond lengths (Å) and angles (°): Sc1–O1 = 2.272(8), Sc1–O2 = 2.263(9), Sc1–S1 = 2.711(5), Sc1–S2 = 2.715(4), Sc1–I1 = 2.915(2), O1–Sc1–O2 = 69.0(3), O1–Sc1–S1 = 71.8(2), O2–Sc1–S2 = 70.7(2), O1–Sc1–I1 = 86.9(3), O2–Sc1–I1 = 86.3(3), S1–Sc1–I1 = 75.17(8), S2–Sc1–I1 = 76.00(8), I1–Sc1–I1 = 94.03(9), S1–Sc1–S2 = 137.16(15).

solutions, but even at low temperatures they remain broad, indicative of dynamic processes. The ⁴⁵Sc NMR resonance, $\delta = 204$, is similar to that in the $[\text{15}] \text{aneO}_3\text{S}_2$ complex, but some 70 ppm to high frequency of the 18-crown-6 complex (Table 1). The reaction of ScI₃ with $[\text{18}] \text{aneO}_4\text{S}_2$ in rigorously anhydrous MeCN produced deep yellow $[\text{ScI}_2([\text{18}] \text{aneO}_4\text{S}_2)]\text{I}$, the structure of which (Fig. 2) reveals a very similar geometry to the chloride. The ⁴⁵Sc NMR resonance observed at $\delta = 206$, seems inconsistent with the presence of coordinated iodide, and it may be that the iodides are displaced in solution by MeCN which would produce a significant low frequency shift.

Replacing $[\text{18}] \text{aneO}_4\text{S}_2$ with the selenium analogue $[\text{18}] \text{aneO}_4\text{Se}_2$ gave extremely moisture sensitive brownish yellow complexes $[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{Se}_2)][\text{FeCl}_4]$ and $[\text{ScI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I}$. Spectroscopically these two complexes, which constitute the first examples with Sc–Se coordination in a neutral ligand, closely resembled the thia-oxa analogues. We were unable to observe ⁴⁵Sc or ⁷⁷Se{¹H} resonances from the iodo-complex, presumably due to exchange, but for $[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{Se}_2)][\text{FeCl}_4]$, the ⁴⁵Sc chemical shift of 205, and a ⁷⁷Se{¹H} shift of +150 ppm compared to the ligand shift²² of +140 ppm, are evidence of the Sc–Se interaction is maintained in solution.

The reaction of $[\text{18}] \text{aneO}_4\text{Te}_2$ with $[\text{ScCl}_3(\text{THF})_3]$ and FeCl₃ in anhydrous MeCN gave a brown precipitated solid with a composition corresponding to $[\text{ScCl}_2([\text{18}] \text{aneO}_4\text{Te}_2)][\text{FeCl}_4]$. The IR spectrum, which showed the presence of the ligand and the absence of MeCN or THF, with $[\text{FeCl}_4]^-$ at 378 cm⁻¹ and a broad feature at ~324 cm⁻¹ assigned to $\nu(\text{ScCl})$, support the formulation. A solution in CD₃CN at ambient temperature rapidly darkens and deposits black tellurium, but from a solution made at 240 K and run immediately it was possible to obtain the ¹H NMR spectrum, which showed very broad



features of the tellura-oxa macrocycle. On standing in solution, new resonances appeared including a doublet at ~ 5.5 ppm which may suggest a vinyl unit, along with a black precipitate. The ^{45}Sc spectrum of a solution of the complex at 240 K contained several broad resonances, the relative intensities of which changed over time, and no useful conclusions could be drawn. This ligand contains quite reactive Te–C bonds in $-\text{Te}(\text{CH}_2)_2-$ units which have a tendency to decompose with elimination of ethene,³¹ and it has limited coordination chemistry. It gives stable complexes bound as a Te_2 donor in planar $[\text{MCl}_2(\text{[18]aneO}_4\text{Te}_2)]$ ($\text{M} = \text{Pd}$ or Pt),²² but decomposes rapidly on reaction with SbX_3 ¹⁶ or $\text{Pb}(\text{BF}_4)_2$ ¹⁷ with precipitation of tellurium, and does not react with (or decompose with) MI_2 ($\text{M} = \text{Ca}$ or Sr) in MeCN.¹⁹ The scandium system seems to be a borderline case, in that a complex precipitates from the concentrated synthesis solution, but decomposes quite rapidly in dilute solution at ambient temperatures.

