Aza-macrocyclic complexes of the Group 1 cations – synthesis, structures and density functional theory study†

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The Group 1 complexes, [M(Me6[18]aneN6)]|BARF| (M = Li−Cs; Me6[18]aneN6 = 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane; BARF = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate), are obtained in high yield by reaction of the macrocycle with BARF in anhydrous CH2Cl2 solution, and characterised spectroscopically (1H, 13C{1H}, 7Li, 23Na, and 133Cs NMR), by microanalysis and, for M = Li, K, and Rb, by single crystal X-ray analysis. The structures show N6-cooordination to the metal ion; the small ionic radius for Li+ leads to a puckered conformation. In contrast, the K+ ion fits well into the N6 plane, with the [BARF]− anions above and below, leading to two K+ species in the asymmetric unit (a hexagonal planar [K(Me6[18]aneN6)]+ cation and a ‘[K(Me6[18]aneN6)(ciτ−BARF)2]− anion’, with long axial K⋯F interactions. The Rb+ ion sits above the N6 plane, with two long axial Rb⋯F interactions in one cation and two long, mutually cis Rb⋯F interactions in the other. The unusual sandwich cations, [M(Me3tacn)2]+ (M = Na, K; distorted octahedral, N6 donor set) and half-sandwich cations [Li(Me3tacn)(thf)]+ (distorted tetrahedron, N3O donor set), [Li(Me2cyclen)(OH)2]+, and [Na(Me4cyclen)(thf)]+ (both distorted square pyramidal with N2O donor sets) were also prepared [Me3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Me4cyclen = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane). Density functional theory (DFT) calculations, using the BP86 and B3LYP functionals, show that the accessibility of the [M(Me3tacn)2]+ sandwich cations depends strongly on the M+ ionic radius, such that it is sufficiently large to avoid steric clashing between the Me groups of the two rings, and small enough to avoid very acute N−M−N chelate angles. The calculations also show that coordination to the Group 1 cation involves significant donation of electron density from the p-orbitals on the N atoms of the macrocycle, rather than purely electrostatic interactions.

Introduction

The coordination chemistry of Group 1 cations with neutral ligands is dominated by oxygen-donor ligands such as alcohols, ethers, and water, including the ubiquitous crown ethers and cryptands which are frequently used as ligands towards Group 1 cations.1,2 The corresponding chemistry with the less studied neutral polyaza macrocycles has been much less studied. We recently reported the preparation of several unusual complexes based upon coordination of Na+ to Me3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane) and Me4cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), including structural characterisation of the sandwich cation salt, [Na(Me3tacn)2][BARF]+ (BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) and [Na(Me4cyclam)(thf)][BARF]+, containing tetradeinate coordination of the macrocycle.3 The Me3tacn complexes were initially isolated serendipitously from reactions of Na[BARF] with SiCl4 in the presence of the N-donor macrocycles, towards preparation of potential precursors for the supercritical fluid electrodeposition (SCFED) of semiconductor materials.4 The Na+ preferentially coordinated to the N-donor macrocycle, and we attributed this unusual behaviour to the low lattice energy of Na[BARF]+, coupled with the high solubility of the [BARF]+ salts in non-competitive, very weakly coordinating solvents, such as CH2Cl2 and toluene.

Neutral diamines (e.g. N,N,N′,N″-tetramethylenediamine) are often used as complexation agents to increase the reactivity of alkyl lithiums5 and to increase the solubility of...
heavier Group 1 alkyls. Whilst a small number of pendant arm functionalised N-donor macrocycles are known to form complexes with alkali metal cations, complexes of neutral N-donor macrocycles with these cations have been very little studied. Earlier work has shown that N-methylated aza macrocycles are more stable towards electrides compared to the analogous crown ethers. Other than the two Na⁺-aza macrocyclic complexes that we reported, four examples involving Me₆tacn coordinated to lithium are known: two lithium-based electrides, a BzLi complex with Me₆tacn and a lithium enolate stabilised by Me₆tacn. Two sodium complexes with Me₆tacn and Me₆cyclen (1,4,7-trimethyl-1,4,7,10-tetraazaacyclododecane) were structurally characterised. No examples of neutral triple- and tetra-aza macrocycles are known for K⁺, Rb⁺, or Cs⁺ and there are very few examples with the N-methylated aza analogue of 18-crown-6, Me₆[18]aneN₆ (1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazaacyclododecane). The structural features of two electrides, [K(Me₆[18]aneN₆)][Na⁺] and [Cs(Me₆[18]aneN₆)][Na⁺], were determined by Dye and co-workers, who also reported NMR spectroscopic evidence for [Rb(Me₆[18]aneN₆)][Na⁺], [Cs(Me₆[18]aneN₆)]²⁻, [Cs(Me₆[18]aneN₆)crown]⁻, and two [Cs(Me₆[18]aneN₆)(crown)]⁻ complexes. We report here the first systematic study of the synthesis, spectroscopic, and structural characterisation of Group 1 cation (Li⁺ to Cs⁺) complexes involving tri-, tetra- and hexa-aza macrocycles. Density functional theory (DFT) with the BP86 and B3LYP functionals has been used to investigate the electronic structure and bonding present in the resulting cations.

