Complexes of Group 2 dications with soft thioether- and selenoether-containing macrocycles†

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A new route to cationic complexes of Mg, Ca, Sr and Ba with 18-membered ring O_4S_2, O_4Se_2 and O_2S_4 donor macrocycles from metal acetonitrile complexes with weakly coordinating $[BAr^F]^-$ anions is described. The precursors used were $[M(MeCN)_x][BAr^F]_2$ (M = Mg, x = 6; M = Ca, x = 8) and $[M'(acacH)(MeCN)_5][BAr^F]_2$ (M' = Sr or Ba). Reaction of these with the heterocrowns, [18]aneO_4S_2 (1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane), [18]aneO_4Se_2 (1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane) or [18]aneO_2S_4 (1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane) in anhydrous CH_2Cl_2 solution gave $[M(heterocrown)(MeCN)_2][BAr^F]_2$ for M = Mg, Ca or Sr, whilst the larger Ba forms $[Ba(heterocrown)(acacH)(MeCN)][BAr^F]_2$. The complexes have been characterised by microanalysis, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. X-ray crystal structures are reported for $[Ca([18]aneO_2S_4)(MeCN)_2][BAr^F]_2$, $[Ca([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$, $[Sr([18]aneO_4S_2)(MeCN)_2][BAr^F]_2$, and $[Sr([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$ which contain 8-coordinate metal centres with *trans*-nitrile ligands and κ^6-heterocrowns, and for the 9-coordinate $[Ba([18]aneO_4Se_2)(acacH)(MeCN)][BAr^F]_2$. Adventitious hydrolysis of the magnesium complexes in solution results in six-coordinate complexes, $[Mg(\kappa^3-[18]aneO_4Se_2)(OH_2)_2(MeCN)][BAr^F]_2$ and $[Mg(\kappa^3-[18]aneO_4S_2)(OH_2)_2(MeCN)][BAr^F]_2$, whose structures were determined. X-ray crystal structures are also reported for $[Mg(MeCN)_6][BAr^F]_2$, $[M(MeCN)_8][BAr^F]_2$ (M = Ca, Sr) and $[Ca(18-crown-6)(MeCN)_2][BAr^F]_2$.

Introduction

The chemistries of the heavier alkaline earth metals (Ca, Sr and Ba) are dominated by the hard M^{2+} cations and their salts with oxo-anions or halides.[1] Barium and strontium salts have niche applications, for example $BaSO_4$ in the oil industry and medicine, but the key importance is of calcium salts, which range from engineering and construction ($CaCO_3$, $CaSO_4$, $Ca(OH)_2$) to apatite in mammalian bones and $CaCO_3$ in corals and shells. For many years their coordination chemistry with neutral ligands was very limited and the organometallic chemistry among the most restricted in the main group.[1–3] However, the last 20 years have seen the development of the coordination chemistry with both charged and neutral oxygen and nitrogen ligands,[4] and despite the synthetic challenges and high reactivities, of a significant organometallic chemistry.[5] The coordination chemistry of magnesium is more familiar, not least because of the importance of chlorophyll and chlorophyll model compounds,[4] while Grignard reagents have been

known for over 100 years.[6] Despite these recent developments, the synthesis of complexes of these elements retains significant challenges, not least the lability of the metal centres, which often results in unpredicted products or mixtures, even in apparently simple systems.[7] We have recently been exploring the use of weakly coordinating fluorinated tetraarylborate anions, such as $[B\{3,5-(CF_3)_2C_6H_3\}_4]^-$ (hereafter BAr^F) to obtain unusual complexes of the Group 1 metal ions, including the synthesis of homoleptic neutral diphosphine complexes of lithium and sodium, $[M(L–L)_3][BAr^F]$ (M = Li or Na; L–L = $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$),[8] the homoleptic octathioether complex of sodium, $[Na([24]aneS_8)][BAr^F]$ ([24]aneS_8 = 1,4,7,10,13,16,19,22-octathiacyclotetracosane),[9] complexes of Li-Cs of N_3-, N_4- and N_6-donor azamacrocycles,[10] and with the heterocrowns, [18]aneO_2S_4 (1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane), [18]aneO_4S_2 (1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane) and [18]aneO_4Se_2 (1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane).[11] These contain rare coordination of the neutral sulfur or selenium donors to the alkali metal centre. Heterocrowns containing S- or Se-donor atoms have an extensive chemistry with d- and p-block metals,[12] but examples with the s-block elements are few. In addition to the Group 1 examples described above, we reported examples of neutral eight-coordinate complexes of CaI_2 and SrI_2 with [18]aneO_4S_2, [18]aneO_2S_4 and [18]aneO_4Se_2.[13] The complex $[Ca(ClO_4)_2([18]aneO_4S_2)]$,[14] the lamellar polymer $[Ba\{Cu(SCN)_3([18]-$

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†Electronic supplementary information (ESI) available: X-ray data on [Sr(MeCN)$_8$][BAr^F]$_2$ and [Ca(18-crown-6)(MeCN)$_2$][BAr^F]$_2$. Spectroscopic data on the complexes. CCDC 1455287–1455298. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00808a

aneO$_4$S$_2$)}],[15] and [Mg(R-benzo[18]aneO$_4$S$_2$)][16] (R-benzo[18]-aneO$_4$S$_2$ = R-benzo-substituted [18]aneO$_4$S$_2$) are also known. The present paper describes the synthesis, structures and spectroscopic properties of complexes of [18]aneO$_4$S$_2$, [18]aneO$_2$S$_4$ and [18]aneO$_4$Se$_2$ with Mg, Ca, Sr and Ba dications, utilising the [BAr^F]$^-$ anions to afford soluble cationic precursor species.

Experimental

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous MgI$_2$, CaI$_2$, SrI$_2$ and BaI$_2$ were purchased from Sigma and used as received. Anhydrous [Sr(acac)$_2$] was prepared by dehydrating commercial [Sr(acac)$_2$(H$_2$O)$_2$] (Sigma): the hydrate was suspended in CH$_2$Cl$_2$ over 4 Å molecular sieves and stirred gently for 2 weeks, then the suspension was decanted away and concentrated to dryness. [Ba(acac)$_2$] was synthesized by reacting BaI$_2$ and K(acac) in a 1 : 2 molar ratio in MeCN followed by extraction of KI with anhydrous acetone. Na[BAr^F] and [H(OEt$_2$)$_2$][BAr^F] were synthesized using Brookhart's procedure.[17] 18-Crown-6 was purchased from Sigma and dried using SOCl$_2$ and the macrocycles [18]aneO$_4$S$_2$, [18]aneO$_2$S$_4$ and [18]aneO$_4$Se$_2$ were synthesized using literature procedures.[18] CH$_2$Cl$_2$ and MeCN were dried by distillation from CaH$_2$ and n-hexane distilled from Na/K alloy. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in CD$_2$Cl$_2$ solution at 298 K using a Bruker AV II-400 spectrometer and are referenced to the residual CH$_2$Cl$_2$ resonance. IR spectra were recorded as mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. Microanalyses were undertaken at London Metropolitan University.

X-ray crystallography

Crystals were obtained as described below. Details of the crystallographic data collection and refinement are in Table 1. Diffractometer: *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_1 = 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.[19] Structure solution and refinement were carried out using WinGX and software packages within.[20] Disorder in the CF$_3$ groups of the [BAr^F]$^-$ anions was present in all of the structures, which is often observed in compounds containing [BAr^F]$^-$,[10,11] and this was satisfactorily modelled using DFIX, DANG, ISOR, DELU, and SIMU restraints. Positional disorder was also present in the macrocycle ligands and was modelled similarly. The dataset for [Ca([18]aneO$_4$S$_2$)(bipy)][BAr^F]$_2$ was collected from a poor-quality crystal which was very weakly diffracting at high angles, thus leading to very high R_{int} values. Repeated attempts at recrystallization of the sample failed to afford better quality crystals. A large amount of residual electron density was located ~1.05 Å from an Se atom in [Ba([18]aneO$_4$Se$_2$)(acacH)-

(MeCN)][BAr^F]$_2$ which could not be satisfactorily modelled as either disordered Se or disordered carbon. H-atoms were placed in geometrically-assigned positions with C–H distances of 0.95 Å (CH), 0.98 Å (CH$_3$) or 0.99 Å (CH$_2$) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C) (CH, CH$_2$) or 1.5U_{eq}(C) (CH$_3$). enCIFer was used to prepare material for publication.[21] CCDC reference numbers 1455287 [Mg(MeCN)$_6$][BAr^F]$_2$, 1455288 [Mg(κ^3-[18]aneO$_4$S$_2$)(OH$_2$)$_2$(MeCN)][BAr^F]$_2$, 1455289 [Mg(κ^3-[18]aneO$_4$Se$_2$)(OH$_2$)$_2$(MeCN)][BAr^F]$_2$, 1455290 [Ca(MeCN)$_8$][BAr^F]$_2$, 1455291 [Ca(18-crown-6)(MeCN)$_2$][BAr^F]$_2$, 1455292 [Ca([18]aneO$_2$S$_4$)(MeCN)$_2$][BAr^F]$_2$, 1455293 [Ca([18]aneO$_4$Se$_2$)(MeCN)$_2$][BAr^F]$_2$, 1455294 [Ca([18]aneO$_4$S$_2$)-(bipy)][BAr^F]$_2$, 1455295 [Sr(MeCN)$_8$][BAr^F]$_2$, 1455296 [Sr([18]aneO$_4$S$_2$)(MeCN)$_2$][BAr^F]$_2$, 1455297 [Sr([18]aneO$_4$Se$_2$)-(MeCN)$_2$][BAr^F]$_2$ and 1455298 [Ba([18]aneO$_4$Se$_2$)(acacH)-(MeCN)][BAr^F]$_2$ contain crystallographic data in CIF format.

