Electronic Supplementary Information

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

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List of Figures

List of Tables

Table S1: X-ray crystallographic parameters[a]

Compound	**[Li(Me$_6$[18]aneN$_6$)]-[BAr^F]**	**[K(Me$_6$[18]aneN$_6$)]-[BAr^F]**	**[Rb(Me$_6$[18]aneN$_6$)]-[BAr^F]**	**[K(Me$_3$tacn)$_2$]-[BAr^F]**
Formula	$C_{50}H_{54}BF_{24}LiN_6$	$C_{50}H_{54}BF_{24}KN_6$	$C_{50}H_{54}BF_{24}N_6Rb$	$C_{50}H_{54}BF_{24}N_6K$
M/g mol^{-1}	1212.74	1244.90	1291.27	1244.90
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$C2/c$ (15)
a/Å	13.180(3)	10.349(2)	10.328(1)	43.534(3)
b/Å	16.887(4)	10.587(3)	10.594(1)	12.7141(9)
c/Å	24.300(5)	25.748(6)	25.779(2)	21.242(2)
α/°	90	81.880(9)	81.581(3)	90
β/°	92.212(3)	83.812(8)	83.317(3)	101.65(1)
γ/°	90	88.221(9)	88.067(3)	90
U/Å^3	5405(2)	2776(1)	2770.8(4)	11515(2)
Z	4	2	2	8
μ(Mo-Kα) /mm^{-1}	0.146	0.217	1.016	0.210
F(000)	2480	1272	1308	5088
Total reflections	25326	37145	36473	21714
Unique reflections	9506	12627	12647	10052
R_{int}	0.053	0.047	0.042	0.112
GooF on F^2	1.020	1.023	1.053	1.032
R_1[b] [$I_o > 2\sigma(I_o)$]	0.084	0.049	0.052	0.099
R_1 (all data)	0.140	0.073	0.072	0.161
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.200	0.120	0.132	0.244
wR_2 (all data)	0.238	0.133	0.143	0.288

[a] Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; ϑ(max) = 27.5°;

[b] $R_1 = \Sigma||F\sigma| - |Fc|| \,/\, \Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2 \,/\, \Sigma wFo^2]^{1/2}$.

Table S1: (continued)

Compound	**[Li(Me$_4$cyclen)-(H$_2$O)][BAr^F]**	**[Na(Me$_4$cyclen)-(thf)][BAr^F]**
Formula	$C_{44}H_{42}BF_{24}LiN_4O$	$C_{48}H_{48}BF_{24}N_4NaO$
M/g mol^{-1}	1116.56	1186.70
Crystal system	Triclinic	Triclinic
Space group (No.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a/Å	12.729(2)	12.7958(9)
b/Å	12.736(2)	12.8488(9)
c/Å	18.368(4)	18.263(1)
α/°	79.00(1)	89.433(4)
β/°	89.45(1)	79.005(4)
γ/°	63.418(7)	64.414(3)
U/Å^3	2604.3(8)	2649.5(3)
Z	2	2
μ(Mo-Kα) /mm^{-1}	0.145	0.155
F(000)	1132	1208
Total reflections	29719	26157
Unique reflections	9170	9346
R_{int}	0.054	0.048
GooF on F^2	1.059	1.049
R_1[b] [$I_o > 2\sigma(I_o)$]	0.096	0.073
R_1 (all data)	0.116	0.104
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.278	0.185
wR_2 (all data)	0.298	0.207

Computational details

DFT computations were carried out to study the structural, electronic, and thermodynamic parameters of the [M(Me$_3$tacn)]$^+$, [M(Me$_3$tacn)$_2$]$^+$, and [M(Me$_6$[18]aneN$_6$)]$^+$ cations. The generalised gradient approximation (GGA) functional BP86[S1] and Becke's three-parameter non-local hybrid exchange correlation B3LYP[S2] functional were used to perform the Berny optimisations.[S3] Several studies involving the coordination of alkali metal cations to macrocycles have proven the reliability of the BP86 and B3LYP functionals.[S4] The standard triple-ζ plus polarisation Pople-style 6-311G(d,p) basis set[S5] was employed for H, C, N, Li, Na, and K atoms. For Rb and

