ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Unexpected neutral aza-macrocycle complexes of sodium†

Cite this: *Chem. Commun.*, 2014, 50, 5843

Received 24th February 2014, Accepted 15th April 2014

DOI: 10.1039/c4cc01407c

www.rsc.org/chemcomm

Matthew Everett, Andrew Jolleys, William Levason, David Pugh and Gillian Reid*

Highly unusual Na^+ complexes with neutral tri- and tetra-amines are isolable in good yield from the reaction of $NaBAr^F$ with the amine in organic media. Structural characterisation reveals primary Na–N bonding, including an unusual sandwich cation $[Na(Me_3tacn)_2]^+$, derived from homoleptic N_6-coordination *via* two Me_3-tacn ligands, and the distorted 5-coordinate $[Na(thf)(Me_4cyclam)]^+$.

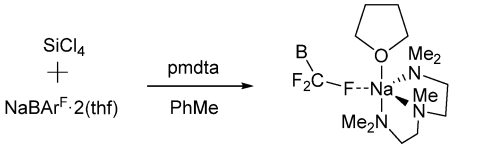
Group 1 metals form hard metal cations with a very strong affinity for both anionic and neutral O-donor ligands. This includes the crown ether macrocycles, with the size of the binding cavity in the macrocycle dictating which alkali metal cation is preferentially coordinated.[1] These complexes are much more soluble in organic solvents than typical Group 1 salts, hence crown ethers often find application as phase transfer catalysts.[1c] Additionally, by encapsulating the Group 1 cation inside a hydrophobic shell and eliminating cation–anion interactions, the nucleophilicity of the associated anion can be increased, leading to increased utility in organic transformations.[1d]

N-donor macrocycles can impart extra stability to alkali metal complexes when compared to the analogous crown ethers. Dye *et al.* used an alkylated N-donor cryptand to encapsulate sodium cations as the key part of a system of room temperature stable electrides.[2a] It is notable that cryptands containing O-donors form electrides which are unstable above −60 °C owing to cleavage of the C–O functionalities.[2b] Despite this, compounds of neutral N-donor macrocyclic ligands with alkali metal cations other than Li^+ are not well studied. Several examples exist where N-donor macrocycles have been functionalised with anionic or neutral donor pendant arms and coordinated to alkali metal cations,[3] but there are no structurally authenticated examples of neutral N-donor macrocycles coordinating to K^+, Rb^+ and Cs^+. Further, only two structurally authenticated examples with Na^+ have been reported: Nöth and co-workers coordinated 1,5,9-trimethyl-1,5,9-trizacyclododecane to $NaBH_4$, and Okuda *et al.* obtained an unexpected complex of NaI with 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane (Me_3cyclen).[4]

As part of our recent work on coordination complexes of silicon[5] and germanium[6] as potential precursors for supercritical fluid electrodeposition (SCFED) processes,[7] we have been utilising the sodium salt of tetrakis(3,5-bis{trifluoromethyl}phenyl)borate (hereafter referred to as $[BAr^F]^-$) both as a supporting electrolyte for use in supercritical fluids[7b,c] and as a halide abstractor in the presence of neutral N-donor ligands (Scheme 1). Unexpectedly, we found that these N-donor ligands have a high affinity for Na^+ under certain conditions. This resulted in coordination of the polyamine to Na^+ rather than halide abstraction from $SiCl_4$ or $[GeCl_2(1,4\text{-dioxane})]$. From the reaction of $SiCl_4$, $NaBAr^F\cdot 2(thf)$ and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdta) we were able to isolate compound **1**, $[Na(pmdta)(thf)(\kappa^1\text{-}BAr^F)]$, as colourless crystals suitable for X-ray diffraction (Fig. 1).

It was also possible to synthesise compound **1** directly, by adding a solution of the ligand in CH_2Cl_2 to a suspension of $NaBAr^F\cdot 2(thf)$ in CH_2Cl_2.[8] Complete dissolution occurred upon addition of the ligand and **1** was isolated as a white solid *via* precipitation with hexane.