**Experimental**

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove box techniques. [Li(thf)₄][BarF]²⁺ and Na[BarF]⁻·2thf were synthesised using a slight modification of the literature procedure. The lithium salt was isolated as [Li(OH₂)₃][BarF]²⁺, which can be converted to the thf adduct by stirring in thf for 16 h over 4 Å molecular sieves. Filtration and removal of solvents affords the thf adduct. Crude Na[BarF]⁻·2thf was recrystallised from thf/n-hexane, resulting in the isolation of Na[BarF]²⁻·2thf. K[BarF]²⁻, Rb[BarF]⁻, and Cs[BarF]⁻ were synthesised via cation exchange of Na[BarF]⁻·2thf in water at 95 °C with excess (5 mol. equiv.) KNO₃, RbNO₃, or CsNO₃, respectively. Me₆tacn was synthesised by a literature procedure. Me₆cyclen was synthesised by methylation of cyclen (Sigma) using formic acid/formaldehyde. Me₆[18]aneN₆ (Sigma) was used as received. CH₂Cl₂ was dried by distillation from CaH₂, toluene distilled from Na, and n-hexane distilled from Na/K alloy. ¹H and ¹³C{¹H} NMR spectra were recorded in CD₂Cl₂ solution at 298 K using a Bruker AV II-400 spectrometer and are referenced to the residual CH₂Cl₂ resonance. ²Li, ²³Na, and ¹³¹Cs NMR spectra were obtained on a Bruker AV II-400 spectrometer at 298 K (unless otherwise stated) and referenced to a 0.1 mol dm⁻³ solution of LiCl, NaCl, or CsNO₃ in D₂O, respectively. 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 S1. Diffraclimeter: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn24+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator (λ₁ = 0.71073 Å) with VHF Varimax optics (70 μm focus). Cell determination and data collection: CrystalClear-SM Expert 3.1 b27, data reduction, cell refinement, and absorption correction: CrystalClear-SM Expert 2.1 b29. Structure solution and refinement were carried out using WinGX and software packages within. Disorder in the CF₃ groups of the [BarF]⁻²⁺ anions was present in all of the structures, which is often observed in compounds containing [BarF]⁻²⁺, and this was satisfactorily modelled using DFIX, DELU, and SIMU restraints. Positional disorder was also present in the –CH₂CH₂– linkers of the macrocycle in [Na(Me₆cyclen)(thf)]⁻·[BarF]⁻ and was modelled similarly. Two locations for the water molecule in [Li(Me₆cyclen)(H₂O)][BarF]⁻ were observed, with the combined electron density consistent with one fully-occupied water molecule. Attempts to model this as other moieties (e.g. methoxide) were unsuccessful. H-atoms were placed in geometrically-assigned positions with C–H distances of 0.95 Å (CH), 0.98 Å (CH₂), or 0.99 Å (CH₃) and refined using a riding model with Uiso = 1.2 Ueq(C) (CH, CH₂) or 1.5 Ueq(C) (CH₃), enCIFer was used to prepare material for publication. CCDC reference numbers 1051099–1051104 contain crystallographic data in CIF format.

**Preparations**

[Li(Me₆[18]aneN₆)][BarF]⁻. [Li(thf)₄][BarF]²⁻ (100 mg, 0.09 mmol) was suspended in CH₂Cl₂ (5 mL) and a solution of Me₆[18]aneN₆ (31 mg, 0.09 mmol) in CH₂Cl₂ (2 mL) was added. The reaction was stirred for 4 h then the product was precipitated by the addition of n-hexane (20 mL). Crystals were obtained by layering a concentrated CH₂Cl₂ solution of the product with n-hexane. White solid. Yield: 97 mg, 89%. Required for C₅₀H₅₄BF₂₄LiN₆: C, 49.51; H, 4.49; N, 6.93. Found: C, 49.52; H, 4.58; N, 6.94%. ¹H NMR (298 K, CD₂Cl₂): δ = 7.73 ([8H], s, BarF H2/6), 7.57 ([4H], s, BarF H4), 2.46 ([24H], br s, NCH₂), 2.29 ([18H], s, NMe). ¹³C{¹H} NMR (298 K, CD₂Cl₂): δ = 162.37 ([8H], s, BarF C4), 135.40 (CH, BarF C1), 132.29 ([18H], s, NMe). ¹³¹C(¹H) NMR (298 K, CD₂Cl₂): δ = 162.37 ([C, q, Jc–f = 49.9 Hz, BarF C1], 135.40 (CH, BarF C2/6), 129.49 (C, qq, ³JC–F = 31.5, 2.9 Hz, BarF C3/5), 125.20 (C, q, Jc–F = 272 Hz, CF₃), 118.06 (CH, septic, ³JC–F = 4.0 Hz, BarF C4), 56.62 (NCH₂), 45.24 (NMe). ¹³Li (298 K, CD₂Cl₂): δ = 0.30.

[Na(Me₆[18]aneN₆)][BarF]⁻. Prepared similarly using Na[BarF]⁻·2thf (100 mg, 0.10 mmol) and Me₆[18]aneN₆ (34 mg, 0.10 mmol). Colourless crystals were obtained by layering a concentrated CH₂Cl₂ solution of the product with n-hexane. Yield: 59 mg, 44%. Required for C₅₀H₅₄BF₂₄Na: C, 48.87; H, 4.43; N, 6.84. Found: C, 48.96; H, 4.35; N, 6.78. ¹H NMR (298 K, CD₂Cl₂): δ = 7.73 ([8H], s, BarF H2/6), 7.57 ([4H], s, BarF H4), 2.54 ([12H], v br s, NCH₂), 2.26 ([30H], br s, NMe + NCH₂). ¹³C(¹H) NMR (298 K, CD₂Cl₂): δ = 162.85 (C, q, Jc–f = 49.9 Hz, BarF C4), 135.40 (CH, BarF C1), 132.29 (C, q, Jc–f = 272 Hz, CF₃), 118.06 (CH, septic, ³JC–F = 4.0 Hz, BarF C4), 56.62 (NCH₂), 45.24 (NMe). ¹³Li (298 K, CD₂Cl₂): δ = 0.30.
BARF C1), 135.39 (CH, BARF C2/6), 129.38 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.20 (C, q, J_C-F = 272 Hz, CF2), 118.05 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 54.16 (NCH3), 44.22 (NMe), 3.3Na (298 K, CD2Cl2); δ = +3.1.