Cs atoms, inner electrons were modeled by a Stuttgart Relativistic Small Core (RSC) 1997 Effective Core Potential (ECP) basis set, which reduces the number of basis functions and also accounts for the scalar relativistic effects.[S6] All stationary points were verified to be minima (absence of negative eigenvalues) on the potential energy hypersurfaces *via* analytic hessian computations. Natural bond orbital analysis (NBO) was also carried out for all the minimum energy structures following the method of Weinhold and coworkers.[S7]

All reported energies were corrected for zero-point energy (ZPE) and these are reported at 298.15 K and 1 atm. The following bond dissociation energies were calculated:

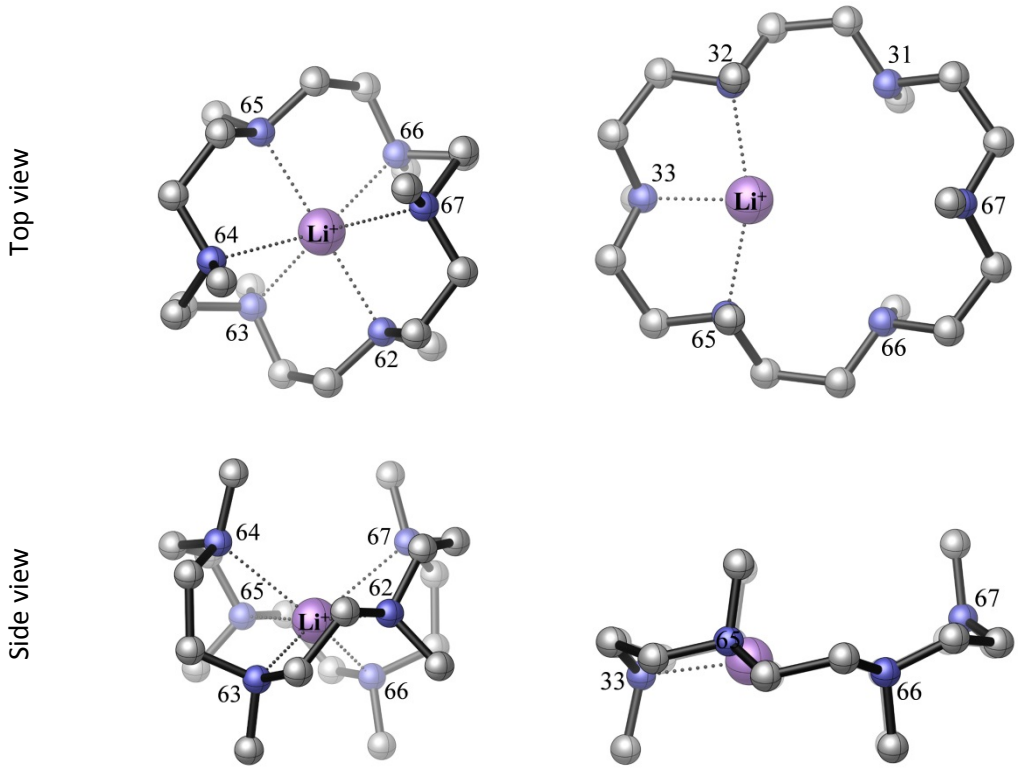
$[M(Me_6[18]aneN_6)]^+ \rightarrow M^+ + Me_6[18]aneN_6$ (1)

$[M(Me_3tacn)]^+ \rightarrow M^+ + Me_3tacn$ (2) and

$[M(Me_3tacn)_2]^+ \rightarrow [M(Me_3tacn)]^+ + Me_3tacn$ (3), where M = Li, Na, K, Rb, and Cs.