Yttrium

Obtaining pure complexes of the macrocycles using YCl_3 in anhydrous MeCN proved to be very difficult, products usually being contaminated with the poorly soluble YCl_3 . However, the 18-crown-6 complex was prepared in this way and crystals were formed directly from the reaction mixture. Structure solution showed these to be $[\text{YCl}_2(\text{18-crown-6})]_3[\text{Y}_2\text{Cl}_9]$. The anion is of the familiar facial bioctahedral type known for many transition metals, and the yttrium species has been reported in $\text{Cs}_3[\text{Y}_2\text{Cl}_9]$ ³² (see ESI[†]). The unit cell contains three eight-coordinate yttrium cations with all six crown oxygen and two chlorines coordinated, but whilst two of the cations have *trans* Cl–Y–Cl arrangement the third is the *cis* isomer (Fig. 3 and 4). In contrast to the seven coordinate $[\text{ScCl}_2(\text{18-crown-6})]^+$,^{3,4} the larger yttrium cation fits within the ring coordinating to all six

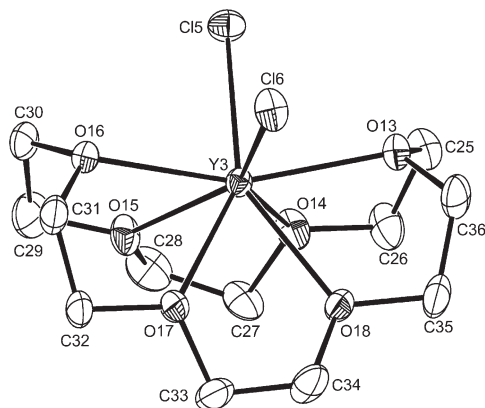


Fig. 3 The structure of the Y3 centred cation in $[\text{YCl}_2(\text{18-crown-6})]_3[\text{Y}_2\text{Cl}_9] \cdot n\text{MeCN}$ ($n = 1.65$) showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y3–O14 = 2.413(4), Y3–O17 = 2.419(4), Y3–O13 = 2.426(3), Y3–O16 = 2.431(3), Y3–O18 = 2.448(4), Y3–O15 = 2.451(4), Y3–Cl5 = 2.5708(15), Y3–Cl6 = 2.5834(15), O14–Y3–O13 = 66.78(13), O17–Y3–O16 = 66.44(12), O17–Y3–O18 = 63.22(13), O13–Y3–O18 = 64.90(13), O14–Y3–O15 = 64.09(13), O16–Y3–O15 = 64.63(13), Cl5–Y3–Cl6 = 89.54(5).

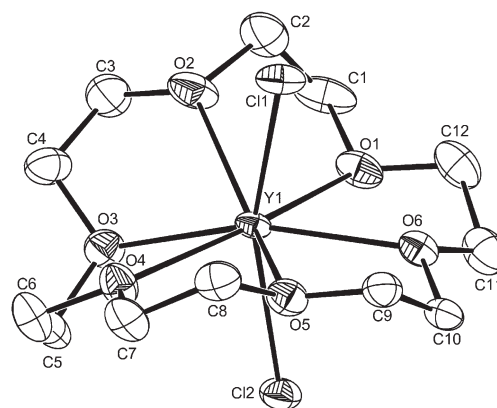


Fig. 4 The structure of the Y1 centred cation in $[\text{YCl}_2(\text{18-crown-6})]_3[\text{Y}_2\text{Cl}_9] \cdot n\text{MeCN}$ ($n = 1.65$) showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–O6 = 2.409(4), Y1–O5 = 2.426(4), Y1–O1 = 2.438(4), Y1–O4 = 2.438(4), Y1–O2 = 2.460(5), Y1–O3 = 2.474(4), Y1–Cl1 = 2.5988(15), Y1–Cl2 = 2.6103(15), O6–Y1–O5 = 65.40(14), O6–Y1–O1 = 65.00(15), O5–Y1–O4 = 63.29(14), O1–Y1–O2 = 65.44(16), O4–Y1–O3 = 63.23(14), O2–Y1–O3 = 62.58(14), Cl1–Y1–Cl2 = 157.91(5).

oxygens. The macrocycle ring is more folded in the *cis* isomer, but the Y–O distances and neighbouring O–Y–O angles are little different between the isomers. In the *trans* form the Cl–Y–Cl angle is 157.9° and the Y–Cl distances are 2.599(2), 2.610(2) Å compared to 89.5° and 2.571(2), 2.583(2) Å in the *cis*. The complex is poorly soluble in dry MeCN in which it exhibits only a singlet in the ^1H NMR spectrum showing exchange processes have made all the methylene groups appear equivalent in the two isomers. Attempts to obtain ^{89}Y NMR data failed; although 100% abundant and with $I = 1/2$, ^{89}Y has a low resonance frequency and long T_1 's which combine to make it an insensitive nucleus and difficult to observe. In the present complex, dynamic processes would account for the absence of an ^{89}Y resonance at ambient temperatures, and the solubility is too poor to obtain a low temperature spectrum.