Compound **1** crystallises in the monoclinic space group *Cc* with evidence for positional disorder present in the coordinated thf molecule as well as in some of the CF_3 groups of the anion. The latter is not unusual in weakly coordinating anions which contain CF_3 groups, but the $[BAr^F]^-$ anion in particular is notorious for being disordered in its solid state structures.[9] Nonetheless, the structure of the molecule is unambiguous with



Scheme 1 Unexpected formation of **1** from the attempted use of $NaBAr^F$ as a halide abstractor. B = remainder of $[BAr^F]^-$ anion (omitted for clarity).

School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK. E-mail: G.Reid@soton.ac.uk; Tel: +44 (0)23 8059 3609

† Electronic supplementary information (ESI) available: Full experimental details, plus all the crystallographic and analytical data for all products. CCDC 987718–987721. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01407c

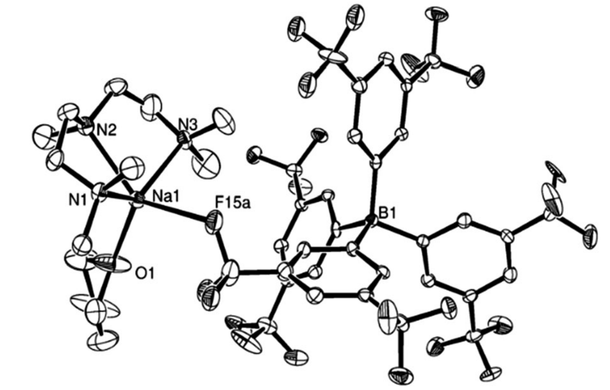


Fig. 1 ORTEP representation of **1** with ellipsoids at 50% probability. H atoms and positional disorder of three CF_3 groups and the thf ring are omitted for clarity. The CF_3 group interacting with Na1 is disordered and only one refined position for the CF_3 group (containing F15a) is shown. Selected bond lengths (Å): N1–Na1 2.473(5), N2–Na1 2.452(5), N3–Na1 2.477(5), O1–Na1 2.262(5), F15a–Na1 2.60(1), F15b–Na1 2.349(6) (not shown).

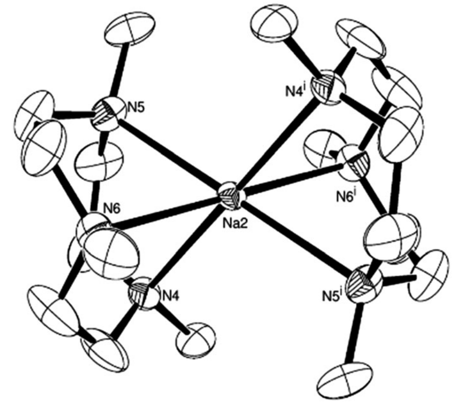


Fig. 2 ORTEP representation showing one of two crystallographically distinct cations in the asymmetric unit of compound **2b**. A picture of the major disorder component from the other cation is shown in the ESI† (Fig. S1). Thermal ellipsoids at 50% probability. The BAr^F anion, which does not interact with the Na^+ centre, and the H atoms are omitted for clarity. Selected bond lengths (Å): N1–Na1 2.554(5), N2–Na1 2.527(5), N3–Na1 2.545(5) (this cation not shown), N4–Na2 2.507(4), N5–Na2 2.600(5), N6–Na2 2.567(5). Range of *cis* N–Na–N angles within the same macrocyclic ring (°): 70.5(2)–72.0(2), between neighbouring rings: 108.1(2)–109.5(2). Symmetry code: $-x + 1/2, -y + 1/2, -z$.

one tridentate pmdta ligand, one thf molecule and one κ^1 Na···F interaction from a CF_3 group completing a 5-coordinate, distorted square-based pyramidal geometry at Na^+. The Na–N bond distances are significantly longer than the Na–O bond distance, reflecting the strong oxophilicity of Na^+, but they are among the shorter range of known Na–N bond lengths in the CSD.[10] The κ^1 interaction between a $[BAr^F]^-$ CF_3 group and Na^+ is only the second example of $[BAr^F]^-$ interacting with any metal,[11] although the positional disorder of the CF_3 group in compound **1** precludes an accurate comparison of Na···F bond distances. However, the observed Na···F distances in **1** are only slightly longer than the sum of the ionic radii for Na^+ and F^- (1.02 and 1.33 Å respectively), and well within the sum of van der Waals radii for Na and F (3.96 Å).[12]