Bond dissociation energies were corrected for Basis Set Superposition Error (BSSE) as implemented by the counterpoise correction of Boys and Bernardi.[S8] All computations were carried out using the Gaussian 09 package[S9] by means of the resources provided by the GridChem Science Gateway[S10] and the UK National Service for Computational Chemistry Software (NSCCS).

A



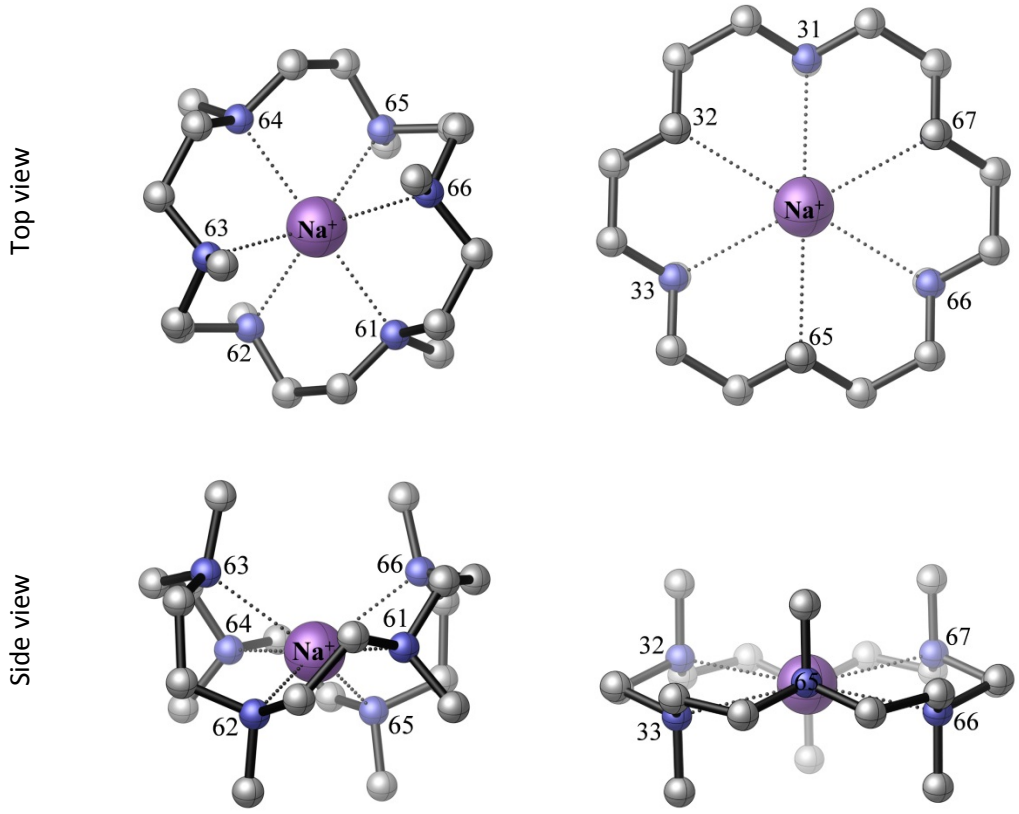
C_2 symmetry
$[Li(Me_6[18]aneN_6)]^+$
-1047.310877 Ha (BP86)
Structure **7**

C_s symmetry
$[Li(Me_6[18]aneN_6)]^+$
-1047.287133 Ha (BP86)
Structure **8**

Two possible minimum energy structures of $[Li(Me_6[18]aneN_6)]^+$, labeled as **7** and **8**, were obtained at the BP86/6-311G(d,p) method. Structure **7** is analogous to the X-ray structure obtained experimentally for $[Li(Me_6[18]aneN_6)]^+$. It is computed to be more stable than structure **8** by 59.6 kJ mol^{-1} at the BP86 level. B3LYP/6-311G(d,p) calculations give similar structures with structure **8** placed 60.7 $kJ.mol^{-1}$ higher in energy than structure **7**. The bond distances, bond angles, and natural charges of ground state minimum energy structure **7** of $[Li(Me_6[18]aneN_6)]^+$ are reported in Tables S2, S3, S4, S12, S13, S18, S19, and S25.