The reaction of $[\text{YCl}_2(\text{THF})_5][\text{YcCl}_4(\text{THF})_2]$ (from YCl_3 and THF)²¹ with FeCl_3 and $[\text{18]aneO}_4\text{S}_2$, gave pale yellow $[\text{YCl}_2(\text{[18]aneO}_4\text{S}_2)]_3[\text{FeCl}_4]$. Crystals grown from MeCN solution by slow evaporation of the solvent showed a *cis*-dichloro arrangement with a Cl–Y–Cl angle of 94.6° (Fig. 5).

The $[\text{YCl}_2(\text{[15]aneO}_3\text{S}_2)]_3[\text{FeCl}_4]$ was obtained similarly, and is assumed to contain a seven coordinate cation. More unusual are $[\text{YCl}_2(\text{[18]aneO}_4\text{Se}_2)]_3[\text{FeCl}_4]$ and $[\text{Yl}_2(\text{[18]aneO}_4\text{Se}_2)]\text{I}$, which contain the first examples of a neutral selenoether function coordinated to yttrium(III). The ^1H NMR spectra of all the yttrium complexes of thia-oxa and seleno-oxa macrocycles show broad resonances without resolved couplings consistent with dynamic behaviour in solution, and as for the 18-crown-6 complex we were unable to observe ^{89}Y NMR spectra. However, for both of the seleno-oxa-crown complexes, $^{77}\text{Se}\{^1\text{H}\}$ NMR resonances were observed with modest low frequency coordination shifts – for $[\text{YCl}_2(\text{[15]aneO}_3\text{S}_2)]_3[\text{FeCl}_4]$ $\delta(^{77}\text{Se}) = 103$ and for $[\text{Yl}_2(\text{[18]aneO}_4\text{Se}_2)]\text{I}$ $\delta(^{77}\text{Se}) = 125$, compared to the ligand value of 140 ppm. If some $[\text{18]aneO}_4\text{Se}_2$ was added, the ^{77}Se



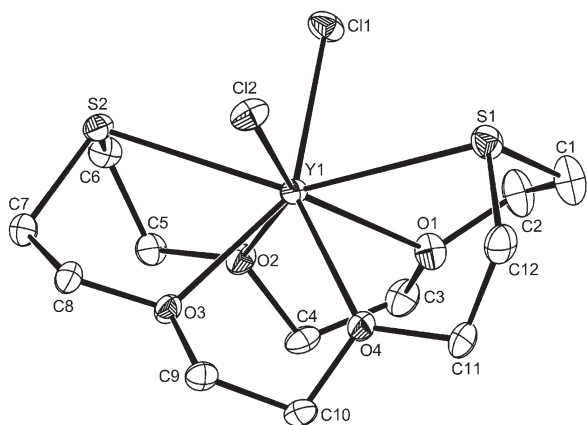


Fig. 5 The structure of the cation in $[\text{YCl}_2([\text{18}]ane\text{O}_4\text{S}_2)][\text{FeCl}_4]$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Y1-O2} = 2.3652(17)$, $\text{Y1-O4} = 2.4012(17)$, $\text{Y1-O3} = 2.4703(17)$, $\text{Y1-O1} = 2.4911(18)$, $\text{Y1-Cl1} = 2.5682(8)$, $\text{Y1-Cl2} = 2.5914(7)$, $\text{Y1-S2} = 2.8955(8)$, $\text{Y1-S1} = 2.9162(8)$, $\text{O4-Y1-O} = 3.67.15(6)$, $\text{O2-Y1-O1} = 66.43(6)$, $\text{Cl1-Y1-Cl2} = 94.63(2)$, $\text{O2-Y1-S2} = 68.09(4)$, $\text{O3-Y1-S2} = 68.26(4)$, $\text{O4-Y1-S1} = 69.20(5)$, $\text{O1-Y1-S1} = 66.58(4)$.

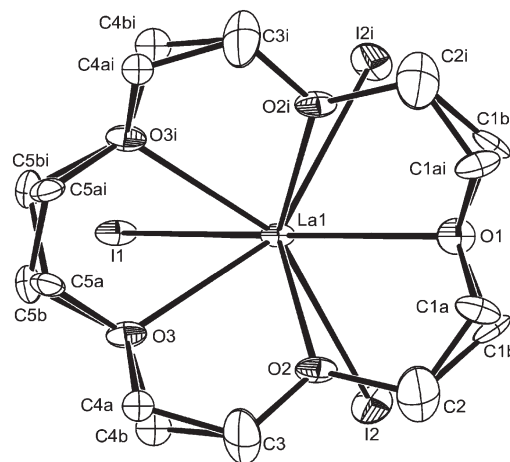


Fig. 6 Structure of $[\text{La}_3(\text{15-crown-5})]\text{MeCN}$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. The molecule has mirror symmetry and carbon atoms C1, C4 and C5 are disordered over two sites (A/B) – both components are shown. Symmetry operation: $i = x, 1/2 - y, z$. Selected bond lengths (\AA) and angles ($^\circ$): $\text{La1-O3i} = 2.587(5)$, $\text{La1-O3} = 2.587(5)$, $\text{La1-O2i} = 2.590(5)$, $\text{La1-O2} = 2.590(5)$, $\text{La1-O1} = 2.626(7)$, $\text{La1-I2i} = 3.1843(9)$, $\text{La1-I2} = 3.1843(9)$, $\text{La1-I1} = 3.2537(11)$, $\text{O3-La1-O3i} = 62.7(2)$, $\text{O3-La1-O2} = 62.27(15)$, $\text{O2-La1-O1} = 61.41(14)$, $\text{I2-La1-I2i} = 95.17(3)$, $\text{I2-La1-I1} = 80.72(2)$.