[Mg(MeCN)$_6$][BAr^F]$_2$. A mixture of MgI$_2$ (0.34 g, 1.21 mmol) and Na[BAr^F] (2.50 g, 2.43 mmol) were dissolved in MeCN (10 mL) and stirred for 24 h. Solvents were removed, the residue extracted with Et$_2$O (20 mL), filtered and dried *in vacuo*. The solid was redissolved in MeCN (5 mL), stirred for 30 min and then taken to dryness again. The resulting solid was dissolved in CH$_2$Cl$_2$ (10 mL) and n-hexane (100 mL) was added to precipitate an off-white solid. Yield: 0.55 g, 23%. Crystals were grown by vapour diffusion of n-hexane into a concentrated solution in CH$_2$Cl$_2$. Anal. Required for C$_{76}$H$_{42}$B$_2$F$_{48}$MgN$_6$ (1997.09): C, 45.71; H, 2.12; N, 4.21. Found: C, 45.61; H, 2.02; N, 4.17%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.74 (s, [16H], BAr^F H2/6), 7.60 (s, [8H], BAr^F H4), 2.16 (s, [18H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.30 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 134.92 (BAr^F C2/6), 129.30 (q, $^2J_{C-F}$ = 32 Hz, BAr^F C3/5), 124.73 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.16 (BAr^F, C4), 117.87 (C, MeCN), 2.18 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2321, 2295 (MeCN), 1611, 1357, 1282, 1261, 1111, 1022, 883, 801, 669, 403.

[Ca(MeCN)$_8$][BAr^F]$_2$. A mixture of CaI$_2$ (0.25 g, 0.85 mmol) and Na[BAr^F] (1.50 g, 1.69 mmol) were dissolved in MeCN (10 mL) and stirred for 24 h, affording a yellow solution. Solvents were removed, the residue extracted with Et$_2$O (20 mL), filtered and dried *in vacuo*. The solid was redissolved in MeCN (5 mL), stirred for 30 min and then concentrated to dryness again. The resulting solid was dissolved in CH$_2$Cl$_2$ (10 mL) and n-hexane (100 mL) was added to precipitate an off-white solid. Yield: 1.06 g, 70%. Crystals were grown by layering a concentrated CH$_2$Cl$_2$ solution with n-hexane. Attempts to obtain accurate elemental analyses failed due to ready loss of MeCN ligands on drying. Samples sent for elemental analysis were consistent with between five and six MeCN ligands coordinated to calcium. The composition with eight MeCN ligands comes from the X-ray structure. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.72 (s, BAr^F H2/6), 7.57 (s, BAr^F H4), 2.07 (s, CH$_3$). IR (Nujol/cm^{-1}): 2310, 2282 (MeCN), 1611, 1282, 1118, 933, 897, 889, 840, 745, 713, 683, 671, 451.

[Sr(acacH)(MeCN)$_5$][BAr^F]$_2$. [Sr(acac)$_2$] (0.071 g, 0.25 mmol) was suspended in MeCN (20 mL) and a solution of [H(OEt$_2$)$_2$][BAr^F] (0.51 g, 0.50 mmol) in MeCN (10 mL) was

Table 1 Crystallographic parameters for the compounds reported

Compound	$[Ca(MeCN)_8][BAr^F]_2$	$[Ca([18]aneO_2S_4)(MeCN)_2][BAr^F]_2$	$[Ca([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$	$[Ca([18]aneO_4S_2)(bipy)][BAr^F]_2$
Formula	$C_{80}H_{48}B_2CaF_{48}N_8$	$C_{80}H_{54}B_2CaF_{48}N_2O_2S_4$	$C_{80}H_{54}B_2CaF_{48}N_2O_4Se_2$	$C_{86}H_{56}B_2CaF_{48}N_2O_4S_2\cdot CH_2Cl_2$
M/g mol^{-1}	2094.96	2177.19	2238.87	2304.07
Crystal system	Tetragonal	Monoclinic	Triclinic	Triclinic
Space group (no.)	$P4/nnc$ (126)	$C2/c$ (15)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a/Å	15.691(3)	18.674(3)	13.201(2)	17.10(1)
b/Å	15.691(3)	18.249(2)	13.554(3)	17.14(1)
c/Å	18.386(5)	26.280(4)	14.019(2)	20.12(2)
α/°	90	90	77.162(9)	111.727(9)
β/°	90	97.626(2)	63.267(7)	94.775(9)
γ/°	90	90	87.06(1)	116.229(6)
U/Å^3	4527(2)	8876(2)	2180.7(6)	4692(6)
Z	2	4	1	2
μ (Mo-Kα)/mm^{-1}	0.216	0.314	1.060	1.631
$F(000)$	2092	4360	1110	2308
Total reflections	31 064	28 599	16 936	58 691
Unique reflections	2009	7839	7679	19 180
R_{int}	0.071	0.044	0.046	0.297
Goodness-of-fit on F^2	1.065	1.043	1.032	0.917
R_1 [$I_o > 2\sigma(I_o)$]	0.082	0.089	0.069	0.091
R_1 (all data)	0.118	0.120	0.101	0.334
wR_2 [$I_o > 2\sigma(I_o)$]	0.263	0.240	0.168	0.146
wR_2 (all data)	0.289	0.272	0.188	0.237

Compound	$[Mg(MeCN)_6][BAr^F]_2$	$[Mg(\kappa^3\text{-}[18]aneO_4S_2)(H_2O)_2(MeCN)][BAr^F]_2\, C_6H_{14}$	$[Mg(\kappa^3\text{-}[18]aneO_4Se_2)(H_2O)_2(MeCN)][BAr^F]_2\, C_6H_{14}$
Formula	$C_{76}H_{42}B_2F_{48}MgN_6$	$C_{78}H_{55}B_2F_{48}MgNO_6S_2\cdot C_6H_{14}$	$C_{78}H_{55}B_2F_{48}MgNO_6Se_2\cdot C_6H_{14}$
M/g mol^{-1}	1997.08	2210.45	2304.25
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group (no.)	$Pnn2$ (34)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a/Å	17.574(4)	12.778(3)	12.792(2)
b/Å	14.570(3)	13.713(4)	13.802(2)
c/Å	16.836(4)	14.080(4)	13.953(2)
α/°	90	84.20(1)	83.273(7)
β/°	90	71.851(9)	73.413(6)
γ/°	90	85.42(1)	84.567(7)
U/Å^3	4311(2)	2329(1)	2339.8(6)
Z	2	1	1
μ (Mo-Kα)/mm^{-1}	0.170	0.212	0.944
$F(000)$	1988	1114	1150
Total reflections	51 977	28 740	21 341
Unique reflections	8528	16 822	15 067
R_{int}	0.084	0.051	0.042
Goodness-of-fit on F^2	1.014	1.017	0.940
R_1 [$I_o > 2\sigma(I_o)$]	0.053	0.081	0.078
R_1 (all data)	0.081	0.137	0.110
wR_2 [$I_o > 2\sigma(I_o)$]	0.131	0.191	0.196
wR_2 (all data)	0.145	0.226	0.218

Compound	$[Sr([18]aneO_4S_2)(MeCN)_2][BAr^F]_2$	$[Sr([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$	$[Ba([18]aneO_4Se_2)(acacH)(MeCN)][BAr^F]_2$
Formula	$C_{80}H_{54}B_2F_{48}N_2O_4S_2Sr$	$C_{80}H_{54}B_2F_{48}N_2O_4Se_2Sr$	$C_{83}H_{59}B_2BaF_{48}NO_6Se_2\cdot 0.75CH_2Cl_2$
M/g mol^{-1}	2192.61	2286.41	2455.89
Crystal system	Triclinic	Triclinic	Triclinic
Space group (no.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a/Å	13.1237(7)	13.181(2)	12.2148(3)
b/Å	13.7167(6)	13.588(2)	18.3147(4)
c/Å	13.8415(8)	13.965(2)	21.778(2)
α/°	76.537(4)	77.134(6)	85.024(6)
β/°	63.147(5)	63.202(5)	82.079(6)
γ/°	87.410(4)	87.516(7)	88.732(6)
U/Å^3	2157.0(2)	2171.8(5)	4814.2(4)
Z	1	1	2
μ (Mo-Kα)/mm^{-1}	0.829	1.613	1.354
$F(000)$	1092	1128	2422
Total reflections	30 737	26 961	55 310
Unique reflections	8828	8858	16 971
R_{int}	0.060	0.059	0.055
Goodness-of-fit on F^2	1.043	1.034	1.036
R_1 [$I_o > 2\sigma(I_o)$]	0.074	0.057	0.098
R_1 (all data)	0.102	0.081	0.122
wR_2 [$I_o > 2\sigma(I_o)$]	0.185	0.150	0.267
wR_2 (all data)	0.203	0.169	0.289