[K(Me18faneN6)][BARF]. Prepared similarly using K[BARF] (50 mg, 0.05 mmol) and Me18faneN6 (17 mg, 0.05 mmol). White crystalline solid. Yield: 51 mg, 76%. Required for C50H42BF24N4Cl: C, 48.24; H, 4.43; N, 6.64%. H1 NMR (298 K, CD2Cl2): δ = 7.72 (8H, s, BARF H2/6), 7.57 ([4H], s, BARF H4), 2.68–2.87, 2.15–2.24 (both [9H], v br s, NCH2), 2.07 ([18H], br s, NMe). 13C{1H} NMR (298 K, CD2Cl2): δ = 162.36 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.39 (CH, BARF C2/6), 129.46 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.20 (C, q, J_C-F = 272 Hz, CF2), 118.07 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 56.17 (NCH3), 38.16 (NMe).

[Rb(Me18faneN6)][BARF]. Prepared similarly using Rb[BARF] (104 mg, 0.10 mmol) and Me18faneN6 (34 mg, 0.10 mmol). White crystalline solid. Yield: 77 mg, 56%. Required for C50H42BF24N4Rb: C, 46.50; H, 4.21; N, 6.51. Found: C, 46.60; H, 4.24; N, 6.45%. 1H NMR (298 K, CD2Cl2): δ = 7.73 ([8H], s, BARF H2/6), 7.57 ([4H], s, BARF H4), 2.59–2.99, 2.10–2.56 (both [12H], v br m, NCH2), 2.05 ([18H], s, NMe). 13C{1H} NMR (298 K, CD2Cl2): δ = 162.36 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.41 (CH, BARF C2/6), 129.47 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.20 (C, q, J_C-F = 272 Hz, CF2), 118.08 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 57.00 (broad, NCH3), 38.48 (broad, NMe).

[Cs(Me18faneN6)][BARF]. Prepared similarly using Cs[BARF] (110 mg, 0.10 mmol) and Me18faneN6 (34 mg, 0.10 mmol). White crystalline solid. Yield: 81 mg, 56%. Required for C50H42BF24N4Cs: C, 44.86; H, 4.06; N, 6.28. Found: C, 44.96; H, 3.99; N, 6.23. 1H NMR (298 K, CD2Cl2): δ = 7.73 ([8H], s, BARF H2/6), 7.57 ([4H], s, BARF H4), 2.40 ([18H], v br m, NCH2), 2.03 ([18H], s, NMe) ([183 K]: 7.73 ([8H], s, BARF H2/6), 7.56 ([4H], s, BARF H4), 2.80–3.00 ([20H], m, NCH3), 2.52–2.76 ([10H], m, NCH2 and NMe), 2.00 ([9H], s, NMe), 1.78–1.96 ([17H], m, NCH2 and NMe), 1.56–1.71 ([14H], m, NMe). 13C{1H} NMR (298 K, CD2Cl2): δ = 162.36 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.42 (CH, BARF C2/6), 129.48 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.21 (C, q, J_C-F = 272 Hz, CF3), 118.08 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 56.79 (broad, NCH3), 40.30 (broad, NMe). 133Cs NMR (298 K, CD2Cl2): δ = 5.40 ([8; 183 K: 73.3, 58.7 (both s). 23Na (298 K, CD2Cl2): δ = 162.36 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.41 (CH, BARF C2/6), 129.50 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.23 (C, q, J_C-F = 272 Hz, CF3), 118.13 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 53.98 (NCH3), 43.46 (NMe). 7Li NMR (298 K, CD2Cl2): δ = 0.41.

[Li(Me4cyclen)(thf)][BARF]. Na[BARF](thf) (250 mg, 0.24 mmol) was suspended in CH2Cl2 (5 mL) and a solution of Me4cyclen (36 mg, 0.16 mmol) in CH2Cl2 (2 mL) was added. The reaction was stirred for 4 h then the product was precipitated by the addition of n-hexane (30 mL). Crystals were obtained by layering a concentrated CH2Cl2 solution of the product with n-hexane. White solid. Yield: 151 mg, 81%. Required for C44H41BF24N4Li: C, 46.57; H, 3.91; N, 4.94. Found: C, 46.67; H, 3.93; N, 4.82%. 1H NMR (298 K, CD2Cl2): δ = 7.74 ([8H], s, BARF H2/6), 7.58 ([4H], s, BARF H4), 2.52–2.59, 2.28–2.37 (both [8H], m, NCH3), 2.27 ([12H], s, NMe). 13C{1H} NMR (298 K, CD2Cl2): δ = 162.40 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.44 (CH, BARF C2/6), 129.54 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.25 (C, q, J_C-F = 272 Hz, CF3), 118.13 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 53.98 (NCH3), 43.46 (NMe). 7Li NMR (298 K, CD2Cl2): δ = 0.41.