shifts of both complex and “free” ligand were unchanged, showing the ligand exchange is low on the NMR timescale. The broadening in the ^1H NMR spectra must be due to processes other than complete dissociation of the macrocycle even in the d^0 complexes; possibilities include reversible dissociation of single donors or inversion. In late d-block metal complexes selenoethers (including $[\text{18}]ane\text{O}_4\text{Se}_2$) usually exhibit high frequency coordination shifts, but with p-block metals and some early transition metals the coordination shifts are erratic, both high and low frequency shifts being observed in different systems.^{12,33}

Lanthanum and lutetium

The complexes formed by 15-crown-5 and 18-crown-6 with LaI_3 and LuI_3 were prepared to provide comparison data for the thia-oxa and seleno-oxa macrocycle systems. The syntheses involving reaction of MI_3 with the crown in anhydrous MeCN were straightforward (ESI^\dagger) and whilst the spectroscopic data were consistent with the formulations, it was necessary to obtain structures to confirm the coordination geometries present. The complexes are very moisture sensitive, especially in solution, and water easily enters the coordination sphere, usually displacing iodide in the process. The structure of $[\text{LaI}_3(\text{15-crown-5})]$ (Fig. 6) shows a neutral, eight-coordinate lanthanum, with some of methylene groups of the backbone disordered over two sites.

The $[\text{LaI}_3(\text{18-crown-6})]$ was isolated by reaction of LaI_3 and the crown in CH_2Cl_2 , but crystals grown from an MeCN solution were found to be $[\text{LaI}_2(\text{18-crown-6})(\text{MeCN})]\text{I}\cdot n\text{MeCN}$ (Fig. 7) again showing the ease with which the iodide is displaced. The Ce and Nd analogues $[\text{MI}_3(\text{18-crown-6})]$ were also isolated, along with crystals of the isomorphous complex $[\text{CeI}_2(\text{18-crown-6})(\text{MeCN})]\text{I}\cdot 0.5\text{MeCN}$ and are described in the

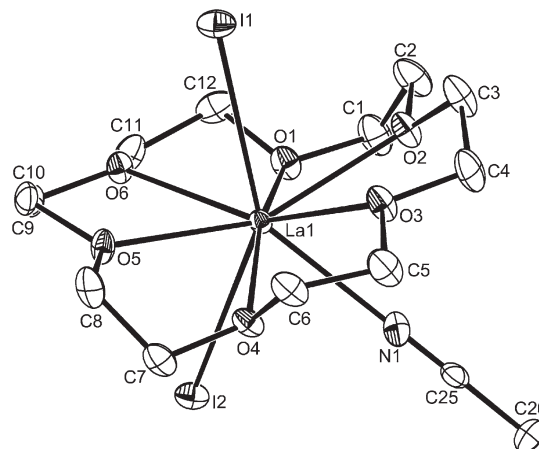


Fig. 7 One of the two crystallographically distinct cations (La1 centred) in $[\text{La}_2(\text{18-crown-6})(\text{MeCN})]\text{I}\cdot n\text{MeCN}$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. La1-O are shown as open bonds. Selected bond lengths (\AA) and angles ($^\circ$): $\text{La1-O5} = 2.569(3)$, $\text{La1-O1} = 2.597(2)$, $\text{La1-O2} = 2.604(3)$, $\text{La1-O4} = 2.605(2)$, $\text{La1-O6} = 2.615(3)$, $\text{La1-N1} = 2.618(4)$, $\text{La1-O3} = 2.639(3)$, $\text{La1-I1} = 3.2152(5)$, $\text{La1-I2} = 3.2304(4)$, $\text{O1-La1-O2} = 62.22(8)$, $\text{O5-La1-O4} = 62.59(8)$, $\text{O5-La1-O6} = 60.83(8)$, $\text{O1-La1-O6} = 62.19(8)$, $\text{O2-La1-O3} = 60.64(8)$, $\text{O4-La1-O3} = 61.24(8)$, $\text{N1-La1-I1} = 140.82(8)$, $\text{N1-La1-I2} = 70.67(8)$, $\text{I1-La1-I2} = 147.857(12)$.