Common items: T = 100 K, λ_1 = 0.71073 Å (Mo Kα), θ_{max} = 27.5°, R_1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR_2 = $[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$.

added *via* a cannula. Most of the solids dissolved and the reaction was stirred for 16 h. After this time solvents were removed and the resulting white solid extracted into CH_2Cl_2 (2 × 30 mL). The extracts were combined and concentrated to ~5 mL, then *n*-hexane (30 mL) was added to precipitate a white solid which was isolated by decanting away the supernatant and drying *in vacuo*. Yield: 0.45 g, 85%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.72 (s, [16H], BAr^F H2/6), 7.57 (s, [8H], BAr^F H4), 3.81 (s, [2H], CH_2, acacH), 2.26 (s, [6H], CH_3, acacH), 2.13 (s, [15H], CH_3, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.32 (q, J_{C-B} = 49.9 Hz, BAr^F, C1), 135.38 (BAr^F, C2/6), 129.47 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F, C3/5), 125.19 (q, J_{C-F} = 272 Hz, CF$_3$), 118.09 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F, C4), 52.89 (CH$_2$, acacH), 32.66 (CH$_3$, acacH), 2.14 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2309 and 2281 (MeCN), 1751, 1714 (acacH) 1611, 1281, 1117, 932, 888, 840, 714, 683, 670. Despite repeated attempts, satisfactory elemental analysis could not be obtained due to the easy loss of the MeCN ligands. A few crystals of [Sr(MeCN)$_8$][BAr^F]$_2$ were obtained by layering a concentrated CH_2Cl_2 solution of the title compound with *n*-hexane.

[Sr(MeCN)$_8$][BAr^F]$_2$. Obtained as a by-product as above: ^1H NMR (CD_2Cl_2, 298 K): δ = 7.72 (s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 2.03 (s, [24H], CH$_3$, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.06 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.37 (BAr^F C2/6), 129.64 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.53 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.05 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 2.20 (s, CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2309, 2281 (MeCN), 1611, 1282, 1126, 888, 816, 683, 670.

[Ba(acacH)(MeCN)$_5$][BAr^F]$_2$. As for the Sr analogue, using [Ba(acac)$_2$] (0.084 g). Yield: 0.33 g of a white solid, 60%. Anal. Required for $C_{79}H_{47}B_2BaF_{48}N_5O_2$ (2169.49): C, 43.74; H, 2.18; N, 3.23. Found: C, 43.63; H, 2.04; N, 3.35%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.72 (s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 2.67 (s, [6H], acacH CH$_3$), 2.24 and 2.20 (each s, [3H], acacH CH$_2$), 2.00 (s, [15H], CH$_3$ MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.32 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.38 (BAr^F C2/6), 129.48 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.19 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.10 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 80.60 (CH$_2$, acacH), 32.65 (CH$_3$, acacH), 1.98 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2307, 2277 (MeCN), 1751 (acacH), 1611, 1281, 1117, 888, 840, 713, 683, 670.

General method for complex synthesis

The Group 2 [BAr^F] salt was suspended in CH_2Cl_2 (5 mL) and a solution of the macrocycle in CH_2Cl_2 (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 the solid *in vacuo*.

[Mg(18-crown-6)(MeCN)$_2$][BAr^F]$_2$. [Mg(MeCN)$_6$][BAr^F]$_2$ (0.050 g, 0.025 mmol) and 18-crown-6 (0.007 g, 0.025 mmol) afforded 0.039 g of a yellow solid in 74% yield. Anal. Required for $C_{80}H_{54}B_2F_{48}MgN_2O_6$ (2097.19): C, 45.82; H, 2.60; N, 1.34. Found: C, 45.64; H, 2.50; N, 1.26%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.73 (s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.85

(s, [24H], OCH$_2$), 2.15 (s, [6H], CH$_3$, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.31 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 135.40 (BAr^F C2/6) 129.48 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz BAr^F, C3/5), 125.18 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 119.33 (C, MeCN), 118.16 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F, C4) 70.02 (s, OCH$_2$) 2.61 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2316, 2289 (MeCN), 1611, 1280, 1122 1106, 889, 839, 802, 682, 670, 402.

[Mg([18]aneO$_4$S$_2$)(MeCN)$_2$][BAr^F]$_2$. [Mg(MeCN)$_6$][BAr^F]$_2$ (0.050 g, 0.025 mmol) and [18]aneO$_4$S$_2$ (0.007 g, 0.025 mmol) afforded 0.044 g of an off-white solid in 82% yield. Anal. Required for $C_{80}H_{54}B_2F_{48}MgN_2O_4S_2 \cdot CH_2Cl_2$ (2214.07): C, 43.94; H, 2.55; N, 1.26. Found: C, 43.67 H, 2.74; N, 1.06%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.75 (br s, [16H], BAr^F H2/6), 7.60 (s, [8H], BAr^F H4), 3.93 (br s, [16H], OCH$_2$), 2.98 (br, t, [8H], SCH$_2$), 2.19 (s, [6H], CH$_3$ MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298K): δ = 161.93 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 135.96 (BAr^F C2/6), 129.06 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 124.78 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.16 (s, $^3J_{CF}$ = 4.0 Hz, BAr^F, C4), 117.72 (C, MeCN), 69.07 (s, OCH$_2$), 31.24 (s, SCH$_2$), 2.14 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2317, 2294 (MeCN), 1611, 1277, 1094, 1019, 887, 801, 682, 669.

[Mg([18]aneO$_2$S$_4$)(MeCN)$_2$][BAr^F]$_2$. [Mg(MeCN)$_6$][BAr^F]$_2$ (0.050 g, 0.025 mmol) and [18]aneO$_2$S$_4$ (0.008 g, 0.025 mmol) afforded 0.034 g of an off-white solid in 63% yield. Anal. Required for $C_{80}H_{54}B_2F_{48}MgN_2O_2S_4$ (2161.09): C, 44.46; H, 2.52; N, 1.30. Found: C, 44.61; H, 2.38; N, 1.32%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.74 (s, BAr^F H2/6), 7.58 (s, BAr^F H4), 3.78 (vbr, s, OCH$_2$), 2.84–2.94 (br s, SCH$_2$), 2.42 (s, CH$_3$, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.13 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 134.88 (BAr^F C2/6), 129.16 (br q, $^2J_{C-F}$ = 31.6 Hz, BAr^F C3/5), 124.78 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.16 (BAr^F C4), 117.93 (C, MeCN), 1.84 (CH$_3$, MeCN) – see text. IR (Nujol/cm^{-1}): 2322, 2296 (MeCN), 1612, 1282, 1115, 1023, 889, 840, 683, 670.

[Mg([18]aneO$_4$Se$_2$)(MeCN)$_2$][BAr^F]$_2$. [Mg(MeCN)$_6$][BAr^F]$_2$ (0.075 g, 0.038 mmol) and [18]aneO$_4$Se$_2$ (0.015 g, 0.038 mmol) afforded 0.057 g of a white powdery solid in 68% yield. Anal. Required for $C_{80}H_{54}B_2F_{48}MgN_2O_4Se_2$ (2223.12): C, 43.22; H, 2.45; N, 1.26. Found: C, 43.16; H, 2.44; N, 1.35%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.75 (br s, [16H], BAr^F H2/6), 7.60 (s, [8H], BAr^F H4), 4.01 (br, s, [16H], OCH$_2$), 2.95 (br s, [8H], SeCH$_2$), 2.15 (s, [6H], MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ = 162.13 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 135.09 (BAr^F C2/6), 129.06 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F, C3/5), 124.78 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.16 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F, C4), 117.78 (C, MeCN), 68.85 (s, OCH$_2$), 23.47 (s, SeCH$_2$), 2.04 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2322, 2295 (MeCN), 1611, 1281, 1112, 888, 839, 683, 669.

[Ca(18-crown-6)(MeCN)$_2$][BAr^F]$_2$. [Ca(MeCN)$_8$][BAr^F]$_2$ (0.100 g, 0.048 mmol) and 18-crown-6 (0.013 g, 0.048 mmol) afforded 0.078 g of a white solid in 77% yield. Anal. Required for $C_{80}H_{54}B_2CaF_{48}N_2O_6$ (2113.28): C, 45.48; H, 2.58; N, 1.33. Found: C, 45.55; H, 2.53; N, 1.41%. ^1H NMR (CD_2Cl_2, 298 K): δ = 7.73 (s, [16H], BAr^F H2/6), 7.57 (s, [8H], BAr^F H4), 3.81 (s, [18H], OCH$_2$), 2.13 (s, [6H], CH$_3$, MeCN). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K$_2$): δ = 162.31 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.37 (BAr^F C2/6), 129.45 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.17

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(q, J_{C-F} = 272 Hz, CF$_3$), 121.11 (C, MeCN), 118.08 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 70.04 (OCH$_2$), 2.29 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2309, 2279 (MeCN), 1611, 1280, 1129, 967, 901, 840, 682, 671, 586, 450.

