Supplementary information

for

Unexpected neutral aza-macrocyclic complexes of sodium

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Experimental

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glove box techniques. 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam) was obtained from Sigma, stored in a glove box and used as received. N,N,N',N'',N''-pentamethyldiethylenetriamine (pmdta) was purchased from Sigma and distilled over CaH_2. 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) was synthesised according to a literature procedure.[1] $NaBAr^F \cdot 2$(thf) was synthesised by a slight modification of Brookhart's procedure.[2] In our hands, the last vestiges of colour were removed by dissolving the tan-coloured product in thf, adding hexane to precipitate a white solid, then drying *in vacuo* to remove excess thf. CH_2Cl_2 was dried by distillation from CaH_2, thf was distilled from a purple solution of sodium benzophenone ketyl, hexane and toluene were distilled over sodium.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in CD_2Cl_2 solutions at 293 K using Bruker AV-300 and DPX-400 spectrometers and are referenced to the residual CH_2Cl_2 resonance. ^{23}Na NMR spectra were obtained at 293 K on a Bruker DPX-400 spectrometer with an approximate 0.25 mM concentration of compound in CH_2Cl_2 and referenced to a 0.1 mol dm^{-3} solution of NaCl in D_2O.[3] Microanalyses were undertaken by Stephen Boyer at London Metropolitan University.

Crystals were obtained as described below. Details of the crystallographic data collection and refinement are in Table S1. 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 100 μm focus). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7.[4] Structure solution and refinement were carried out using WinGX and software packages within.[5] All compounds contained positional disorder of some of the CF_3 groups; a common issue with weakly-coordinating anions containing CF_3 groups, but especially $[BAr^F]^-$.[6] Some

positional disorder was also noted for the thf molecule in compound **1**, and for the macrocyclic ring in compounds **2b**, **3** and the by-product [Me_3tacnH][BAr^F] (below). This disorder was modelled satisfactorily using suitable restraints. H atoms attached to C 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). The NH proton in [Me_3tacnH][BAr^F] was initially located in the Fourier difference map but added as an idealised proton (AFIX 13) with an N–H distance of 0.93 Å and U_{iso}(H) = 1.2U_{eq}(N). enCIFer was used to prepare CIFs for publication.[7] CCDC reference numbers 987718-987721 contain crystallographic data in CIF format.

General synthetic method:

$NaBAr^F \cdot 2$(thf) (240 mg, 0.23 mmol) was suspended in CH_2Cl_2 (5 mL) and a solution of the amine in CH_2Cl_2 (2 mL) was added. The reaction was stirred for 4 hours then the product was precipitated by the addition of hexane (30 mL). Crystals were obtained by layering a concentrated CH_2Cl_2 solution of the product with hexane.

(tetrahydrofuran)(pmdta)sodium (κ^1-tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) (1)

40 mg (0.23 mmol) of pmdta was used. Yield: 144 mg of a white solid, 71%.

δ_H (400.1 MHz, CD_2Cl_2): 7.74 (8H, s, BAr^F H2/6), 7.59 (4H, s, BAr^F H4), 3.69–3.75 (4H, m, OCH_2), 2.42–2.74 (7H, br m, NCH_3 and CH_2), 2.32–2.42 (4H, br m, CH_2), 2.22 (12H, br s, $N(CH_3)_2$), 1.85–1.92 (4H, m, $OCH_2C\underline{H}_2$) ppm.

δ_C (100.6 MHz, CD_2Cl_2): 161.38 (C, q, $J_{C–B}$ = 49.9 Hz, BAr^F C1), 135.44 (CH, BAr^F C2/6), 129.51 (BAr^F C3/5), 125.24 (C, q, $J_{C–F}$ = 272 Hz, CF_3), 118.13 (CH, BAr^F C4), 69.22 (OCH_2), 57.64, 48.80 (NCH_2) 45.89, 45.26 (NCH_3), 26.02 ($OCH_2\underline{C}H_2$) ppm.

δ_{Na} (105.8 MHz, CD_2Cl_2): 2.1 ppm.