ESI^\dagger If the reaction of LaI_3 and 18-crown-6 is conducted in MeCN solution in the presence of $[\text{NH}_4]\text{PF}_6$, the product is $[\text{LaI}_2(\text{18-crown-6})]\text{PF}_6$. Lanthanum easily switches between eight- and nine-coordinate depending upon the ligand set and the conditions. We also carried out conductivity measurements of several $[\text{MI}_3(\text{crown})]$ complexes in $10^{-3} \text{ mol dm}^{-3}$ MeCN and found the values (Experimental section) were much higher than expected for 1 : 1 electrolytes, showing that in the



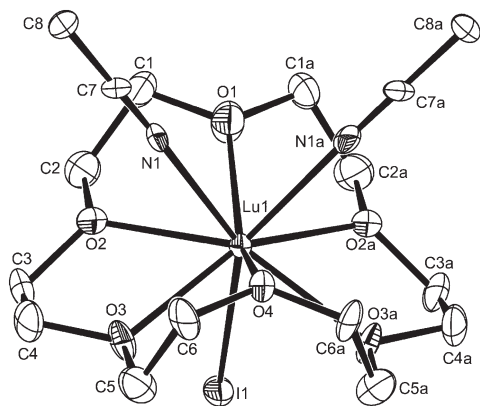


Fig. 8 The structure of the cation in $[\text{LuI}(18\text{-crown-6})(\text{MeCN})_2]_2$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The cation has mirror symmetry. Symmetry operation: $a = x, 1/2 - y, z$. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Lu1-O1} = 2.353(13)$, $\text{Lu1-O2} = 2.405(9)$, $\text{Lu1-O3} = 2.423(8)$, $\text{Lu1-N1} = 2.425(11)$, $\text{Lu1-O4} = 2.432(11)$, $\text{Lu1-I1} = 3.075(2)$, $\text{O1-Lu1-O2} = 64.8(2)$, $\text{O2-Lu1-O3} = 64.5(3)$, $\text{N1-Lu1-N1a} = 71.7(5)$, $\text{O3-Lu1-O4} = 66.0(3)$, $\text{N1-Lu1-I1} = 143.1(2)$.

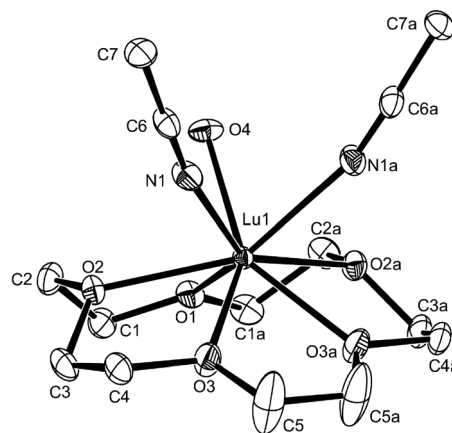


Fig. 9 The structure of the cation in $[\text{Lu}(15\text{-crown-5})(\text{MeCN})_2(\text{OH}_2)]_3$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The cation has mirror symmetry. Symmetry operation: $a = x, 1/2 - y, z$. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Lu1-O4} = 2.257(5)$, $\text{Lu1-O3} = 2.303(4)$, $\text{Lu1-O1} = 2.317(5)$, $\text{Lu1-O2} = 2.361(3)$, $\text{Lu1-N1} = 2.401(4)$, $\text{O3-Lu1-O3a} = 65.30(18)$, $\text{O3-Lu1-O2} = 67.09(13)$, $\text{O1-Lu1-O2} = 67.78(9)$, $\text{N1-Lu1-N1a} = 70.3(2)$.

very dilute solutions, the iodide ligands are displaced.³⁴ In contrast, $[\text{La}(\text{O}_3\text{SCF}_3)_2(18\text{-crown-6})][\text{O}_3\text{SCF}_3]$, prepared from $\text{La}(\text{O}_3\text{SCF}_3)_3$ and the crown in MeCN (see ESI[†]), is a 1:1 electrolyte, showing that the hard triflate ligands are not easily displaced, contrasting with the soft iodide. All attempts to observe ^{139}La NMR spectra from iodide complexes failed, attributed to fast quadrupolar relaxation in the low symmetry environments. However, for $[\text{La}(\text{O}_3\text{SCF}_3)_2(18\text{-crown-6})]^+$ in which the O_8 donor set would be expected to produce a smaller electric field gradient, a broad resonance was observed at $\delta = -112$ ($W_{1/2} = 3000$ Hz).

Lutetium is significantly smaller than lanthanum and hence might be expected to favour a lower coordination number and/or smaller ligands. The complexes $[\text{Lu}_2(15\text{-crown-5})\text{I}]$ and $[\text{LuI}(18\text{-crown-6})(\text{MeCN})_2]_2$ were isolated from MeCN solutions of the constituents. Crystals of the latter showed (Fig. 8) the two nitrile ligands arranged on one side and the iodide on the other side of the puckered macrocycle ring. Comparisons of the bond lengths from the structures in Fig. 7 and 8 clearly show the effect of the decreased radius of Lu^{3+} .