[Ca([18]aneO$_4$S$_2$)(MeCN)$_2$][BAr^F]$_2$. [Ca(MeCN)$_8$][BAr^F]$_2$ (0.100 g, 0.048 mmol) and [18]aneO$_4$S$_2$ (0.014 g, 0.048 mmol) afforded 0.078 g of a white solid in 76% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$CaF$_{48}$N$_2$O$_4$S$_2$ (2145.23): C, 44.79; H, 2.54; N, 1.31. Found: C, 44.63; H, 2.45; N, 1.27%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.73 (s, [16H], BAr^F H2/6), 7.57 (s, [8H], BAr^F H4), 3.86–3.89 (m, [16H], OCH$_2$), 2.89 (br s, [8H], SCH$_2$), 2.10 (s, [6H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.33 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.48 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.19 (q, J_{C-F} = 272 Hz, CF$_3$), 119.06 (C, MeCN), 118.11 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 70.95, 70.70 (OCH$_2$), 31.73 (SCH$_2$), 2.30 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2307, 2276 (MeCN), 1611, 1279, 1117, 901, 889, 839, 744, 682, 670, 449.

[Ca([18]aneO$_2$S$_4$)(MeCN)$_2$][BAr^F]$_2$. [Ca(MeCN)$_8$][BAr^F]$_2$ (0.100 g, 0.048 mmol) and [18]aneO$_2$S$_4$ (0.016 g, 0.048 mmol) afforded 0.074 g of a white solid in 71% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$CaF$_{48}$N$_2$O$_2$S$_4$ (2177.19): C, 44.13; H, 2.50; N, 1.29. Found: C, 43.91; H, 2.41; N, 1.38%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.72 (s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.90 (t, J = 5.2 Hz, [8H], OCH$_2$), 3.01 (s, [8H], SCH$_2$), 2.92 (t, J = 5.0 Hz, [8H], SCH$_2$), 2.13 (s, [6H], CH$_3$ MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.34 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.40 (BAr^F C2/6), 129.49 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.21 (C, q, J_{C-F} = 272 Hz, CF$_3$), 120.25 (C, MeCN), 118.12 (CH, septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 70.97 (OCH$_2$), 32.12, 31.99 (SCH$_2$), 2.57 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2307, 2275 (MeCN), 1611, 1279, 1120, 901, 839, 682, 671.

[Ca([18]aneO$_4$Se$_2$)(MeCN)$_2$][BAr^F]$_2$. [Ca(MeCN)$_8$][BAr^F]$_2$ (0.100 g, 0.048 mmol) and [18]aneO$_4$Se$_2$ (0.019 g, 0.048 mmol) afforded 0.077 g of a white solid in 72% yield. Anal. calc. for C$_{80}$H$_{54}$B$_2$CaF$_{48}$N$_2$O$_4$Se$_2$ (2239.21): C, 42.91; H, 2.43; N, 1.25. Found: C, 42.82; H, 2.36; N, 1.16%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.72 (s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.95 (t, J = 5.6 Hz, [8H], OCH$_2$), 3.91 (s, [8H], OCH$_2$), 2.87 (br s, [8H], SeCH$_2$), 2.15 (s, [6H], CH$_3$ MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.33 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.47 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.20 (q, J_{C-F} = 272 Hz, CF$_3$), 120.63 (C, MeCN), 118.10 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.45, 71.32 (OCH$_2$), 25.53 (SCH$_2$), 2.63 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2307, 2275 (MeCN), 1611, 1280, 1130, 903, 840, 671.

[Sr(18-crown-6)(MeCN)$_2$][BAr^F]$_2$. [Sr(acacH)(MeCN)$_5$][BAr^F]$_2$ (0.100 g, 0.047 mmol) and 18-crown-6 (0.012 g, 0.047 mmol) afforded 0.069 g of a white solid in 68% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$F$_{48}$N$_2$O$_6$Sr (2160.82): C, 44.47; H, 2.52; N, 1.30. Found: C, 44.34; H, 2.38; N, 1.39%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.72 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.73 (s, [24H], OCH$_2$), 2.13 (s, [6H], CH$_3$ MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.31 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.48 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.18 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 119.33 (C, MeCN), 118.10

(septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 70.70 (OCH$_2$), 2.23 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2308, 2278 (MeCN), 1611, 1282, 1120, 1092, 974, 932, 900, 886, 839, 745, 682, 670, 448, 366.

[Sr([18]aneO$_4$S$_2$)(MeCN)$_2$][BAr^F]$_2$. [Sr(acacH)(MeCN)$_5$][BAr^F]$_2$ (0.100 g, 0.047 mmol) and [18]aneO$_4$S$_2$ (0.014 g, 0.047 mmol) afforded 0.089 g of a white solid in 86% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$F$_{48}$N$_2$O$_4$S$_2$Sr (2192.78): C, 43.82; H, 2.48; N, 1.28. Found: C, 43.69; H, 2.53; N, 1.25%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.73 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.82 (s, [8H], OCH$_2$), 3.78 (br s, [8H], OCH$_2$), 2.85 (v br s, [8H], SCH$_2$), 2.12 (s, [6H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.31 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.38 (BAr^F C2/6), 129.46 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.18 (C, q, J_{C-F} = 272 Hz, CF$_3$), 119.50 (C, MeCN), 118.10 (CH, septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.38, 70.16 (OCH$_2$), 31.50 (SCH$_2$), 2.28 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2303, 2275 (MeCN), 1612, 1282, 1148, 1090, 888, 682, 670, 580, 481, 450, 393.

[Sr([18]aneO$_2$S$_4$)(MeCN)$_2$][BAr^F]$_2$. [Sr(acacH)(MeCN)$_5$][BAr^F]$_2$ (0.100 g, 0.047 mmol) and [18]aneO$_2$S$_4$ (0.015 g, 0.047 mmol) afforded 0.085 g of a white solid in 86% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$F$_{48}$N$_2$O$_2$S$_4$Sr (2224.73): C, 43.19; H, 2.45; N, 1.26. Found: C, 43.25; H, 2.37; N, 1.18%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.73 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.87 (t, J = 5.1 Hz, [8H], OCH$_2$), 2.95 (s, [8H], SCH$_2$), 2.89 (t, J = 5.2 Hz, [8H], SCH$_2$), 2.08 (s, [6H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.32 ($^1J_{C-B}$ = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.43 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.19 (q, J_{C-F} = 272 Hz, CF$_3$), 119.24 (C, MeCN), 118.11 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.04 (OCH$_2$), 32.56, 32.41 (SCH$_2$), 2.26 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2308, 2280 (MeCN), 1611, 1281, 1127, 932, 899, 889, 839, 745, 683, 670, 383, 365.

[Sr([18]aneO$_4$Se$_2$)(MeCN)$_2$][BAr^F]$_2$. [Sr(acacH)(MeCN)$_5$][BAr^F]$_2$ (0.100 g, 0.047 mmol) and [18]aneO$_4$Se$_2$ (0.018 g, 0.047 mmol) afforded 0.077 g of a white solid in 72% yield. Anal. Required for C$_{80}$H$_{54}$B$_2$F$_{48}$N$_2$O$_4$Se$_2$Sr (2286.75): C, 42.02; H, 2.38; N, 1.22. Found: C, 42.14; H, 2.29; N, 1.25%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.73 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.82–3.94 (m, [16H], OCH$_2$), 2.87 (v br s, [8H], SeCH$_2$), 2.15 (s, [6H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.33 (q, $^1J_{C-B}$ = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.46 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.20 (q, J_{C-F} = 272 Hz, CF$_3$), 120.20 (C, MeCN), 118.11 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.43, 71.33 (OCH$_2$), 25.24 (SeCH$_2$), 2.40 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2305, 2275 (MeCN), 1611, 1284, 1140, 1117, 897, 886, 838, 682, 670, 579, 448, 392, 366.

[Ba([18]aneO$_2$S$_4$)(acacH)(MeCN)][BAr^F]$_2$. [Ba(acacH)(MeCN)$_5$][BAr^F]$_2$ (0.100 g, 0.046 mmol) and [18]aneO$_2$S$_4$ (0.015 g, 0.046 mmol) afforded 0.074 g of a white solid in 69% yield. Anal. Required for C$_{83}$H$_{59}$B$_2$BaF$_{48}$NO$_4$S$_4$ (2333.50): C, 42.72; H, 2.55; N, 0.60. Found: C, 42.60; H, 2.63; N, 0.71%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.73 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.86 (t, J = 5.0 Hz, [8H], OCH$_2$), 3.84 (s, [2H], acacH CH$_2$), 2.94 (s, [8H], SCH$_2$), 2.86 (t, J = 4.9 Hz, [8H], SCH$_2$), 2.29 (s, [6H], acacH CH$_3$), 2.05 (s, [6H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 209.66 (acacH CO), 162.34 (q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.40 (BAr^F C2/6), 129.48 (qq, $^2J_{C-F}$ = 31.6,
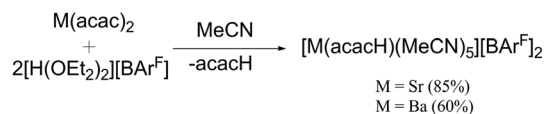
2.9 Hz, BAr^F C3/5), 125.21 (q, J_{C-F} = 272 Hz, CF$_3$), 118.12 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.11 (OCH$_2$), 53.63 (CH$_2$, acacH), 33.05 (CH$_3$, acacH), 32.89, 32.61 (SCH$_2$), 2.24 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2306, 2268 (MeCN), 1737 (acacH), 1611, 1283, 1117, 937, 887, 839, 683, 670.