Analysis: Calc. for $C_{45}H_{43}N_3OBF_{24}Na$ (1131.62): C, 47.76; H, 3.83; N, 3.71. Found: C, 47.57; H, 3.75; N, 3.81.

(tetrahydrofuran)(Me_3tacn)sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (2a)

40 mg (0.23 mmol) of Me_3tacn was used. Yield: 179 mg of a white crystalline solid, 88%.

δ_H (400.1 MHz, CD_2Cl_2): 7.73 (8H, s, BAr^F H2/6), 7.58 (4H, s, BAr^F H4), 3.69–3.76 (4H, m, OCH_2), 2.54–2.64 (6H, m, NCH_2), 2.28–2.49 (15H, m, NCH_2 and NCH_3), 1.84–1.91 (4H, m, thf $OCH_2C\underline{H}_2$) ppm.

δ_C (100.6 MHz, CD_2Cl_2): 162.35 (C, q, $J_{C–B}$ = 49.9 Hz, BAr^F C1), 135.42 (CH, BAr^F C2/6), 129.65 (BAr^F C3/5), 125.23 (C, q, $J_{C–F}$ = 272 Hz, CF_3), 118.11 (CH, BAr^F C4), 69.24 (OCH_2), 54.70, 54.20 (NCH_2) 47.95, 46.70 (NCH_3), 25.99 ($OCH_2\underline{C}H_2$) ppm.

δ_{Na} (105.8 MHz, CD_2Cl_2): 3.7 ppm.

Analysis: Calc. for $C_{45}H_{41}N_3OBF_{24}Na$ (1129.77): C, 47.84; H, 3.66; N, 3.72. Found: C, 47.75; H, 3.75; N, 3.70.

Bis(Me_3tacn)sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (2b)

80 mg (0.46 mmol) of Me_3tacn was used. Yield: 206 mg of a white solid, 93%.

δ_H (400.1 MHz, CD_2Cl_2): 7.75 (8H, s, BAr^F H2/6), 7.59 (4H, s, BAr^F H4), 2.51–2.68 (16H, m), 2.30–2.51 (26H, br s) ppm.

δ_C (100.6 MHz, CD_2Cl_2): 162.56 (C, q, J_{C-B} = 49.9 Hz, BAr^F C1), 135.44 (CH, BAr^F C2/6), 129.55 (C, qq, $^2J_{C-F}$ = 31.6, 2.9 Hz, BAr^F C3/5), 125.25 (C, q, J_{C-F} = 272 Hz, CF_3), 118.11 (CH, septet, $^3J_{C-F}$ = 3.7 Hz, BAr^F C4), 60.00 (CH_2), 54.98 (CH_2) 48.09 (CH_3) ppm.

δ_{Na} (105.8 MHz, CD_2Cl_2): 6.2 ppm.

Analysis: Calc. for $C_{50}H_{54}N_6BF_{24}Na$ (1228.94): C, 48.87; H, 4.43; N, 6.84. Found: C, 49.68; H, 4.35; N, 6.70.