The atom numbering continues from that in the main manuscript.

B

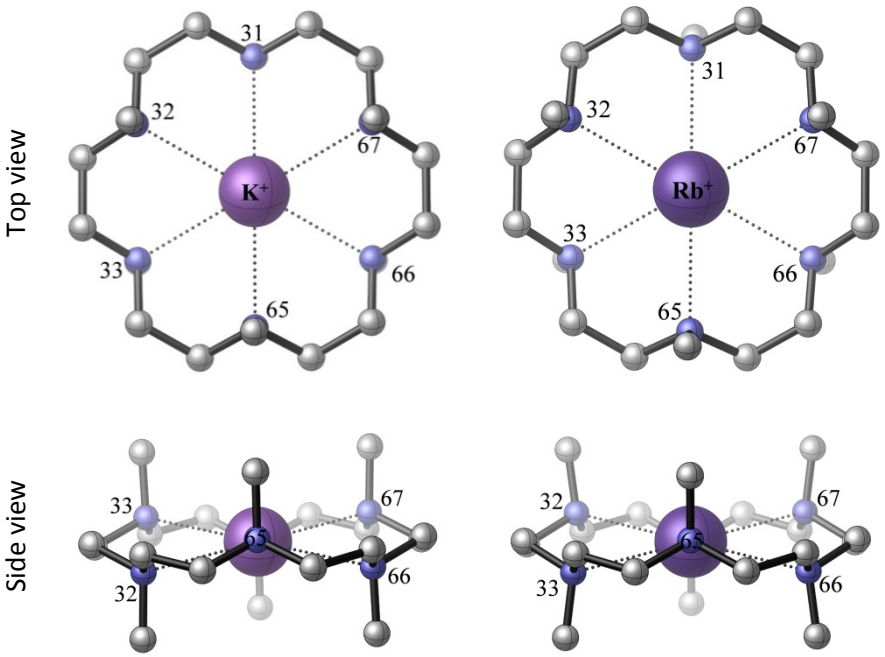


C_2 symmetry
$[Na(Me_6[18]aneN_6)]^+$
-1046.713396 Ha (BP86)
Structure **1**

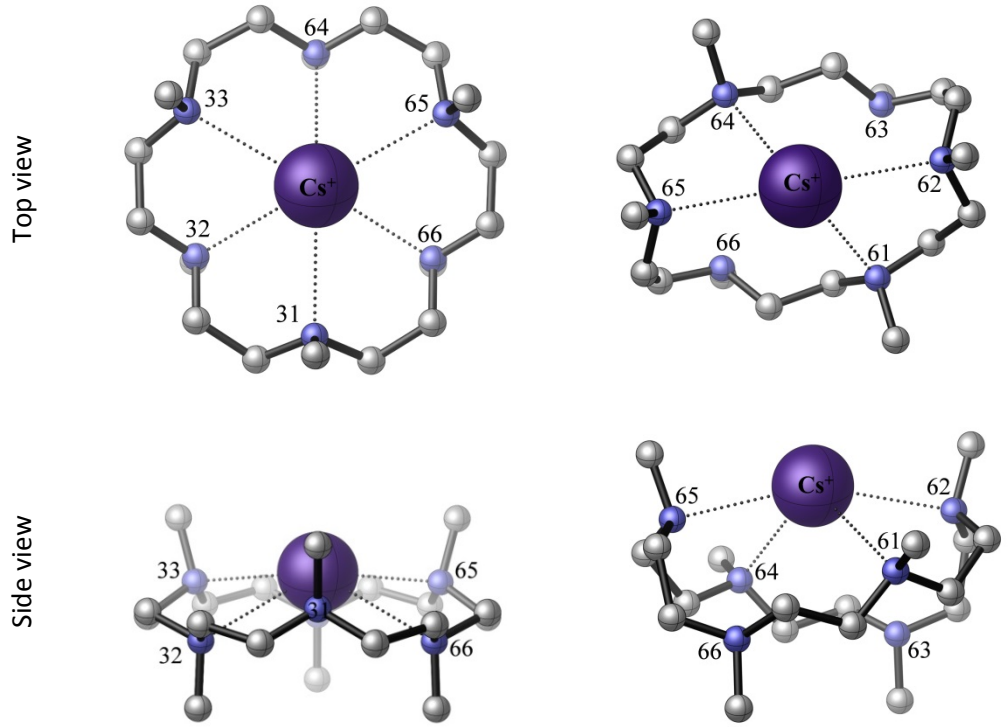
D_{3d} symmetry
$[Na(Me_6[18]aneN_6)]^+$
-1046.690682 Ha (BP86)
Structure **2**