[Ba([18]aneO$_4$Se$_2$)(acacH)(MeCN)][BAr^F]$_2$. [Ba(acacH)(MeCN)$_5$]-[BAr^F]$_2$ (0.100 g, 0.046 mmol) and [18]aneO$_4$Se$_2$ (0.018 g, 0.046 mmol) afforded 0.086 g of a white solid in 78% yield. Anal. Required for C$_{83}$H$_{59}$B$_2$BaF$_{48}$NO$_6$Se$_2$ (2409.52): C, 41.62; H, 2.48; N, 0.58. Found: C, 41.51; H, 2.35; N, 0.63%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.72 (br s, [16H], BAr^F H2/6), 7.58 (s, [8H], BAr^F H4), 3.88 (t, J = 5.4 Hz, [8H], OCH$_2$), 3.85 (s, [2H], acacH CH$_2$), 3.80 (s, [8H], OCH$_2$), 2.89 (t, J = 5.4 Hz, [8H], SeCH$_2$), 2.30 (s, [6H], CH$_3$, acacH), 2.06 (s, [3H], CH$_3$, MeCN). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 209.76 (acacH CO), 162.32 (q, $^1J_{C-B}$ = 49.9 Hz, BAr^F C1), 135.39 (BAr^F C2/6), 129.47 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.19 (q, J_{C-F} = 272 Hz, CF$_3$), 120.06 (C, MeCN), 118.10 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 71.47, 71.08 (OCH$_2$), 53.53 (CH$_2$, acacH), 33.07 (CH$_3$, acacH), 25.43 (SeCH$_2$), 2.27 (CH$_3$, MeCN). IR (Nujol/cm^{-1}): 2299, 2266 (MeCN), 1740 (acacH), 1611, 1283, 1116, 1007, 885, 839, 744, 682, 669 448, 366.

[Ca([18]aneO$_4$S$_2$)(2,2′-bipyridyl)][BAr^F]$_2$. [Ca([18]aneO$_4$S$_2$)-(MeCN)$_2$][BAr^F]$_2$ (0.030 g, 0.014 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and a solution of 2,2′-bipyridyl (0.002 g, 0.014 mmol) in CH$_2$Cl$_2$ (5 mL) was added. The reaction was stirred for 16 h, then concentrated to ~5 mL and hexane was layered on top. Colourless crystals were produced which were isolated by decanting away the solvent and drying *in vacuo*. Yield: 0.031 g, 99%. Anal. Required for C$_{86}$H$_{56}$N$_2$O$_4$B$_2$CaF$_{48}$S$_2$ (2219.31): C, 46.54; H, 2.54; N, 1.26. Found: C, 46.39; H, 2.41; N, 1.35. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ = 7.84–8.59 (br m, [8H], bipy), 7.73 (br s, [16H], BAr^F H2/6), 7.57 (s, [8H], BAr^F H4), 4.08 (vbr s, [8H], OCH$_2$), 3.94 (br s, [8H], OCH$_2$), 2.77 (vbr s, [8H], SCH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ = 162.34 (q, $^1J_{C-B}$ = 50.0 Hz, BAr^F C1), 135.40 (BAr^F C2/6), 129.48 (qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.20 (q, $^1J_{C-F}$ = 272 Hz, CF$_3$), 118.01 (septet, $^3J_{C-F}$ = 4.0 Hz, BAr^F C4), 69.54, 68.20 (OCH$_2$), 31.75 (SCH$_2$).

Results and discussion

Metal synthons

We initially attempted to prepare the MeCN complexes [M(MeCN)$_x$][BAr^F]$_2$ (M = Mg, x = 6; M = Ca, Sr or Ba, x = 8) by salt metathesis between the appropriate MI$_2$ and Na[BAr^F] in anhydrous MeCN solution (Scheme 1), since it was anticipated

that these compounds would serve as more readily soluble synthons for accessing soft donor macrocyclic complexes for the Group 2 cations, while incorporating weakly coordinating [BAr^F]$^-$ anions. This was successful for M = Mg and Ca, yielding [Mg(MeCN)$_6$][BAr^F]$_2$ and [Ca(MeCN)$_8$][BAr^F]$_2$ after purification as described in the Experimental section. However, for M = Sr, salt metathesis resulted in products which retained a large amount of Na[BAr^F], and although a small number of crystals formed in one reaction which were identified as [Sr(MeCN)$_8$][BAr^F]$_2$ (see below), this complex could not be obtained in sufficient yield or purity to be a useful synthon. The salt metathesis also failed in the barium case. As an alternative route, the reaction of [M(acac)$_2$] (M = Sr or Ba, acacH = acetylacetone) with [H(OEt$_2$)$_2$][BAr^F][17] in anhydrous MeCN was used to prepare [M(MeCN)$_5$(acacH)][BAr^F]$_2$, (M = Sr or Ba) which proved to be readily isolated (Scheme 2). These complexes were characterised by microanalysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Their IR spectra are consistent with coordination of neutral acacH.[22] Colourless, moisture sensitive crystals of [Mg(MeCN)$_6$][BAr^F]$_2$ were grown from CH$_2$Cl$_2$/n-hexane, and the X-ray crystal structure showed the expected regular octahedral cation (Fig. 1). The cation has been structurally characterised in several salts including [Mg(MeCN)$_6$][MgBr$_4$][7] and [Mg(MeCN)$_6$][AlCl$_4$]$_2$,[23] and the dimensions are comparable: the present structure serves to confirm the identity of the reagent.

The ^{1}H and ^{13}C{^{1}H} NMR spectra show the [BAr^F]$^-$ anions, with resonances due to the CH$_3$ group of MeCN at δ = 2.16 and δ = 2.18 respectively, shifted from the liquid resonances at

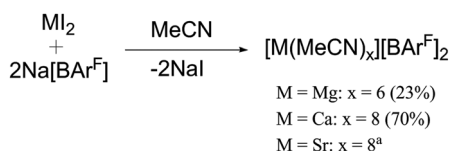Scheme 2   Synthesis of [M(acacH)(MeCN)$_5$][BAr^F]$_2$ (M = Sr, Ba).

Fig. 1 ORTEP representation of the dication of [Mg(MeCN)$_6$][BAr^F]$_2$. Ellipsoids are shown at the 50% probability level and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Mg–N1 = 2.165(5), Mg–N2 = 2.143(5), Mg–N3 = 2.135(4). Symmetry code: (i) −x, −y, z.

Scheme 1 Synthesis of [M(MeCN)$_x$][BAr^F]$_2$ (M = Mg, Ca, Sr). [a]Product contaminated with Na[BAr^F].
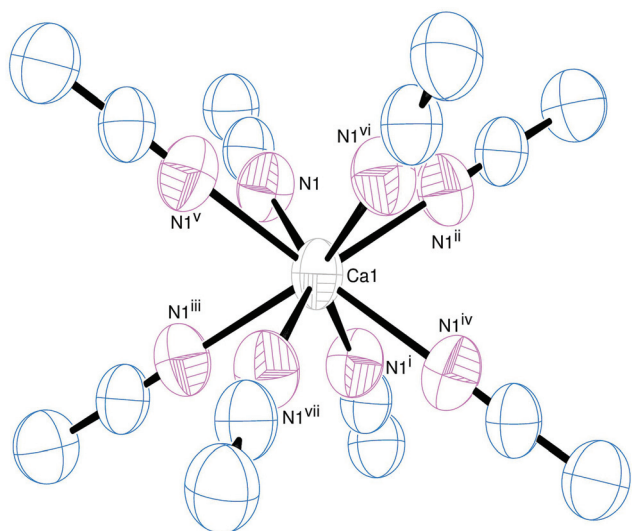
Fig. 2 ORTEP representation of the dication $[Ca(MeCN)_8]^{2+}$. Ellipsoids are shown at the 50% probability level and hydrogen atoms omitted for clarity. Bond lengths (Å): Ca–N = 2.514(5), N–C = 1.136(7). Symmetry codes: (i) x, $0.5 - y$, $0.5 - z$; (ii) $0.5 - x$, y, z; (iii) $0.5 - x$, $0.5 - y$, $0.5 - z$; (iv) x, $0.5 - y$, z; (v) $0.5 - x$, y, $0.5 - z$; (vi) $0.5 - x$, $0.5 - y$, z; (vii) x, y, $0.5 - z$.