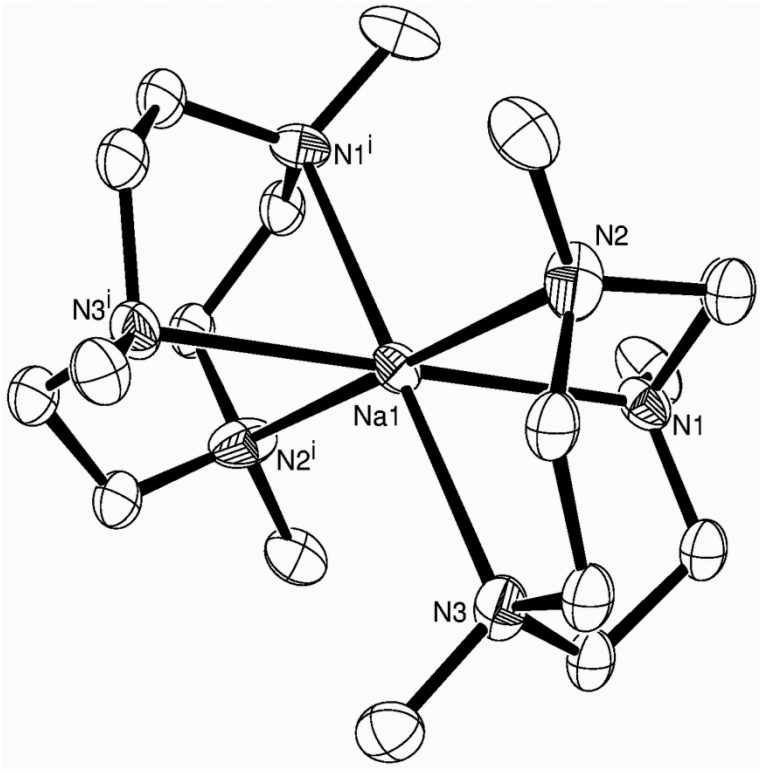

Figure S1. ORTEP representation of the major component of the disordered cation in the asymmetric unit of compound **2b**. The other cation was not disordered and a picture is shown in the main manuscript, along with relevant bond lengths and angles (Figure 2). Thermal ellipsoids at 50% probability. The BAr^F anion, which does not interact with the Na^+ centre, and the H atoms are omitted for clarity. Symmetry code: –x, y, –z + 0.5.

(tetrahydrofuran)(Me_4cyclam)sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (3)

60 mg (0.23 mmol) of Me_4cyclam was used. Yield: 199 mg of a white solid, 91%.

δ_H (300.1 MHz, CD_2Cl_2): 7.69 (8H, s, BAr^F H2/6), 7.57 (4H, s, BAr^F H4), 3.68–3.75 (4H, m, OCH_2),2.56–2.67 (4H, m, $NC\underline{H}_2CH_2C\underline{H}_2N$), 2.40 (8H, br s, $NC\underline{H}_2C\underline{H}_2N$), 2.31–2.36 (4H, m, $NC\underline{H}_2CH_2C\underline{H}_2N$), 2.17 (12H, s, NCH_3), 1.75–1.93 (6H, m, $CH_2C\underline{H}_2CH_2$ and thf $OCH_2C\underline{H}_2$), 1.46–1.55 (2H, m, $CH_2C\underline{H}_2CH_2$) ppm.

δ_C (75.5 MHz, CD_2Cl_2): 161.33 (C, q, J_{C-B} = 49.8 Hz, BAr^F C1), 135.39 (CH, BAr^F C2/6), 128.46 (BAr^F C3/5), 125.19 (C, q, J_{C-F} = 272 Hz, CF_3), 118.07 (CH, BAr^F C4), 68.70 (OCH_2), 57.14 ($N\underline{C}H_2$) 42.64 (NCH_3), 25.88 ($OCH_2\underline{C}H_2$), 23.59 ($CH_2\underline{C}H_2CH_2$) ppm.

δ_{Na} (105.8 MHz, CD_2Cl_2): 11.4 ppm.

Analysis: Calc. for $C_{50}H_{52}N_4OBF_{24}Na$ (1214.76): C, 49.41; H, 4.32; N, 4.61. Found: C, 49.35; H, 4.24; N, 4.61.

1*H*-1,4,7-trimethyl-1,4,7-triazacyclononane tetrakis{3,5-bis(trifluoromethyl)phenyl}borate

These crystals were obtained from a synthesis of compound **2a** which had been inadvertently exposed to air. A few crystals were grown by layering a concentrated CH_2Cl_2 solution of the hydrolysed product with hexane.