Analysis of the product (^{1}H and ^{13}C{^{1}H} NMR spectroscopy, elemental analysis) supported the formulation observed crystallographically, although it is noteworthy that the signals for the triamine ligand in the ^{1}H NMR spectrum were very broad at room temperature as a result of the amine-coordinated cations undergoing fast ligand exchange in solution, as is typical of labile alkali metal complexes. Solution ^{23}Na NMR spectroscopy showed a signal at +2.1 ppm (relative to a 0.1 mol dm^{-3} solution of NaCl in D_2O), which is ~6 ppm to high frequency of $NaBAr^F{\cdot}2(thf)$ (−4.8 ppm in CH_2Cl_2) and reflects the difference between a homoleptic O-donor environment at Na and one with significant N-donation.

Following the new procedure,[8] two complexes of $NaBAr^F$ with the macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) were also synthesised using a 1 : 1 ratio of macrocycle to Na (**2a**) and a 2 : 1 ratio (**2b**). Whilst crystals of compound **2a** did not give a viable X-ray data set, spectroscopic analysis indicated that a product with similar composition to compound **1** was obtained and elemental analysis supported the formulation $[Na(Me_3tacn)(thf)][BAr^F]$. ^{1}H NMR spectroscopy at room temperature showed broad resonances for the macrocycle protons. The ^{23}Na NMR shift of +3.7 ppm is similar to that observed from compound **1**, consistent with N-donor atom coordination to Na^+.

Compound **2b**, $[Na(Me_3tacn)_2][BAr^F]$, crystallises in the monoclinic space group *C*2/*c* with two symmetry-independent half cations and one disordered anion comprising the asymmetric unit. One half-cation also contained positional disorder of the ethylene linkers within the macrocyclic ring, but the nitrogen atoms were not disordered and the coordination environment around both half cations is clearly that of a sandwich complex with two macrocycles surrounding one Na^+ cation. Despite the oxophilicity of the alkali metal cations, no thf is retained in the structure, presumably due to the strong preference for the Me_3tacn ligand for tridentate coordination (Fig. 2).

The Na–N bond distances for **2b** are slightly longer (by ~0.1 Å) than those in **1**. This may simply be due to the increased coordination number at Na^+. The solution ^{23}Na NMR spectrum shows a singlet at +6.2 ppm.

It is notable that **2b** is only the second structurally characterised example of a sandwich complex of any metal with Me_3tacn as ligand. The other was reported by Wieghardt *et al.* with Ag(I), which has a larger ionic radius than Na(I) (1.15 Å and 1.02 Å, respectively, for 6-coordination).[13] The *cis* N–Na–N angles around Na are significantly distorted away from the ideal 90°; those within a ring are about 40° smaller than those between neighbouring macrocycles and this is almost certainly due to steric repulsion between the methyl groups on alternating macrocyclic rings causing the Na–N bond distance to increase, thus reducing the intra-macrocycle bond angles. This is consistent with the Ag(I) structure reported by Wieghardt which also showed a large disparity between the inter-ring and intra-ring N–M–N angles.

We observed that Me_3tacn was readily protonated in the presence of even trace water; one attempted synthesis of **2a** was inadvertently exposed to the atmosphere forming the hydrolysis product $[Me_3tacnH][BAr^F]$ (see ESI†). This suggests that judicious choice of conditions (solvent and anion) is required in order to access the potentially very rich coordination chemistry of alkali metal cations with a wider range of Lewis bases.

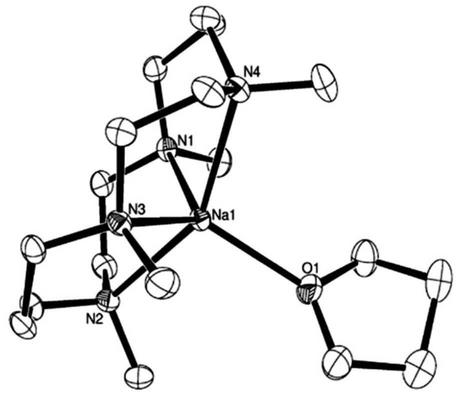


Fig. 3 ORTEP representation of the cation of compound **3**. Thermal ellipsoids at 50% probability. The BAr^F anion, which does not interact with the Na^+ centre, and the H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–Na1 2.438(2), N2–Na1 2.454(2), N3–Na1 2.451(2), N4–Na1 2.473(2), O1–Na1 2.313(2). N1–Na1–N3 123.91(7), N2–Na1–N4 150.33(7), N1–Na1–N2 77.94(7), N1–Na1–N4 89.49(7), N2–Na1–N3 88.00(6), N3–Na1–N4 76.82(6).