$\delta = 1.96$ and $\delta = 1.79$. The IR spectrum (liquid film) shows two resonances at 2252 and 2293 cm^{-1} assigned as $\nu(CN)$ and $\nu(C–C) + \delta(CH_3)$ of similar intensity due to Fermi resonance.[24] In $[Mg(MeCN)_6][BAr^F]_2$ both bands are found at higher frequency (2295, 2321 cm^{-1}), consistent with coordination to the metal. Similar patterns were observed for all the complexes in this work, confirming the MeCN is coordinated in all cases.

Extremely moisture sensitive crystals of $[Ca(MeCN)_8][BAr^F]_2$ were grown from CH_2Cl_2/n-hexane, but these partially lose MeCN on drying with both microanalysis and integration of the ^1H NMR spectrum showing ~6 MeCN/Ca in the vacuum-dried product.[25] The structure (Fig. 2) shows a square antiprismatic cation with no interaction with the $[BAr^F]^-$ anions. This cation has not been reported previously, although the Ca–NCMe bond lengths are similar to those in other calcium complexes including $[Ca(18\text{-crown-6})(MeCN)_2][SbCl_6]_2$,[13] $[Ca(18\text{-crown-6})(MeCN)_2][BPh_4]_2$[26] and $[Ca(MeCN)_5I_2]$.[7]

The spectroscopic properties of $[Sr(MeCN)_8][BAr^F]_2$ are similar to those of the calcium analogue. A few modest quality crystals of this complex were formed as a by-product from the salt metathesis reaction and also deposited from an MeCN solution of $[Sr(MeCN)_5(acacH)][BAr^F]_2$. The X-ray structure showed them to contain a square antiprismatic cation (see Fig. S1, ESI†).

The $[M(acacH)(MeCN)_5][BAr^F]_2$ (M = Sr, Ba) proved to be useful synthons for the heterocrown complexes. The IR spectra show coordinated MeCN and acacH, and although X-ray quality crystals were not obtained, they probably contain seven-coordinate metal centres.

Heterocrown complexes

The reaction of $[Ca(MeCN)_8][BAr^F]_2$ with $[18]aneO_2S_4$, $[18]aneO_4S_2$, $[18]aneO_4Se_2$ and 18-crown-6 afforded complexes

$[Ca(crown)(MeCN)_2][BAr^F]_2$. In all cases the ^1H and $^{13}C\{^1H\}$ NMR spectra show small high frequency shifts for the CH_2O, CH_2S/Se and CH_3CN groups consistent with coordination. The IR spectra are dominated by the $[BAr^F]^-$ anion vibrations, but show small high frequency shifts in the vibrations due to MeCN. X-ray quality crystals were grown for the adducts with $[18]aneO_2S_4$, $[18]aneO_4Se_2$ (Fig. 3) and 18-crown-6 (Fig. S2, ESI†).

For each complex an eight-coordinate Ca^{2+} centre sitting in the middle of a hexadentate macrocycle with *trans* MeCN ligands was observed. Similar structures have been reported for $[Ca(18\text{-crown-6})I_2]$,[27] $[Ca(18\text{-crown-6})(hmpa)_2]^{2+}$ (hmpa = hexamethylphosphoramide)[26] and $[Ca(18\text{-crown-6})(MeCN)_2]$-$[SbCl_6]_2$,[13] although in contrast $[Ca(heterocrown)I_2]$ (hetero-crown = $[18]aneO_4Se_2$ or $[18]aneO_2S_4$),[13] $[Ca(18\text{-crown-6})$-$(O_3SCF_3)_2]$[13] and $[Ca([18]aneO_4S_2)(OH_2)_2]I_2$[13] contain puckered macrocycles with *cis* coordinated monodentate ligands. It is probable that the energy difference between the different arrangements is small and the cation geometry may be influenced by intermolecular interactions and crystal packing. Eight coordination, either dodecahedral or square antiprismatic, is relatively common for the heavier alkaline earth metals,[2,4] and whilst the geometry is readily established for those containing eight monodentate ligands,[28] the distortions resulting with polydentates can make identifying the coordination sphere difficult. Lippard and Russ[29] detailed a method for mathematically distinguishing between the two polyhedra, which required the identification of the plane of best fit which encompassed the metal centre and four of the eight coordinating atoms, then calculating the dihedral angle between this plane and the plane defined by the metal centre and the remaining four coordinating atoms. For an ideal dodecahedron this angle will be 90° whereas for an ideal square antiprism this angle will be 77.4°. A "τ_8" parameter can be defined as $(\theta - 77.4)/12.6$ where θ is the dihedral angle between the two planes of best fit. A τ_8 value of 0 would correspond to an ideal square antiprismatic geometry and a τ_8 value of 1 would correspond to an ideal dodecahedral geometry, with intermediate values indicating the degree of distortion away from the two ideals.

For the $[18]aneO_2S_4$ complex the τ_8 parameter is calculated to be 0.29 and for the $[18]aneO_4Se_2$ complex the τ_8 parameter is 0.93. This indicates that the latter complex is very close to an ideal dodecahedral geometry, whereas the former is better described as square antiprismatic, but with a high degree of distortion (Fig. 3(c) and (d)). This contrasts markedly with the $[Ca(heterocrown)I_2]$ complexes where the macrocycle conformation was significantly folded because the iodide ligands bound in a *cis* manner and the geometry of the complexes was close to square antiprismatic. The $[Ca(18\text{-crown-6})(MeCN)_2]^{2+}$ dication (Fig. S2, ESI†) has a τ_8 value of 0.90 indicating that it is close to a dodecahedral geometry.

Changes in the macrocyclic coordination geometry do not significantly affect the Ca–S and Ca–Se bond lengths which are very similar between the iodide[13] and MeCN complexes, although there are some slight differences in the Ca–O bond
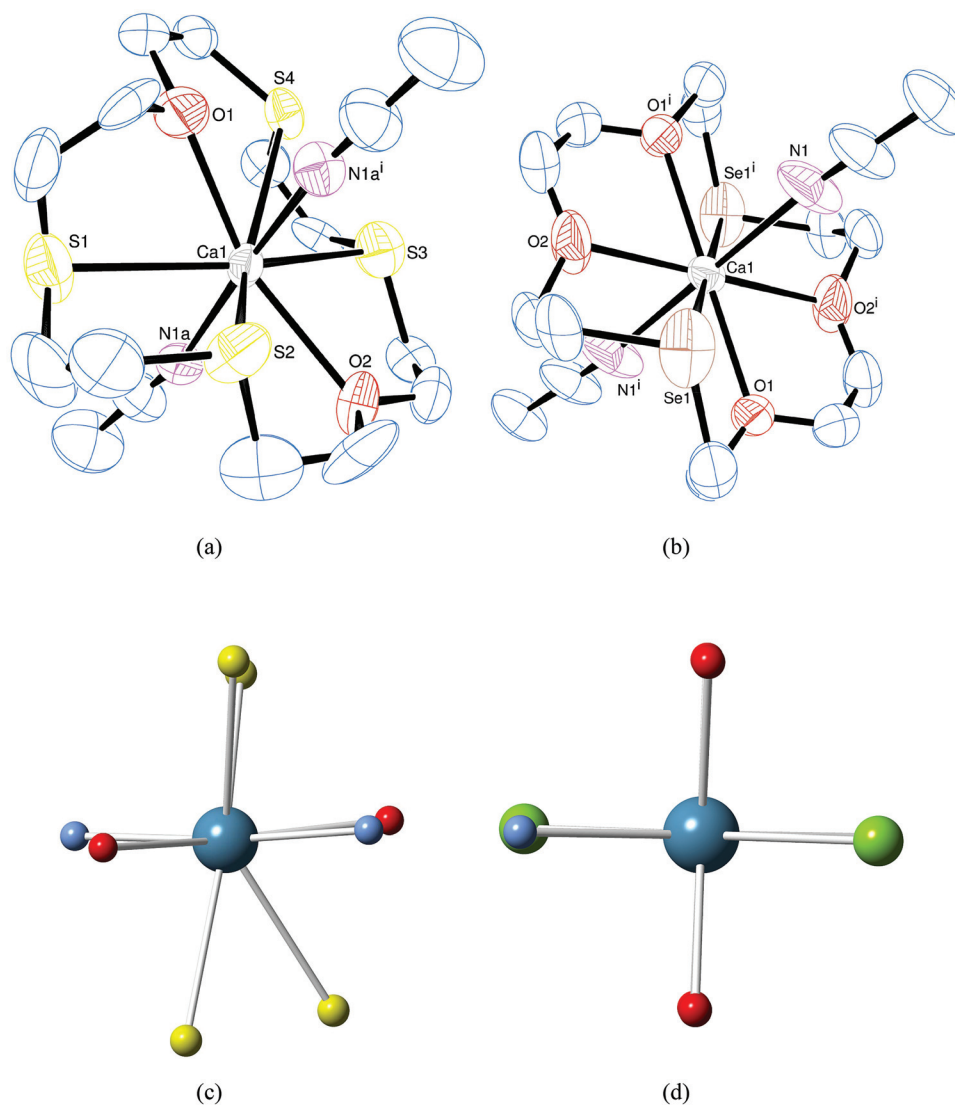
Fig. 3 (a) the cation of $[Ca([18]aneO_2S_4)(MeCN)_2][BAr^F]_2$ with the positional disorder and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ca–O1 = 2.52(1), Ca–O2 = 2.668(8), Ca–S1 = 2.986(4), Ca–S2 = 2.954(2), Ca–S3 = 2.906(4), Ca–S4 = 2.962(3), Ca–N1a = 2.37(1); O1–Ca–S1 = 65.3(2), S1–Ca–S2 = 73.1(1), S2–Ca–O2 = 68.3(2) O2–Ca–S3 = 70.1(2), S3–Ca–S4 = 54.2(1), S4–Ca–O1 = 59.2(2), S1–Ca–S3 = 153.8(1), S2–Ca–S4 = 146.0(1), O1–Ca–O2 = 154.3(3). (b) The cation of $[Ca([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$ with hydrogens and $[BAr^F]^-$ anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ca–O1 = 2.461(4), Ca–O2 = 2.455(5), Ca–Se1 = 3.1526(9), Ca–N1 = 2.488(5); O1–Ca–Se1 = 67.0(1), O2–Ca–Se1 = 66.0(1), O1–Ca–O2^i = 64.7(1). Symmetry code: (i) 1 – x, 1 – y, –z. View of the metal coordination sphere for $[Ca([18]anO_2S_4)]^{2+}$ (c) and $[Ca([18]aneO_4Se_2)]^{2+}$ (d) illustrating the differences from the (near) dodecahedral geometry present in the latter (colour key: blue = N, red = O, yellow = S, green = Se).