[Me4cyclen(OH)][BARF]. [Li(OH)2][BARF] (150 mg, 0.16 mmol) was dissolved in CH2Cl2 (5 mL) and a solution of Me4cyclen (36 mg, 0.16 mmol) in CH2Cl2 (2 mL) was added. The reaction was stirred for 4 h then all volatiles were removed. Crystals were obtained by layering a concentrated CH2Cl2 solution of the product with n-hexane. White solid. Yield: 151 mg, 81%. Required for C44H41BF24LiOH: C, 46.57; H, 3.91; N, 4.94. Found: C, 46.67; H, 3.93; N, 4.82%. 1H NMR (298 K, CD2Cl2): δ = 7.74 ([8H], s, BARF H2/6), 7.58 ([4H], s, BARF H4), 2.52–2.59, 2.28–2.37 (both [8H], m, NCH3), 2.27 ([12H], s, NMe). 13C{1H} NMR (298 K, CD2Cl2): δ = 162.40 (C, q, J_C-F = 49.9 Hz, BARF C1), 135.44 (CH, BARF C2/6), 129.54 (C, qq, J_C-F = 31.5, 2.9 Hz, BARF C3/5), 125.25 (C, q, J_C-F = 272 Hz, CF3), 118.13 (CH, septet, J_C-F = 4.0 Hz, BARF C4), 53.98 (NCH3), 43.46 (NMe). 7Li NMR (298 K, CD2Cl2): δ = 0.41.
The reaction of \([\text{Li(thf)}_4][\text{BArF}]\) with Me₆[18]aneN₆ in CH₂Cl₂

Hexa-aza macrocyclic complexes are collected in the ESI.

Results and discussion

In view of the limited literature examples of aza-macroyclic complexes with Group 1 cations, their expected lability in solution, and the lack of diagnostic spectroscopic signatures for these complexes, X-ray crystallographic data provide the key characterisation method. We therefore describe the solid state data first, comparing these with computed structures obtained using DFT, followed by their solution NMR spectroscopic data.

DFT calculations were performed on the isolated cations [M(Me₃tacn)]⁺, [M(Me₃tacn)₂]⁺, and [M(Me₆[18]aneN₆)]⁺, with M = Li, Na, K, Rb, and Cs, using the BP86 and B3LYP functionals. In general, these functionals perform equally well in replicating bond distances and angles in the cations investigated (Tables S2 and S3). The results from the BP86 functional are discussed in the main manuscript, while those computed with the B3LYP functional are collected in the ESI.

Hexa-aza macrocyclic complexes

The reaction of [Li(thf)]⁺[BArF] with Me₆[18]aneN₆ in CH₂Cl₂ led to the isolation of a white crystalline solid (Scheme 1), which was formulated as [Li(Me₆[18]aneN₆)][BArF] on the basis of microanalytical, ¹H, ¹³C{¹H}, and ⁷Li NMR spectroscopic data. The crystal structure (Fig. 1) shows the [Li(Me₆[18]aneN₆)]⁺ cation contains an N₆ donor set (without retention of thf) and the macrocycle is in a puckered conformation; the distortion from an ideal octahedron is severe, as seen by two of the ‘trans’ N–Li–N angles which show a large deviation from 180°, whilst the Li–N bond lengths vary by ca. 0.3 Å. They are longer than the sum of ionic radii for Li (6-coordinate) and N (2.39 Å),²⁰ but significantly shorter than the sum of van der Waals radii (3.78 Å),²¹ consistent with the mismatch between the small Li⁺ cation and the 18-membered ring. The ¹H NMR spectrum is broad at 298 K, indicating dynamic behaviour in solution, while the ⁷Li NMR spectrum shows a singlet at −0.30 ppm.

The computed minimum energy geometry of the isolated [Li(Me₆[18]aneN₆)][BArF] cation (Fig. 2) has C₂ symmetry. The macrocycle is puckered as in the crystal structure, and overall the computed geometric parameters are in close agreement with the experimental values (Tables S2 and S3).

Fig. 3 shows the isodensity plots of the frontier molecular orbitals (FMOs) of [Li(Me₆[18]aneN₆)]. The results show that the highest occupied molecular orbital (HOMO) is centred on the six N atoms of the Me₆[18]aneN₆ ring, and is composed of the N 2p lone pairs with their associated lobes oriented in the direction of the Li⁺ ion. Population analysis shows that the low-lying HOMOs (HOMO–1 to HOMO–5) are also dominated by the N 2p lone pairs, however, an increasing contribution of Li⁺ is observed from HOMO–1 to HOMO–5 (i.e. HOMO–1, HOMO–3, HOMO–4, and HOMO–5 have 3%, 6%, 6%, and 10% contributions from the 2pₓ, 2pₓ, 2pᵧ, and 2s orbitals of Li⁺, respectively). LUMO and LUMO+1 are antibonding molecular orbitals (ABMOs) and correspond predominantly to the 2s and 2p orbitals of the Li⁺ centre.

[Na(Me₆[18]aneN₆)][BArF] was also isolated as a white solid from the reaction of Na[BArF]₂·2thf with Me₆[18]aneN₆ and similarly characterised. Whilst we were unable to grow crystals...
Fig. 2  The optimised BP86 DFT geometry of the [Li(Me₆[18]aneN₆)]⁺ cation with C₂ symmetry and ¹A electronic ground state. The reference axes are shown (in red).