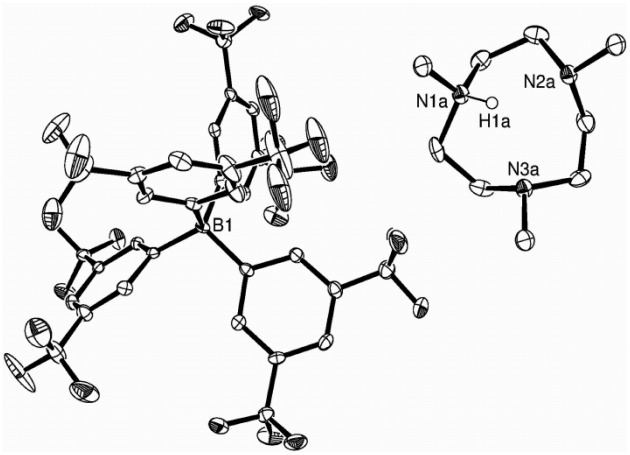

Figure S2. ORTEP representation of [Me_3tacnH][BAr^F]. Thermal ellipsoids at 50% probability, hydrogen atoms (bar NH) are omitted for clarity.

Compound	**[Na(pmdta)(thf)(BAr^F)] (1)**	**[Na(Me_3tacn)$_2$][BAr^F] (2b)**	**[Na(Me_4cyclam)(thf)][BAr^F] (3)**	**[Me_3tacnH][BAr^F]**
Formula	$C_{45}H_{43}BF_{24}N_3NaO$	$C_{50}H_{54}BF_{24}N_6Na$	$C_{50}H_{52}BF_{24}N_4NaO$	$C_{41}H_{34}BF_{24}N_3$

M/g mol^{-1}	1131.62	1228.79	1214.76	1035.52
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group (No.)	*Cc* (9)	*C*2/*c* (15)	*P*-1 (2)	*P*1 (1)
a/Å	14.492(4)	43.057(2)	12.784(2)	9.677(1)
b/Å	14.229(4)	12.624(1)	12.896(2)	10.771(1)
c/Å	24.850(7)	21.279(2)	18.089(2)	10.824(1)
α/°	90	90	91.602(2)	83.284(6)
β/°	103.181(4)	100.930(7)	98.258(3)	82.174(6)
γ/°	90	90	114.446(2)	82.924(6)
U/Å^3	4989(2)	11356(1)	2674.1(7)	1103.5(3)
Z	4	8	2	1
μ(Mo-Kα) /mm^{-1}	0.160	0.147	0.155	0.163
F(000)	2296	5024	1240	522
Total reflections	11845	50872	27281	10486
Unique reflections	8832	10019	12176	7226
R_{int}	0.024	0.100	0.021	0.021
Goodness-of-fit on F^2	1.050	1.057	1.062	1.031
R_1[b] [$I_o > 2\sigma(I_o)$]	0.072	0.092	0.058	0.051
R_1 (all data)	0.087	0.164	0.067	0.064
wR_2[b] [I_o >	0.161	0.235	0.136	0.105

$2\sigma(I_o)$]				
wR_2 (all data)	0.173	0.271	0.142	0.112

Table S1: crystallographic data for the compounds reported in this paper. All datasets were collected at 100(2) K. Note: for compound **2b**, positional disorder of the $[BAr^F]^-$ anion and one of the macrocycle rings was severe. This required the use of a lot of restraints resulting in high weighted R-factors. Other indicators of data quality such as the standard uncertainties on the unit cell lengths and the C–C bond lengths were acceptable.

References

1) K. Wieghardt, P. Chaudhuri, B. Nuber, J. Weiss, *Inorg. Chem.*, 1982, **21**, 3086.

2) M. Brookhart, B. Grant, A. F. Volpe Jr., *Organometallics*, 1992, **11**, 3920.

3) ^{23}Na: 100%, I = $^3/_2$, Ξ = 26.42 MHz, R_c = 524, Q = 0.10 x 10^{-28} m^2.

4) CrystalClear-SM Expert 2.0 r13, Rigaku Corporation, Tokyo, Japan, 2011.

5) L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.

6) A. B. Chaplin, A. S. Weller, *Eur. J. Inorg. Chem.*, 2010, 5124.

7) F. H. Allen, O. Johnson, G. P. Shields, B. R. Smith, M. Towler, *J. Appl. Cryst.*, 2004, **37**, 335.