Crystals grown from an MeCN solution of $[\text{Lu}_2(15\text{-crown-5})\text{I}]$ were found to be $[\text{Lu}(15\text{-crown-5})(\text{MeCN})_2(\text{OH}_2)]_3$, where all three iodides had been displaced by MeCN and adventitious water (Fig. 9).

The complexes $[\text{LaI}_3([15]\text{aneO}_3\text{S}_2)]$, $[\text{LaI}_3([18]\text{aneO}_4\text{S}_2)]$, $[\text{LaI}_3([18]\text{aneO}_4\text{Se}_2)]$, $[\text{NdI}_3([18]\text{aneO}_4\text{Se}_2)]$, $[\text{Lu}_2([18]\text{aneO}_4\text{S}_2)\text{I}]$ and $[\text{Lu}_2([18]\text{aneO}_4\text{Se}_2)\text{I}]$ were isolated from reaction of the appropriate lanthanide iodide with the ligands in anhydrous MeCN. The spectroscopic data and microanalyses are consistent with the formulations, but the main interest lies in the structures. The $[\text{LaI}_3([18]\text{aneO}_4\text{S}_2)]$ and $[\text{LaI}_3([18]\text{aneO}_4\text{Se}_2)]$ are isomorphous and contain nine-coordinate lanthanum centres with the metal *endo*-coordinated to all six donors of the

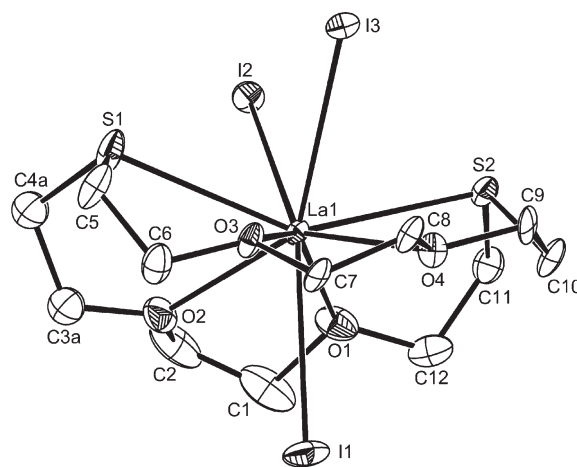


Fig. 10 Structure of $[\text{La}_3([18]\text{aneO}_4\text{S}_2)]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. C3 and C4 were disordered and modelled as two sites A/B. Only the 3A and 4A sites are shown in the figure. Selected bond lengths (\AA) and angles ($^\circ$): $\text{La1-O3} = 2.582(4)$, $\text{La1-O2} = 2.618(4)$, $\text{La1-O4} = 2.622(4)$, $\text{La1-O1} = 2.635(4)$, $\text{La1-S2} = 3.004(1)$, $\text{La1-S1} = 3.015(2)$, $\text{La1-I2} = 3.2678(6)$, $\text{La1-I3} = 3.2999(7)$, $\text{La1-I1} = 3.3124(6)$, $\text{O3-La1-O4} = 63.74(12)$, $\text{O2-La1-O1} = 63.1(2)$, $\text{O4-La1-S2} = 66.23(9)$, $\text{O1-La1-S2} = 65.20(10)$, $\text{O3-La1-S1} = 64.68(9)$, $\text{O2-La1-S1} = 66.26(11)$, $\text{S2-La1-S1} = 144.76(4)$, $\text{I2-La1-I3} = 77.877(13)$, $\text{I2-La1-I1} = 141.33(2)$, $\text{I3-La1-I1} = 140.735(14)$.

puckered ring and with two iodides above and one below the plane (Fig. 10 and 11). The La-O and La-I bond distances are not significantly different between the two structures, but interestingly the La-S and La-Se differ only by ~ 0.01 \AA , compared to the differences in covalent radii of the chalcogens of 0.015 \AA .³⁵ Whilst this could be seen as evidence of stronger interaction with the selenium donors, this seems unlikely and a possible explanation is that the constraints of the macrocycle ring play a significant role in the M-S/Se bond lengths. The

^{139}La $I = 7/2$, 99.9%, $\Xi = 14.13$ MHz, $Q = -0.21 \times 10^{-28}$ m², $R_c = 336$.