Fig. 3  Frontier molecular orbitals (isovalue of 0.02 electrons Bohr⁻³) for the [Li(Me₆[18]aneN₆)]⁺ complex obtained from BP86 DFT calculations. The energy and symmetry of the molecular orbitals are given in eV and in parentheses, respectively. The dark red (+) and green (−) lobes represent the signs of the angular part of the AO contributing to a MO.
suitable for X-ray analysis, hexadentate coordination of the macrocycle is likely. Two possible minimum energy structures of [Na(Me$_6$[18]aneN$_6$)]$^+$ (1 and 2 in Fig. 4) were located in the BP86 DFT calculations. Structure 1 ($C_2$ symmetry) is analogous to the computed minimum energy structure of [Li(Me$_6$[18]aneN$_6$)]$^+$, while structure 2 ($D_{3d}$ symmetry) has a geometry similar to its K$^+$ and Rb$^+$ counterparts (vide infra). Structure 1 is more stable than 2 by 28.2 kJ mol$^{-1}$ in the gas phase (Tables S12, S13, S18 and S19†). It is important to note that the presence of the [BArF]$^-$ anions in the crystal will influence the relative stabilities of structures 1 and 2 in the isolated solids.

[K(Me$_6$[18]aneN$_6$)][BArF]$^-$ was isolated and characterised similarly. Its X-ray structure (Fig. 5) showed two half-cations in the asymmetric unit, with the K$^+$ ions occupying crystallographic inversion centres. [K(Me$_6$[18]aneN$_6$)]$^+$ shows hexagonal planar N$_6$ coordination at K$^+$, with the NMe groups alternating ‘up-down’ around the ring. The difference between the two K$^+$ cations in the asymmetric unit is found in the long-range interactions to the [BArF]$^-$ anions. There are two K2⋯F1 interactions.

![Top view](image1)

![Side view](image2)

**Fig. 4** The BP86 DFT optimised geometries of [Na(Me$_6$[18]aneN$_6$)]$^+$ structures 1 ($C_2$ symmetry) and 2 ($D_{3d}$ symmetry). The reference axes are shown (in red). Structure 1 is computed to be more stable than structure 2 by 28.2 kJ mol$^{-1}$.

![View of the K2 centred cation (left) and the K1 cation (right)](image3)

**Fig. 5** (a) View of the K2 centred cation (left) and (b) the K1 cation (right) of [K(Me$_6$[18]aneN$_6$)][BArF]$^-$]. Thermal ellipsoids are drawn at 50% probability. H atoms and the [BArF]$^-$ anions (bar F1) are omitted for clarity. Selected bond lengths (Å) and angles (°): K1–N1 2.883(2), K1–N2 2.896(2), K1–N3 2.911(2), K2–N4 2.918(2), K2–N5 2.866(2), K2–N6 2.911(2); N1–K1–N2 61.86(5), N2–K1–N3 61.35(5), N1–K1–N3i 60.67(5), N4–K2–N5 61.79(5), N5–K2–N6 61.35(5), N4–K1–N6 61.04(5). Symmetry codes: (i) 1 − x, −y, 1 − z; (ii) −x, 1 − y, −z.
actions of 3.658(1) Å perpendicular to the N6 plane ($\Sigma$ vdW = 4.19 Å), which gives K2 an overall hexagonal bipyramidal arrangement (Fig. 5a). The other potassium cation (K1) contains no K⋯F interactions and is therefore hexagonal planar (Fig. 5b).

[Rb(Me$_6$[18]aneN$_6$)][BARF] also crystallises with two Rb$^+$ cations in the asymmetric unit, with the Rb$^+$ ion sitting out of the N$_6$ plane by 0.561(3) Å (Rb1) and 0.382(3) Å (Rb2). For Rb1, this has the effect that one Rb⋯F interaction is much shorter than the other. The Rb1–F12 distance of 3.235(2) Å is much shorter than the sum of van der Waals radii (4.67 Å) (Fig. 6a), and is also significantly shorter than the corresponding K⋯F distance. The Rb1⋯F12 distance (4.128(1) Å) is also within the sum of van der Waals radii. Rb2 has two long Rb⋯F distances of 3.951(1) and 4.233(1) Å, both of which are on the same side of the N$_6$ ring (Fig. 6b).

The BP86 DFT calculations satisfactorily reproduce the experimental X-ray structures of [M(Me$_6$[18]aneN$_6$)]$^+$ (M = K and Rb) with $D_{3d}$ symmetry (Fig. 7), which contrasts with $C_2$ symmetry identified for the Li$^+$ counterpart. In the computed structures both metal cations lie within the plane of the Me$_6$[18]aneN$_6$ ring, with six equivalent bond distances (K–N =...
2.984 Å; Rb–N = 3.062 Å), indicating that despite the [BArF]− anion being large and usually considered as very weakly interacting, in some cases it still influences the experimentally determined geometry.

Fig. 8 and S3† show the isodensity plots of the frontier MOs (FMOs) of the [M(Me6[18]aneN6)]+ (M = K or Rb, respectively), which are very similar. As for the Li+ complex discussed above, the HOMO (and LUMO+1) correspond predominantly to the ns (np) orbitals of K+ and Rb+ respectively; the main metal contribution is in the lower HOMO−3 to HOMO−5 orbitals.

The relevant charge densities for the complex cations are shown in Table 1, together with those for Me6[18]aneN6 itself (which has two conformers of very similar energy, structures 3 and 4, Fig. S2†). This shows that electron density is transferred from the bonding σ C–H and σ C–N orbitals and N 2p non-bonding orbitals of [M(Me6[18]aneN6)]+ to the ns and np valence orbitals of the metal. The metal ion in the [M(Me6[18]aneN6)]+ species is more positively charged on going from Li+ → K+ → Rb+, consistent with more electron density being retained on the ligand as Group 1 is descended.