lengths. Additionally, a slight shortening of the Ca–NCCH$_3$ bond lengths is observed for the macrocyclic complexes compared to $[Ca(MeCN)_8][BAr^F]_2$, although it should be noted that there was a significant amount of positional disorder present in the $[18]aneO_2S_4$ complex (including the MeCN ligands) and care is needed in making the comparisons.

The MeCN ligands can be displaced by neutral donors, for example 2,2′-bipyridyl, which formed $[Ca([18]aneO_4S_2)(bipy)]$-$[BAr^F]_2$. The ^1H and $^{13}C\{^1H\}$ NMR spectra contained broad resonances indicative of a dissociating system in CD$_2$Cl$_2$ solution at ambient temperatures, but the identity was confirmed by the X-ray crystal structure (Fig. 4).

In order to accommodate the bidentate bipy ligand the $[18]aneO_4S_2$ coordination becomes puckered, closer to that previously observed for the $[Ca(18-aneO_4S_2)I_2]$ where the iodide ligands were *cis* and the geometry is close to dodecahedral, $\tau_8 = 0.82$.

Heterocrown complexes of strontium were obtained through reaction of $[Sr(acacH)(MeCN)_5][BAr^F]_2$ with $[18]aneO_4S_2$, $[18]aneO_2S_4$ and $[18]aneO_4Se_2$, forming $[Sr(heterocrown)(MeCN)_2]$-$[BAr^F]_2$. Notably the acacH ligand is lost but two MeCN ligands were retained, as shown by the ^1H and $^{13}C\{^1H\}$ NMR data. This was confirmed by the X-ray structures of $[Sr([18]aneO_4S_2)$-$(MeCN)_2][BAr^F]_2$ and $[Sr([18]aneO_4Se_2)(MeCN)_2][BAr^F]_2$ (Fig. 5).
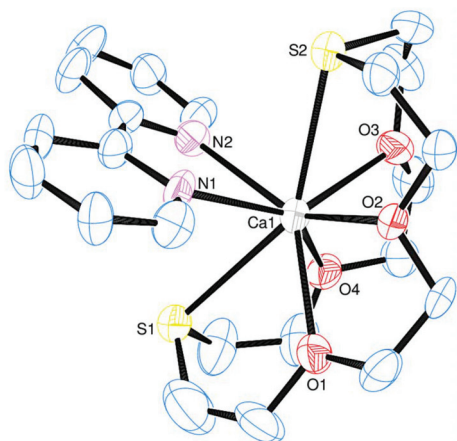
Fig. 4 The cation of [Ca([18]aneO$_4$S$_2$)(bipy)][BAr^F]$_2$. Ellipsoids are shown at the 50% probability level and the hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ca–O1 = 2.497(6), Ca–O2 = 2.433(6), Ca–O3 = 2.514(6) Ca–O4 = 2.462(6), Ca–S1 = 2.943(4), Ca–S2 = 2.935(4), Ca–N1 = 2.461(7), Ca–N2 = 2.458(7); S1–Ca–S2 = 145.23(9), S1–Ca–O1 = 67.7(2), O1–Ca–O4 = 87.0(2).

The structures revealed that both complexes adopted 8-coordinate geometries with a hexadentate macrocycle and two *trans* MeCN ligands. The τ_8 parameter for the [18]aneO$_4$S$_2$ complex was 0.73 and for the [18]aneO$_4$Se$_2$ complex it was 0.89 indicating that distorted dodecahedral is the best description, albeit severely distorted for the former. The Sr–S and Sr–Se bond lengths are very similar to those reported for the 9-coordinate [Sr(macrocycle)(OH$_2$)$_3$]I$_2$ complexes,[13] although the Sr–O bond lengths are slightly shorter than those previously reported which may be a result of lower coordination number

(8 *vs.* 9). No evidence for any Sr···[BAr^F] interactions was observed, although such interactions were found with the larger alkali metals.[11]

The only example of an oxathia-crown complex of barium is in the polymer [Ba{Cu(SCN)$_3$([18]aneO$_4$S$_2$)}],[15] and previous attempts to use BaI$_2$ as a metal source failed to result in any complexes.[13] The reaction of [Ba(acacH)(MeCN)$_5$][BAr^F]$_2$ with [18]aneO$_2$S$_4$ and [18]aneO$_4$Se$_2$ in MeCN produced the complexes [Ba(heterocrown)(acacH)(MeCN)][BAr^F]$_2$, in which the acacH ligand was retained, contrasting with the strontium complexes. This was confirmed by the crystal structure of [Ba([18]aneO$_4$Se$_2$)(acacH)(MeCN)][BAr^F]$_2$ (Fig. 6) the first barium complex containing neutral selenoether coordination. The larger Ba^{2+} (1.43 Å) compared to 1.27 Å for Sr^{2+} (ref. 30) results in an increase in coordination number to nine, composed of the six donor atoms from the heterocrown, two oxygens from the neutral acacH and one MeCN, in a geometry that can be described as distorted tricapped trigonal prismatic. Coordination numbers of 8–10 have been found in complexes of 18-crown-6 with Ba^{2+} with similar bond lengths and irregular geometries.[15,26,27,31–33]

The complexes of these heterocrowns with the much smaller magnesium ion (r^{2+} = 0.78 Å) were expected to differ from those described above. The reaction of [Mg(MeCN)$_6$][BAr^F]$_2$ with 18-crown-6, [18]aneO$_2$S$_4$, [18]aneO$_4$S$_2$ and [18]aneO$_4$Se$_2$ in anhydrous CH$_2$Cl$_2$ gave yellow or off-white solids of composition [Mg(crown)(MeCN)$_2$][BAr^F]$_2$. Repeated attempts to obtain X-ray quality crystals were unsuccessful, although structures of two hydrolysis products were obtained (Fig. 6). The spectroscopic data on [Mg(crown)(MeCN)$_2$][BAr^F]$_2$ (crown = 18-crown-6, [18]aneO$_4$S$_2$ and [18]aneO$_4$Se$_2$) show the presence of coordinated MeCN and the absence of water. The