Two minimum energy $[Na(Me_6[18]aneN_6)]^+$ structures (**1** and **2**) obtained using the BP86 and B3LYP functionals. Structure **1** (C_2 symmetry) has a geometry analogous to the computed ground state minimum energy $[Li(Me_6[18]aneN_6)]^+$ structure **7**, while structure **2** (D_{3d} symmetry) has a geometry similar to its K and Rb counterparts. The functionals predict structure **1** to be more stable than structure **2** by 28.2 (BP86) and 35.6 (B3LYP) kJ mol^{-1}. Structure **1** maximises the effective coordination between the small Na^+ cation and the six N atoms. The bond distances, angles, and natural charge of only structure **1** are reported in Table S18, S19, and S26.

c


Top view
Side view
31
32
67
K+
33
66
65
Rb+
D3d symmetry
[K(Me6[18]aneN6)]+
D3d symmetry
[Rb(Me6[18]aneN6)]+

D

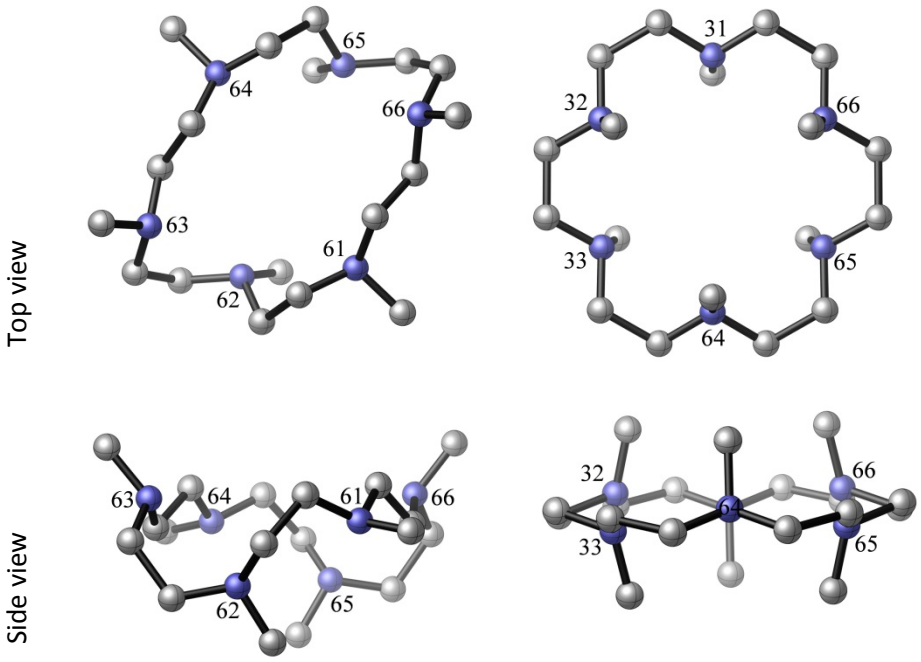


C_{3v} symmetry
$[Cs(Me_6[18]aneN_6)]^+$
-1059.9646816 Ha (BP86)
Structure **5**

C_2 symmetry
$[Cs(Me_6[18]aneN_6)]^+$
-1059.9488067 Ha (BP86)
Structure **6**

Two possible minimum energy structures for the $[Cs(Me_6[18]aneN_6)]^+$ complex, labeled as **5** and **6** located by the DFT computations. Structure **5** (planar) is more stable than that of **6** (puckered conformation) by a relative energy of 43.1 kJ mol^{-1} (BP86).