Crystals of [Cs(Me6[18]aneN6)][BArF] all showed severe disorder, although microanalytical and spectroscopic data were consistent with the formulation [Cs(Me6[18]aneN6)][BArF]. Two possible minimum energy structures for the [Cs(Me6[18]aneN6)]+ complex, 5 and 6, are located by the BP86 DFT computations, with structure 5 lower in energy than structure 6 by 43.1 kJ mol−1 (Fig. 9). In 5, the Cs+ ion lies out of the N6 plane by 0.869 Å, similar to the experimentally derived [Rb(Me6[18]aneN6)]+ structure. Notably, the reported [Cs(Me6[18]aneN6)]+ is structurally very different.11a

The bond dissociation energies calculated for [M(Me6[18]aneN6)]+ → M+ + Me6[18]aneN6 (1) (Table 2) decrease on going from Li+ to Cs+, as expected.

Tri-aza macrocyclic complexes

Based upon our earlier work on Na-Me3tacn complexes,3 we also attempted to extend the chemistry of Me3tacn to the other members of Group 1 (Scheme 2).

Using a 1:2 molar ratio of [Li(thf)4][BArF]:Me3tacn in toluene resulted in the isolation of the half-sandwich complex [Li(Me3tacn)(thf)][BArF] in good yield. This contrasts with the
analogous reaction with Na’, for which both the sandwich and half-sandwich complexes were obtained depending upon the molar ratio of metal : ligand used. Further attempts to form the sandwich [Li(Me₃tacn)₂]⁺ cation from [Li(thf)₄][BARF] and 2 mol. equiv. of Me₃tacn in CH₂Cl₂ instead led to a quaternary ammonium cation as its chloride salt (Scheme 2), which was identified by ¹H NMR spectroscopy and from comparison with the literature unit cell.²² No evidence for the [Li(Me₃tacn)₂]⁺ cation was observed.

Although attempts to crystallise the [Li(Me₆[18]aneN₆)]⁺ structures 5 (C₃ᵥ symmetry) and 6 (C₂ symmetry). The reference axes are shown (in red). Structure 5 is computed to be 43.1 kJ mol⁻¹ lower than structure 6.

Table 2 Zero-point and BSSE corrected BP86 bond dissociation energies [kJ mol⁻¹] for dissociation [M(Me₆[18]aneN₆)]⁺ → M⁺ + Me₆[18]aneN₆ (1), M = Li, Na, K, Rb, or Cs

<table>
<thead>
<tr>
<th>M</th>
<th>D(M) (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>423.3 (421.5)</td>
</tr>
<tr>
<td>Na</td>
<td>341.0 (339.2)</td>
</tr>
<tr>
<td>K</td>
<td>264.6 (262.9)</td>
</tr>
<tr>
<td>Rb</td>
<td>209.1 (207.3)</td>
</tr>
<tr>
<td>Cs</td>
<td>151.9 (150.1)</td>
</tr>
</tbody>
</table>

The reported values were obtained using the energy of the Me₆[18]aneN₆, structure 4 (Fig. S2). The values in parentheses were obtained using the energy of the Me₆[18]aneN₆, structure 3 (Fig. S2).

Scheme 2 Products from the reaction of M[BARF] with 2 mol. equiv. of Me₆tacn (M = Li, Na, K). Conditions: (i) 0.5 mol. equiv. [Li(thf)₄][BARF], CH₂Cl₂; (ii) 0.5 or 1 mol. equiv. [Li(thf)₄][BARF], toluene; (iii) M = Na: 0.5 mol. equiv. Na[BARF]·2thf, CH₂Cl₂; M = K: 0.5 mol. equiv. K[BARF], CH₂Cl₂.
[K(Me₃tacn)₂][BARF] was successfully prepared and isolated similarly to the Na⁺ analogue and is isostructural (Fig. 11), forming a centrosymmetric very distorted octahedral cation. This contrasts with the hexagonal planar coordination present in [K(Me₆[18]aneN₆)]⁺, although the bond distances and angles at K⁺ are actually quite similar.

The K–N bonds are 0.2–0.3 Å longer than the corresponding Na–N bonds, while the intra-macroyclic N–K–N angles are more acute by 8–9°. These differences may reflect a poorer match between the large K⁺ cation and the small nine-membered Me₃tacn ring, although as we have noted, they are similar to the angles in [K(Me₆[18]aneN₆)]⁺. As shown in Fig. 11, the Me groups of the two rings are well separated.

In contrast to the BP86 DFT optimised [Li(Me₃tacn)⁺] and [Na(Me₃tacn)₂]⁺ complexes (S₆ symmetry), [K(Me₃tacn)₂]⁺ is computed to have D₃ symmetry (Fig. 12). The computed K–N bond distances are 2.915 Å; slightly longer than the experimental values (2.765(5)–2.880(5) Å), while the calculated N–K–N bond angles within the five-membered chelate rings (63.0°) are closely comparable to the crystallographic values.

The calculations on [K(Me₃tacn)₂]⁺ show that the HOMO and HOMO–1 are doubly degenerate (as are HOMO–2 and HOMO–3) (Fig. 13), and they are mainly located on the N atoms of the Me₃tacn ring, corresponding to N 2p valence orbitals. The LUMO, LUMO+1 and LUMO+2 are mainly localised on K⁺. The LUMO corresponds to the 4s orbital of K⁺, while LUMO+1 and LUMO+2 correspond mainly to the 4pₓ and 4pᵧ orbitals, respectively. The FMOs of the [Na(Me₃tacn)₂]⁺ analogue follow similar trends (Fig. S5†).