(a)	(b)
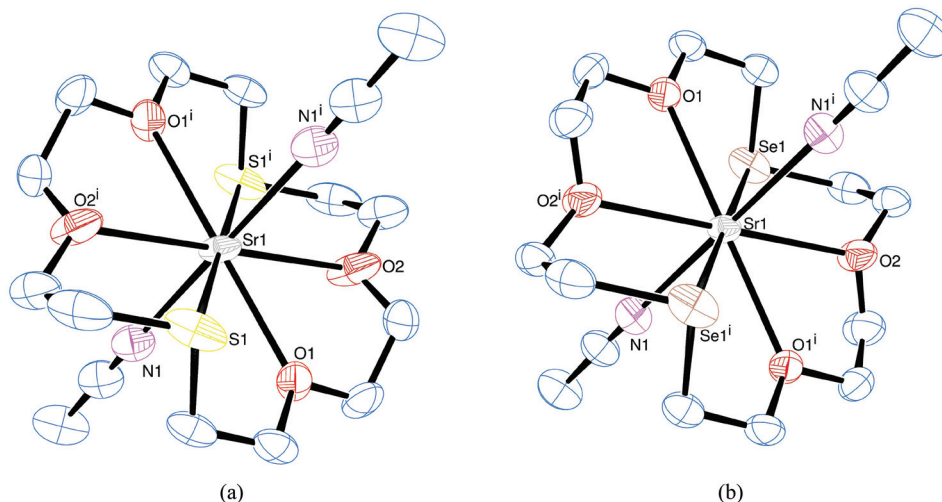
Fig. 5 (a) The cation of [Sr([18]aneO$_4$S$_2$)(MeCN)$_2$][BAr^F]$_2$ with the [BAr^F]$^-$ anions and hydrogen atoms omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Sr–O1 = 2.593(3), Sr–O2 = 2.624(4), Sr–S1 = 3.122(1), Sr–N1 = 2.611(5); O1–Sr–S1 = 63.15(9), O2^i–Sr–S1 = 64.4(1), O1–Sr–O2 = 61.8(1). Symmetry code: (i) −x, 2 − y, 2 − z. (b) The cation of [Sr([18]aneO$_4$Se$_2$)(MeCN)$_2$][BAr^F]$_2$ with hydrogen atoms and [BAr^F]$^-$ anions omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Sr–O1 = 2.606(3), Sr–O2 = 2.611(3), Sr–Se1 = 3.2216(6), Sr–N1 = 2.620(4); O1–Sr–Se1 = 65.02(7), O2–Sr–Se1 = 65.59(7), O1–Sr–O2^i = 61.96(9). Symmetry code: (i) −x, −y, −z.
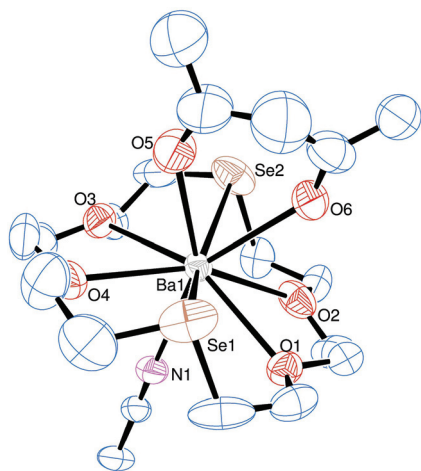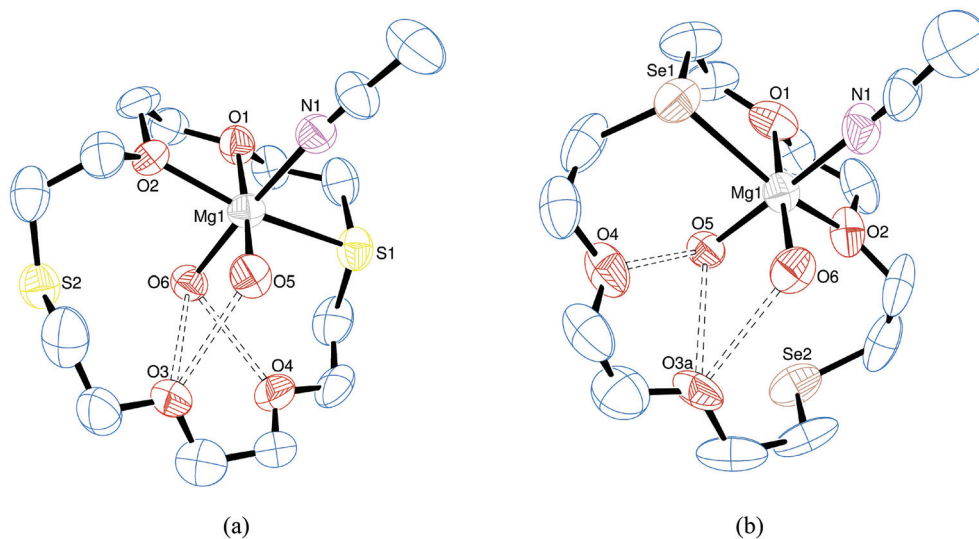
Fig. 6 The cation of [Ba([18]aneO$_4$Se$_2$)(acacH)(MeCN)][BAr^F]$_2$ with the positional disorder of the macrocycle, CH$_2$Cl$_2$ solvent molecule and hydrogen atoms omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Ba–O1 = 2.791(6), Ba–O2 = 2.786(7), Ba–O3 = 2.787(6), Ba–O4 = 2.813(7), Ba–O5 = 2.733(8), Ba–O6 = 2.770(7), Ba–Se1 = 3.363(1), Ba–Se2 = 3.366(1), Ba–N1 = 2.920(8); Se1–Ba–O1 = 62.9(1), O1–Ba–O2 = 61.0(2), O2–Ba–Se2 = 60.8(2), Se2–Ba–O3 = 62.3(2), O3–Ba–O4 = 63.3(2), O4–Ba–Se1 = 63.8(2) O5–Ba1–O6 = 63.7(2).

^{1}H NMR resonances of the crown ligands show small high frequency shifts relative to the unbound ligands,[18] but are rather broad. The CH$_2$O and CH$_2$S resonances of [Mg([18]aneO$_2$S$_4$)(MeCN)$_2$][BAr^F]$_2$ are very broad both in the ^{1}H NMR and ^{13}C{^{1}H} spectra which probably indicates substantial solution lability of the heterocrown, which contains four soft thioether

donors on the hard magnesium centre. Since the steric demands of the linear MeCN groups are small, it is possible that the [Mg(crown)(MeCN)$_2$]$^{2+}$ cations contain eight-coordinate magnesium in the solid state, although the coordination number could be lower, whilst the ring undergoes a fast dynamic process in solution. Seven-coordination is known with κ^5-18-crown-6 in [Mg(18-crown-6)(HCl$_2$)$_2$][34] and [Mg(κ^5-18-crown-6)Cl$_2$],[35] which contain near planar MgO$_5$ units with *trans* coordinated anions above and below the plane.

During attempts to grow crystals of [Mg(crown)(MeCN)$_2$][BAr^F]$_2$ from CH$_2$Cl$_2$/n-hexane in a freezer, crystals of [Mg(crown)(MeCN)(OH$_2$)$_2$][BAr^F]$_2$ (crown = [18]aneO$_4$S$_2$ or [18]aneO$_4$Se$_2$) were obtained, no doubt due to ingress of adventitious water. The structures are isomorphous (Fig. 7) and contain κ^3-crown, one MeCN and two water ligands. The crown is coordinated O$_2$S/Se in a *mer* geometry – providing extremely rare examples of Mg^{2+} coordinated to neutral thio- and seleno-ether functions, with *cis*-diaquo ligands. Hydrogen-bonding is present between the coordinated H$_2$O ligands and the remaining O-atoms of the crown. κ^3-Coordination of 18-crown-6 is present in the five-coordinate [Mg(18-crown-6)(^{i}Bu)(2,6-^{t}Bu$_2$C$_6$H$_4$O)].[36]

Adventitious hydrolysis of some [M(heterocrown)I$_2$] (M = Ca or Sr) complexes displaced the iodide ligands to give [M(heterocrown)(OH$_2$)$_2$]I$_2$ [13] but κ^6-coordination of the crown remained. The different behaviour of Mg *versus* Ca and Sr in these systems may be largely attributable to the smaller size of the magnesium. We note that mixed aqua-crown complexes are also well established for some 3d metals, *e.g.* [Cr(κ^2-18-crown-6)(OH$_2$)Cl$_3$] or [V(κ^2-18-crown-6)(OH$_2$)Cl$_3$].[37,38]

(a)

(b)

Fig. 7 (a) The cation of [Mg(κ^3-[18]aneO$_4$S$_2$)(OH$_2$)$_2$(MeCN)][BAr^F]$_2$, with positional disorder of the macrocycle and all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mg–O1 = 2.113(8), Mg–O2 = 2.081(7), Mg–S1 = 2.625(4), Mg–O5 = 2.025(8), Mg–O6 = 2.037(8), Mg–N1 = 2.14(1); S1–Mg–O2 = 158.5(3), O1–Mg–O2 = 77.5(3), S1–Mg–O1 = 81.2(2). (b) The cation of [Mg(κ^3-[18]aneO$_4$Se$_2$)(OH$_2$)$_2$(MeCN)][BAr^F]$_2$ with the [BAr^F]$^-$ anions, positional disorder of the macrocycle and hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): Mg–O1 = 2.107(8), Mg–O2 = 2.064(8), Mg–Se1 = 2.794(4), Mg–O5 = 2.027(8), Mg–O6 = 2.022(8), Mg–N1 = 2.12(1); Se1–Mg–O2 = 158.6(3), O1–Mg–O2 = 77.9(4), Se1–Mg–O1 = 80.8(3).

Conclusions

A range of cationic complexes of the Group 2 metals Mg–Ba with heterocrown ethers have been prepared from acetonitrile synthons taking advantage of the solubility in weak donor solvents conferred by the $[BAr^F]^-$ anions. The new complexes have been fully characterised spectroscopically and in many cases by X-ray crystallography. They include the first example of coordination of a neutral selenoether function to Ba^{2+}, and rare examples with seleno- and thio-ether coordination to the other hard metal centres. The heterocrown-nitrile complexes should prove to be useful synthons for incorporation of other donor types to the metal centre, as demonstrated by the characterisation of $[Ca([18]aneO_4S_2)(bipy)][BAr^F]_2$, whilst more generally, the $[M(MeCN)_x][BAr^F]_2$ (M = Mg, x = 6; M = Ca, x = 8) or $[M'(acacH)(MeCN)_5][BAr^F]_2$ (M' = Sr, Ba) may offer a route into other Group 2 complexes with soft donor atoms. Further work to explore these possibilities is currently underway.

Acknowledgements

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