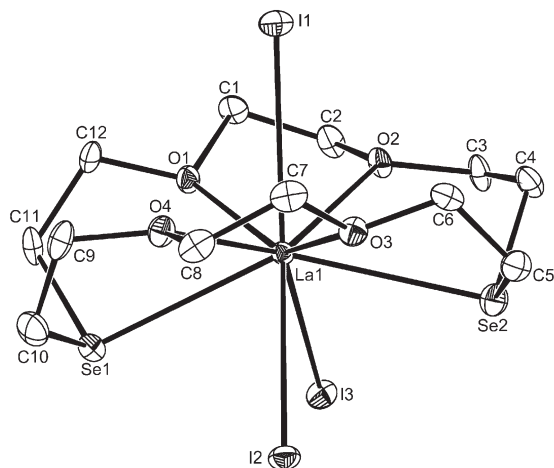


Fig. 11 Structure of $[\text{LaI}_3([\text{18}] \text{aneO}_4\text{Se}_2)]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): La1–O1 = 2.560(3), La1–O2 = 2.604(3), La1–O4 = 2.609(4), La1–O3 = 2.634(3), La1–Se2 = 3.0885(7), La1–Se1 = 3.0971(7), La1–I2 = 3.2658(6), La1–I3 = 3.3244(7), La1–I1 = 3.3565(6), O1–La1–O2 = 64.27(10), O4–La1–O3 = 63.88(11), O2–La1–Se2 = 67.96(7), O3–La1–Se2 = 66.56(8), O1–La1–Se1 = 64.51(7), O4–La1–Se1 = 67.62(8), Se2–La1–Se1 = 140.63(2), I2–La1–I3 = 78.705(11), I2–La1–I1 = 141.297(14), I3–La1–I1 = 139.502(13).

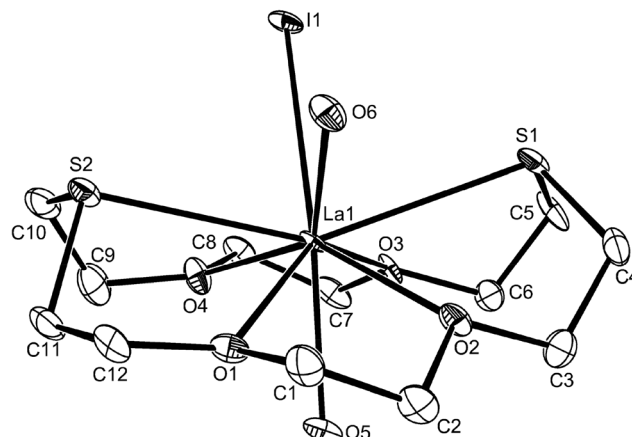


Fig. 12 Structure of the cation in $[\text{LaI}([\text{18}] \text{aneO}_4\text{S}_2)(\text{OH}_2)_2]_2 \cdot \text{H}_2\text{O}$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms on C are omitted for clarity. H atoms were not identified on the water ligands. Selected bond lengths (Å) and angles ($^\circ$): La1–O5 = 2.508(5), La1–O6 = 2.519(5), La1–O3 = 2.568(5), La1–O2 = 2.588(5), La1–O1 = 2.606(5), La1–O4 = 2.608(6), La1–S2 = 3.012(2), La1–S1 = 3.063(2), La1–I1 = 3.2385(7), O5–La1–O6 = 136.3(2), O3–La1–O2 = 104.60(15), O2–La1–O1 = 64.18(15), O3–La1–O4 = 62.92(15), O1–La1–S2 = 65.15(11), O4–La1–S2 = 66.27(12), O3–La1–S1 = 64.67(11), O2–La1–S1 = 64.34(11), S2–La1–S1 = 147.69(5), O5–La1–I1 = 147.54(13), O6–La1–I1 = 76.13(12).

structure was also obtained of the hydrolysis product $[\text{LaI}([\text{18}] \text{aneO}_4\text{S}_2)(\text{OH}_2)_2]_2 \cdot \text{H}_2\text{O}$ (Fig. 12).

The lutetium complexes $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{S}_2)]\text{I}$ and $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I}$ are isomorphous and contain eight-coordinate metal centres, reflecting the decreasing metal radius compared to lanthanum. The structure of $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I}$ shows the macrocycle ring is more folded and both iodides are on the same side of the metal, but compared to the geometry in $[\text{LaI}_3([\text{18}] \text{aneO}_4\text{Se}_2)]$, the differences in bond lengths are much as expected given the reduced metal radius of Lu^{3+} .

The ^1H NMR spectra of this series of compounds show broad singlets for the inequivalent methylene groups, but again couplings are not resolved. For the $[\text{LaI}_3([\text{18}] \text{aneO}_4\text{Se}_2)]$ and $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I}$ the $^{77}\text{Se}\{^1\text{H}\}$ spectra show small low frequency coordination shifts of -3 (La) and -32 (Lu), and in the presence of free $[\text{18}] \text{aneO}_4\text{Se}_2$ the chemical shifts are unchanged, showing exchange of the macrocycle is slow on the NMR timescale (Fig. 13).