Table 3 shows the charge densities on the metal and N atoms of Me₃tacn, [M(Me₃tacn)]⁺ and [M(Me₃tacn)₂]⁺, M = Na and K. The natural charge on K⁺ is lower than the formal charge of +1, showing a significant electron density transfer from the ligands. The charge densities on the N atoms for [M(Me₃tacn)]⁺ and [M(Me₃tacn)₂]⁺ are more negative than in the ‘free’ ligand, because electron density is withdrawn from σ C–H and σ C–N orbitals of the ligand.

As in the [M(Me₆[18]aneN₆)]⁺ analogues, the charge densities on M show that less electron density is transferred to the metal in the K⁺ case, suggesting a relatively weaker interaction between the K⁺ and the Me₃tacn ligand(s), and correspondingly longer K–N distances, than in the Na⁺ case.

Attempts to prepare analogous complexes with Rb⁺ and Cs⁺ ions failed; the optimised minimum energy structures of [M(Me₃tacn)₁]⁺ (M = Rb, Cs) are presented in Tables S16, S17, S22 and S23.†
Zero-point and BSSE corrected bond dissociation energies (kJ mol$^{-1}$) for the dissociation [M(Me$_3$tacn)$_2$]$^+ \rightarrow M^+ +$ Me$_3$tacn (2), M = Li, Na, K, Rb, and Cs, decrease on going down Group 1 (Table 4), correlating with the increase in the ionic radii, and the poorer fit with the small triaza macrocycle. A similar trend in zero-point corrected bond dissociation energies is observed for the dissociation of [M(Me$_3$tacn)$_2$]$^+ \rightarrow [M(Me$_3$tacn)]^+ +$ Me$_3$tacn (3), except for the dissociation energy of the [Li(Me$_3$tacn)$_2$]$^+$ complex which is much lower. This appears to be mainly a consequence of the inaccessibility of the small lithium ion to accommodate six-coordination because the presence of the Me substituents on one macrocycle sterically impedes the approach of the second.

It seems clear, therefore, that isolation of the [M(Me$_3$tacn)$_2$]$^+$ cations is a fine balance between the metal ion being sufficiently large to avoid significant steric clashing between the Me groups of the two rings, but small enough to avoid very acute N–M–N chelate angles.

Tetra-aza macrocyclic complexes
Changing the ligand from Me$_3$tacn to Me$_4$cyclen has the effect of both increasing the denticity and expanding the macro cyclic binding cavity. Reaction of [Li(OH)$_2$]$_3$[BARF] with Me$_4$cyclen in

![Fig. 13](image-url)
CH₂Cl₂ (Scheme 3) led to the formation of [Li(Me₄cyclen)(OH₂)][BArF].

The crystal structure shows a five-coordinate square pyramidal (τ = 0.02) cation with the macrocycle tetradentate and one apical water molecule (Fig. 14). The NMe groups all lie on the same side of the N₄ plane as the metal, with the Li cation displaced out of the N₄ plane by 0.758(7) Å. The same product is obtained irrespective of the ratio of Me₄cyclen : Li[BArF] used.

The reaction between Me₄cyclen and Na[BArF]·2thf in CH₂Cl₂ yielded [Na(Me₄cyclen)(thf)][BArF], with the thf ligand apical (Fig. 15). The τ value of 0.00 confirms an ideal square-pyramidal geometry. Although sandwich complexes of the Group 1 cations with 12-crown-4, e.g. [Na(12-crown-4)]⁺, are well known, over the course of our studies we found no evidence for [M(Me₄cyclen)]⁺ salts with the heavier Group 1 cations (K⁺, Rb⁺, Cs⁺) resulted only in the isolation of [Me₄cyclenH][BArF].

**Solution multinuclear NMR spectroscopy**

The ¹H and ¹³C{¹H} NMR spectra (Experimental) each show the presence of the coordinated aza-macrocycle. The ¹H NMR spectra of Me₁₈[18]aneN₆ complexes of K⁺, Rb⁺, and Cs⁺ salts at ambient temperatures show broad CH₃ and CH₂ resonances. On cooling the solutions the resonances broaden and then split, the effects being most evident in the Cs⁺ salt, but even at 185 K the resonances are still broad and lack resolved couplings, showing that the low temperature limiting spectra have not been reached. These effects are reversible with temperature. Upon cooling the [Cs(Me₆[18]aneN₆)][BArF] solution, the broad signal for the CH₂ protons resolved into complex multiplets and the resonance for the methyl protons split into sharp singlets. This behaviour is most likely a result of two major stereoisomers (arising from the different orientations of the Me groups: ‘all-up’ and alternating ‘up-down’) for which the separate resonances are evident at low temperature as their rate of interconversion slows.

The Group 1 elements offer several nuclei, suitable for NMR spectroscopic studies. Lithium-7 NMR spectra on the aza complexes each show singlet resonances close to δ = 0 (see Experimental). Like the Na⁻-aza macrocyclic cations in our earlier work, the ²³Na NMR spectra of the new complexes are sharp resonances with chemical shifts to high frequency of Na⁺ in water (δ = 0): [Na(Me₆[18]aneN₆)][BArF] +3.1; [Na(Me₄cyclen)(thf)][BArF] +12.7; [Na(Me₄cyclam)(thf)][BArF] +11.4; [Na-(Me₃tacn)(thf)][BArF] +3.7; [Na(Me₅tacn)(thf)][BArF] +6.2. Although

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Fig. 14 View of the cation in [Li(Me₄cyclen)(OH₂)][BArF]. Thermal ellipsoids are drawn at 50% probability. H atoms and the [BArF]⁻ anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Li₁–N₁ 2.186(8), Li₁–N₂ 2.206(8), Li₁–N₃ 2.179(8), Li₁–N₄ 2.154(9), Li₁–O₁a 1.981(1); N₁–Li₁–N₂ 82.8(3), N₂–Li₁–N₃ 82.1(3), N₃–Li₁–N₄ 84.7(3), N₁–Li₁–N₄ = 82.6(3).