Reaction of $NaBAr^F{\cdot}2(thf)$ with the tetradentate N-donor macrocycle, Me_4cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) yielded colourless crystals of **3**. Structural analysis (Fig. 3) revealed a tetradentate coordination mode for the macrocycle, with the Me groups in the 'all-up' configuration, directed towards the same side of the N_4 plane as the metal, with one thf molecule completing a distorted 5-coordinate geometry at sodium. The sodium cation lies above the N_4-plane by 0.889(1) Å, reflecting a mismatch between the Na^+ cation size and the macrocyclic binding cavity. The τ value[14] of 0.44 indicates that the geometry at Na^+ is almost half-way between ideal square based pyramidal and ideal trigonal bipyramidal. The Na–O bond length is about 0.05 Å longer than the corresponding distance in compound **1**, while the Na–N bond lengths are identical to **1** (within experimental error) and they are also in accord with the Na–N bond lengths found in [Na(Me_3cyclen)I], the only other neutral tetradentate macrocyclic ligand coordinated to sodium.[4b]

Although the amine-coordinated cations are very likely to be undergoing fast ligand exchange in solution, as is typical of labile alkali metal complexes, ^{23}Na NMR studies show that the Na–N coordination is clearly detectable in solution. ^{23}Na NMR studies of homoleptic O-donor complexes (*e.g.* $NaBPh_4$ with dibenzo-18-crown-6 and dibenzo-24-crown-8) show $\delta(^{23}Na)$ to low frequency of the zero reference, typically *ca.* 0 to −16 ppm.[15] However, for complexes **1–3**, $\delta(^{23}Na)$ is significantly to high frequency (to *ca.* +10 ppm). This effect of N-coordination on $\delta(^{23}Na)$ was also seen by Lin and Popov, who measured $\delta(^{23}Na)$ of $NaBPh_4$ with 15-crown-5 in a variety of solvents.[16] With O-donor solvents, $\delta(^{23}Na)$ was always to low frequency of the reference irrespective of the concentration of crown ether, but when pyridine was used as the solvent with a low concentration of crown ether (*i.e.* significant N-coordination to Na is present), a shift to high frequency relative to the reference was observed. Thus it seems that the ^{23}Na chemical shifts are sensitive to both the nature and number of the donor atoms coordinated.

We have shown that neutral alkylated multidentate N-donor ligands have a surprisingly high affinity for Na^+ cations. The reagent $NaBAr^F$ readily forms complexes with N-donor ligands in preference to abstracting a halide from Lewis acids such as $SiCl_4$ and [$GeCl_2$(1,4-dioxane)], and the complexes have also been synthesised without the Lewis acid. The complexes exhibit a rich range of structural interactions, including a very rare example of two Me_3tacn macrocycles forming a sandwich complex and only the second example of a $[BAr^F]^-$ anion interacting with a metal. The successful formation of these new species may be a result of the low lattice energy of $NaBAr^F$ when compared to other Group 1 ionic salts, coupled with the high solubility of the $[BAr^F]^-$ anion in organic media which do not compete with the N-donor ligand, and suggests that judicious choice of solvent and anion may lead to the unveiling of a rich area of coordination chemistry of softer donor ligands with hard Group 1 cations. Further investigations into extending this study to other alkali metal cations and ligands are underway.

This work was funded by EPSRC (through a Programme Grant EP/I033394/1 and also through EP/I010890/1). The SCFED Project (www.scfed.net) is a multidisciplinary collaboration of British universities investigating the fundamental and applied aspects of supercritical fluids.