Conclusions

A series of oxa-thia and oxa-selenium macrocycle complexes of trivalent Sc, Y, La and Lu have been prepared and characterised spectroscopically and in many cases by X-ray crystallography. The new complexes contain rare examples of these hard metal ions coordinated to neutral sulfur donor centres, and include

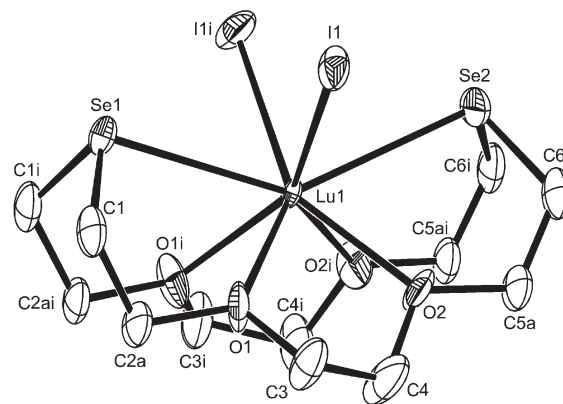


Fig. 13 The structure of the cation in $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{Se}_2)]\text{I} \cdot 2\text{MeCN}$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The cation has mirror symmetry. Symmetry operation: $i = x, 1/2 - y, z$. Selected bond lengths (Å) and angles ($^\circ$): Lu1–O2 = 2.348(8), Lu1–O1 = 2.368(8), Lu1–Se2 = 2.8959(18), Lu1–Se1 = 2.9034(17), Lu1–I1 = 2.9974(10), O2–Lu1–O1 = 68.1(3), O2–Lu1–Se2 = 69.8(2), O1–Lu1–Se1 = 71.32(18), Se2–Lu1–Se1 = 139.19(5), I1–Lu1–I1i = 94.67(4).

the first examples of coordination with neutral selenium donor groups. All contain *endo*-coordinated macrocycles with all of the neutral donors bonded to the metal centres. The use of the MI_3 ($\text{M} = \text{Sc}, \text{Y}, \text{La}$ or Lu) for preparing complexes of this type offers considerable benefits in solubility over the corresponding chlorides, allowing direct reaction of MI_3 with the macrocycle (not possible with MCl_3 and the heterocrowns), although the resulting iodo-complexes are extremely moisture sensitive. The data on the crown ether complexes show that the coordinated halides are readily displaced by traces of water

|| Poor quality crystals of $[\text{LuI}_2([\text{18}] \text{aneO}_4\text{S}_2)]\text{I} \cdot 2\text{MeCN}$ were isomorphous with the seleno-oxo-crown analogue. $a = 15.440(6)$, $b = 11.847(4)$, $c = 14.821(6)$, $\alpha = \beta = \gamma = 90$, $V = 2711.2(18)$, $z = 4$. The crystal quality was poor and refined to give R_1 ($I > 2\sigma I$) = 0.0986.



and, in some cases, partially by MeCN. More significantly, in the oxa-thia and oxa-selena crown complexes, similar displacement of halide occurs, while the M–S(Se) coordination is retained. The high coordination numbers and the irregular coordination geometries adopted, mean that detailed comparisons of the structural data must be made with care, but overall it is clear that the flexibility of the ligands allows them to fit well to the range of metal ions studied ($r M^{3+} = 0.74\text{--}1.22 \text{ \AA}$); indeed there is evidence in the Sc systems that the larger sulfur donor atoms allow less strained coordination in the 18-membered rings than in the crown ether analogue. Comparison of the M–O and M–S distances show the latter are longer by an amount approximating to the increase in covalent radius³⁵ of the donor, which shows the M–S interactions, even on these hard metals, are significant. However, as noted above, the further increase in metal–donor bond lengths on going to M–Se is rather less than expected. Although the strength of the bonds to soft metal centres increases down Group 16 (*i.e.* S < Se),³³ this seems unlikely to be the case with the hard M³⁺ cations, and the observed effect probably reflects the mutual accommodation of the donors within the constraints of the macrocycle ring.

The ¹H NMR spectra of the complexes in solution at ambient temperatures show resonances broadened to varying degrees and without resolved couplings, indicative of dynamic processes. However, use of ⁷⁷Se NMR spectroscopy to study the selena-oxa crown complexes both with and without added macrocycle, show that ligand exchange between coordinated and ‘free’ macrocycle is slow on the NMR timescale, hence the dynamic processes seen in the ¹H NMR spectra would seem to be due to reversible dissociation of single donor centres, rather than intermolecular ligand exchange. The stability of the thia-oxa and selena-oxa macrocyclic complexes raises the prospect that complexes of macrocycles with higher chalcogen content, or even of homoleptic large thia- or selena-crowns, may be obtainable under appropriate anhydrous conditions and using the MI₃ or MCl₃ + chloride abstractor synthon strategy, and this will form the basis of a further study.

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