Figure S1: The optimised geometry of the $[M(Me_6[18]aneN_6)]^+$ complexes, M = Li (A), Na (B), K/Rb (C), and Cs (D) obtained at the BP86/6-311G(d,p) method. The Stuttgart RSC 1997 ECP basis set was used for the Rb and Cs atoms.



C_2 symmetry
$Me_6[18]aneN_6$
-1039.269335 Ha (BP86)
Structure **3**

D_{3d} symmetry
$Me_6[18]aneN_6$
-1039.268664 Ha (BP86)
Structure **4**

Structure **3** (puckered conformation) is more stable than structure **4** (planar) by a relative energy of 1.8 (BP86) and 4.4 (B3LYP) kJ.mol^{-1}. These two structures of $Me_6[18]aneN_6$ were considered to calculate the bond dissociation energies for the dissociation $[M(Me_6[18]aneN_6)]^+ \rightarrow M^+ + Me_6[18]aneN_6$ (1), where M =Li–Cs.

Figure S2: The optimised structures of the metal free $Me_6[18]aneN_6$ ligand obtained at the BP86/6-311G(d,p) method.

Table S2: Comparison of selective experimental and computed bond distances (Å) for the $[M(Me_6[18]aneN_6)]^+$ systems, M = Li (A), K (B), and Rb (C). The N atom numberings of the BP86 and B3LYP optimised geometries are given in brackets.

A

$[Li(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
Li-N1 (N62)	2.274(9)	2.326	2.332
Li-N2 (N63)	2.384(9)	2.428	2.418
Li-N3 (N64)	2.587(9)	2.688	2.704
Li-N4 (N65)	2.315(9)	2.326	2.332
Li-N5 (N66)	2.45(1)	2.428	2.418
Li-N6 (N67)	2.554(9)	2.688	2.704

B

$[K(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
K-N1 (N31)	2.883(2)	2.984	2.982
K-N2 (N32)	2.896(2)	2.984	2.982
K-N3 (N33)	2.911(2)	2.984	2.982
K-N1^i (N65)	2.883(2)	2.984	2.982
K-N2^i (N66)	2.896(2)	2.984	2.982
K-N3^i (N67)	2.911(2)	2.984	2.982

C

$[Rb(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
Rb-N1 (N31)	2.899(2)	3.062	3.058
Rb-N2 (N32)	2.980(2)	3.062	3.058
Rb-N3 (N33)	2.948(2)	3.062	3.058
Rb-N1^i (N65)	3.066(2)	3.062	3.058
Rb-N2^i (N66)	2.890(2)	3.062	3.058
Rb-N3^i (N67)	3.012(2)	3.062	3.058

Table S3: Comparison of selected experimental and computed bond angles (°) for the $[M(Me_6[18]aneN_6)]^+$ systems, M = Li (A), K (B), and Rb (C). The N atom numberings of the BP86 and B3LYP optimised geometries are given in brackets.