Fig. 15 View of the cation present in [Na(Me₄cyclen)(thf)][BArF]. Thermal ellipsoids are drawn at 50% probability. H atoms, the [BArF]⁻ anion, and disorder of the ethylene linkers within the Me₄cyclen ring are omitted for clarity. Selected bond lengths (Å) and angles (°): Na–N₁ 2.463(4), Na–N₂ 2.461(3), Na–N₃ 2.453(4), Na–N₄ 2.444(4), Na–O₁ 2.244(3); N₁–Na–N₂ 75.4(1), N₂–Na–N₃ 75.6(1), N₃–Na–N₄ 76.0(1), N₁–N₁–N₄ 75.5(2).

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*Notes: Li: I = ⁹/₁, N = 92.6%, Rₑ = 1.54 × 10⁻⁴, Q = 3.7 × 10⁻³² m⁴, Ξ = 38.87 MHz; Na: I = ⁹/₁, N = 100%, Rₑ = 5.24 × 10⁻⁶, Q = 0.10 × 10⁻²⁸, Ξ = 26.41; K: I = ⁹/₁, N = 93.3%, Rₑ = 2.69, Q = 5.5 × 10⁻³⁰, Ξ = 8.67; Rb: I = ⁹/₁, N = 72.1%, Rₑ = 43.4, Q = 0.25 × 10⁻²⁸, Ξ = 9.69; Cs: I = ⁹/₁, N = 100%, Rₑ = 2.75 × 10⁻², Q = 0.3 × 10⁻³⁰, Ξ = 13.21.*
the cations are expected to be exchanging rapidly in solution, these values can be compared with the Na⁺-crown ether cations which have chemical shifts to low frequency of 0 ppm, and therefore indicate that the azacrown complexation is retained in CH₂Cl₂ solution.

Solutions of the potassium complexes in CH₂Cl₂ solution do not show a ⁴¹⁷K resonance at room temperature (295 K) or on cooling to 185 K. Studies of K⁺-crown ether cations over a range of temperatures and K⁺:crown ether ratios in a range of donor solvents show that often only the ‘free’ K⁺ resonance is seen. The [K(crown)]⁻ is often not observed most likely due to fast quadrupolar relaxation in the low symmetry environment. In [K(Me₆[¹⁸]aneN₆)]⁻ and [K(Me₆tacn)₂]⁻ it is probable that fast ligand exchange in solution produces low symmetry environments and fast quadrupolar relaxation (the corresponding ¹H NMR spectra show only broad singlets for the macrocyclic CH₂ groups). For similar reasons, no ⁸⁵Rb resonance was observed at any temperature between 298 and 185 K.

The Q value for the ¹³³Cs nucleus is small, hence NMR spectra are readily observed. The VT ¹³³Cs NMR data for [Cs(Me₆[¹⁸]aneN₆)][BARF] show a singlet at 54.1 ppm (298 K) and this splits into two singlets at 73.3 and 58.7 ppm at 183 K, which we attribute to the slowing of dynamic processes and the presence of two significant stereoisomers (‘all up’ and alternating ‘up-down’). These chemical shifts are also significantly to high frequency of those typically observed in crown ether adducts.

Conclusions

By taking advantage of the lower lattice energies associated with [BARF]⁺ precursors, which leads to increased solubility in very weak donor solvents such as CH₂Cl₂, the unusual Group 1 cation complexes [M(Me₆[¹⁸]aneN₆)][BARF] can be obtained in good yield for all members from M = Li to Cs. Structural characterisation of several of these (M = Li, K, and Rb) allows comparisons down the Group, as well as the rarely observed bis-Me₆tacn sandwich cations, [M(Me₆tacn)₂][BARF], isolated for M = Na and K. The combined experimental and DFT study indicates that the isolation of the [M(Me₆tacn)₂]⁺ cations requires a fine balance of, on one hand, the metal ion being sufficiently large to avoid significant steric clashing between the Me groups of the two rings, and on the other, the ion being sufficiently small to avoid extremely acute N–M–N chelate angles. In contrast, the very small Li⁺ ion forms only the half-sandwich [Li(Me₆tacn)[thf]]⁺ cation. These complex cations show significant structural differences which correlate closely with the trends in ionic radii down Group 1 and the available macrocyclic binding cavity. The [BARF]⁻ anions also show quite significant M⁻F interactions, particularly towards the larger metal ions (K⁺ and beyond), despite being large, diffuse ions with delocalised charge.

DFT calculations show very good agreement with the experimentally determined structures and confirm significant donation of electron density from the N atoms of the ligand upon complexation, which is accompanied by transfer of some electron density to N from the σ C–H and σ C–N bonding orbitals. The nature of the FMOs show that contributions from the metal orbitals are only significant in the lower energy valence occupied orbitals, while the HOMO itself is dominated by the N 2p orbitals. The calculations also show that coordination of the azacrown to the Group 1 cation in these complexes involves significant donation of electron density from the p-orbitals on the N atoms, rather than purely electrostatic interactions.

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Notes and references