Notes and references

1 (*a*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, West Sussex, 2nd edn, 2009, p. 116; (*b*) J. S. Bradshaw, R. M. Izatt, A. V. Bordunov, C. Y. Zhu and J. K. Hathaway, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Elsevier, Oxford, 1996, p. 35; (*c*) T. Hashimoto and K. Maruoka, in *Asymmetric Phase Transfer Catalysis*, ed. K. Maruoka, Wiley, Weinheim, 2008, p. 1; (*d*) J. McMurry, *Organic Chemistry*, Brooks/Cole, California, 8th edn, 2010, p. 690.
2 (*a*) M. Y. Redko, J. E. Jackson, R. H. Huang and J. L. Dye, *J. Am. Chem. Soc.*, 2005, **127**, 12416; (*b*) P. M. Cauliez, J. E. Jackson and J. L. Dye, *Tetrahedron Lett.*, 1991, **32**, 5039.
3 See, for example: (*a*) G. R. Giesbrecht, A. Gebauer, A. Shafir and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 2000, 4018; (*b*) H. Misake, H. Miyake, S. Shinoda and H. Tsukube, *Inorg. Chem.*, 2009, **48**, 11921.
4 (*a*) H.-H. Giese, T. Habereder, H. Nöth, W. Ponikwar, S. Thomas and M. Warchhold, *Inorg. Chem.*, 1999, **38**, 4188; (*b*) S. Standfuss, T. P. Spaniol and J. Okuda, *Eur. J. Inorg. Chem.*, 2010, 2987.
5 (*a*) K. George, A. L. Hector, W. Levason, G. Reid, G. Sanderson, M. Webster and W. Zhang, *Dalton Trans.*, 2011, **40**, 1584; (*b*) W. Levason, D. Pugh and G. Reid, *Inorg. Chem.*, 2013, **52**, 5185.
6 (*a*) M. F. Davis, W. Levason, G. Reid and M. Webster, *Dalton Trans.*, 2008, 2261; (*b*) F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Inorg. Chem.*, 2010, **49**, 752; (*c*) P. N. Bartlett, C. Y. Cummings, W. Levason, D. Pugh and G. Reid, *Chem. – Eur. J.*, 2014, **20**, 5019–5027.
7 (*a*) J. Ke, W. Su, S. M. Howdle, M. W. George, D. Cook, M. Perdjon-Abel, P. N. Bartlett, W. Zhang, F. Cheng, W. Levason, G. Reid, J. Hyde, J. Wilson, D. C. Smith, K. Mallik and P. Sazio, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 14768; (*b*) P. N. Bartlett, D. C. Cook, M. W. George, J. Ke, W. Levason, G. Reid, W. Su and W. Zhang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 190; (*c*) J. Ke, P. N. Bartlett, D. Cook, T. L. Easun, M. W. George, W. Levason, G. Reid, D. Smith, W. Su and W. Zhang, *Phys. Chem. Chem. Phys.*, 2014, DOI: 10.1039/C3CP54955K.
8 A typical procedure is as follows: to a suspension of $NaBAr^F{\cdot}2(thf)$ (240 mg, 0.23 mmol) in anhydrous CH_2Cl_2 (5 mL) was added a solution of the ligand (1 mol eq.) in CH_2Cl_2 (2 mL). The solution was stirred under N_2 for 4 h, then layered with anhydrous hexane (30 mL) to produce colourless crystals. Full experimental details, crystallographic and analytical data for all products are contained in the ESI†.
9 A. B. Chaplin and A. S. Weller, *Eur. J. Inorg. Chem.*, 2010, 5124.

10 F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.
11 S. I. Pascu, T. Jarrosson, C. Naumann, S. Otto, G. Kaiser and J. K. M. Sanders, *New J. Chem.*, 2005, **29**, 80.
12 S. Alvarez, *Dalton Trans.*, 2013, **42**, 8617.
13 C. Stockheim, K. Wieghardt, B. Nuber, J. Weiss, U. Flörke and H.-J. Haupt, *J. Chem. Soc., Dalton Trans.*, 1991, 1487.
14 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
15 (*a*) H. D. H. Stöver, A. Deville and C. Detellier, *J. Am. Chem. Soc.*, 1985, **107**, 4167; (*b*) A. Deville, H. D. H. Stöver and C. Detellier, *J. Am. Chem. Soc.*, 1987, **109**, 7293.
16 J. D. Lin and A. I. Popov, *J. Am. Chem. Soc.*, 1981, **103**, 3773.