A

$[Li(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
N1 (N62)-Li-N2 (N63)	77.3(3)	78.3	78.4
N1 (N62)-Li-N3 (N64)	104.5(3)	101.6	101.8
N2 (N63)-Li-N3 (N64)	73.1(3)	72.9	72.9
N4 (N65)-Li-N5 (N66)	77.7(3)	78.3	78.4
N4 (N65)-Li-N6 (N67)	102.6(3)	101.6	101.8

N5 (N66)-Li-N6 (N67)	73.5(3)	72.9	72.9
N1 (N62)-Li-N4 (N65)	177.7(4)	174.0	173.6
N1 (N62)-Li-N5 (N66)	103.4(4)	104.7	104.7
N1 (N62)-Li-N6 (N67)	75.9(3)	74.7	74.2
N2 (N63)-Li-N4 (N65)	104.0(3)	104.7	104.7
N2 (N63)-Li-N5 (N66)	117.4(4)	121.5	122.3
N2 (N63)-Li-N6 (N67)	152.9(4)	152.1	151.6
N3 (N64)-Li-N4 (N65)	74.3(3)	74.7	74.2
N3 (N64)-Li-N5 (N66)	151.8(4)	152.1	151.6
N3 (N64)-Li-N6 (N67)	109.7(3)	105.8	105.3

B

$[K(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
N1 (N31)-K-N2 (N32)	61.86(5)	62.0	62.0
N1 (N31)-K-N3 (N33)	119.33(5)	118.0	118.0
N2 (N32)-K-N3 (N33)	61.35(5)	62.0	62.0
$N1^i$ (N65)-K-$N2^i$ (N66)	61.86(5)	62.0	62.0
$N1^i$ (N65)-K-$N3^i$ (N67)	119.33(5)	118.0	118.0
$N2^i$ (N66)-K-$N3^i$ (N67)	61.35(5)	62.0	62.0
N1 (N31)-K-$N1^i$ (N65)	180.0	180.0	180.0
N1 (N31)-K-$N2^i$ (N66)	118.14(5)	118.0	118.0
N1 (N31)-K-$N3^i$ (N67)	60.67(5)	62.0	62.0
N2 (N32)-K-$N1^i$ (N65)	118.14(5)	118.0	118.0
N2 (N32)-K-$N2^i$ (N66)	180.0	180.0	180.0
N2 (N32)-K-$N3^i$ (N67)	118.65(5)	118.0	118.0
N3 (N33)-K-$N1^i$ (N65)	60.67(5)	62.0	62.0
N3 (N33)-K-$N2^i$ (N66)	118.65(5)	118.0	118.0
N3 (N33)-K-$N3^i$ (N67)	180.0	180.0	180.0

C

$[Rb(Me_6[18]aneN_6)]^+$	Expt	BP86	B3LYP
N1 (N31)-Rb-N2 (N32)	61.78(6)	62.3	62.3
N1 (N31)-Rb-N3 (N33)	120.47(6)	117.7	117.7
N2 (N32)-Rb-N3 (N33)	60.09(6)	62.3	62.3
$N1^i$ (N65)-Rb-$N2^i$ (N66)	60.84(6)	62.3	62.3
$N1^i$ (N65)-Rb-$N3^i$ (N67)	113.28(6)	117.7	117.7
$N2^i$ (N66)-Rb-$N3^i$ (N67)	60.35(6)	62.3	62.3
N1 (N31)-Rb-$N1^i$ (N65)	163.02(2)	180.0	180.0
N1 (N31)-Rb-$N2^i$ (N66)	119.93(6)	117.7	117.7
N1 (N31)-Rb-$N3^i$ (N67)	60.95(6)	62.3	62.3
N2 (N32)-Rb-$N1^i$ (N65)	111.98(6)	117.7	117.7
N2 (N32)-Rb-$N2^i$ (N66)	162.53(2)	180.0	180.0

N2 (N32)-Rb-N3^{i} (N67)	114.45(6)	117.7	117.7
N3 (N33)-Rb-N1^{i} (N65)	59.80(6)	62.3	62.3
N3 (N33)-Rb-N2^{i} (N66)	119.29(6)	117.7	117.7
N3 (N33)-Rb-N3^{i} (N67)	162.75(2)	180.0	180.0

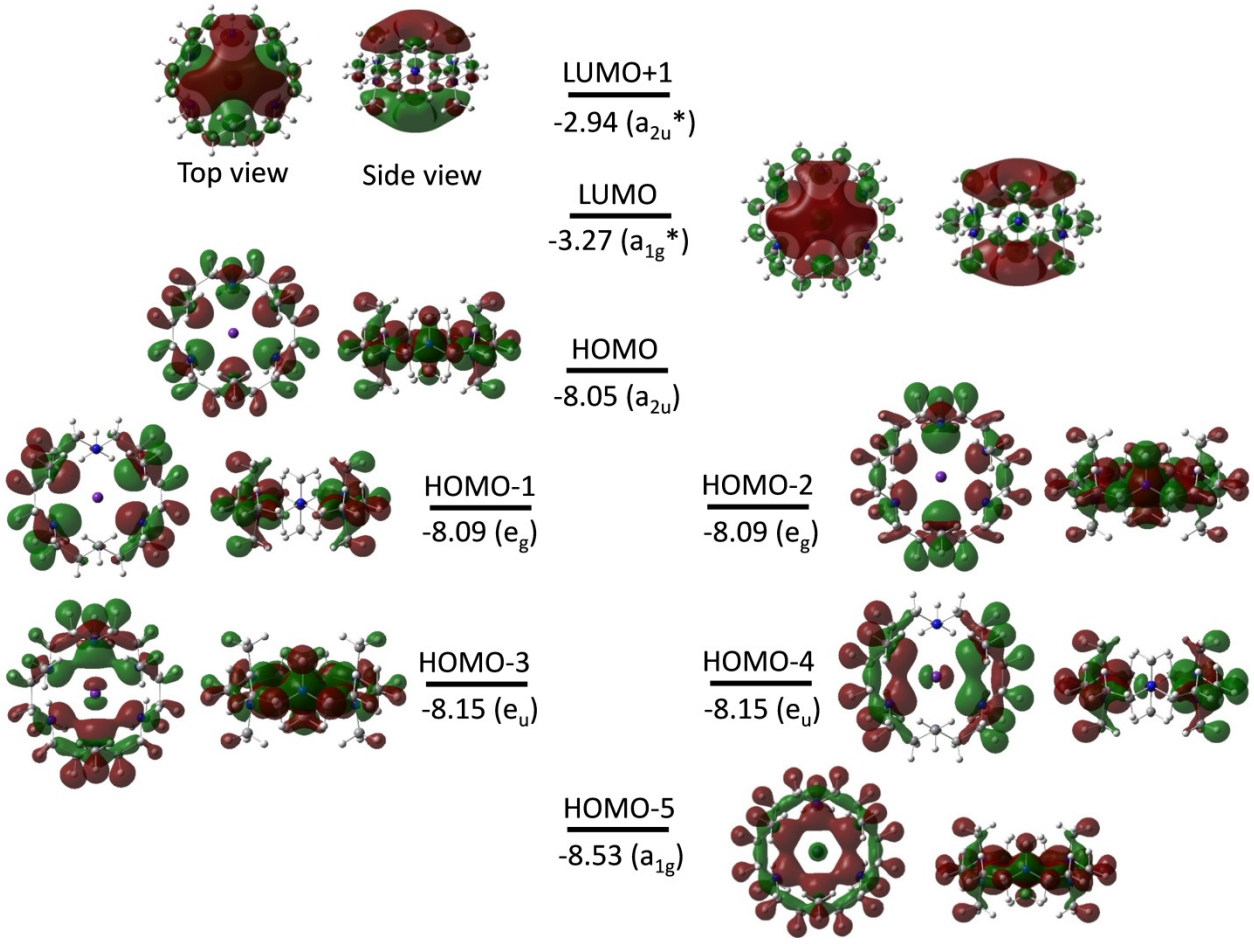


Figure S3: FMOs (isovalue of 0.02 electrons Bohr^{-3}) for the [Rb(Me$_6$[18]aneN$_6$)]$^+$ system obtained using the BP86 functional. The energy and symmetry of the MOs are given in eV and in parentheses, respectively. The dark red (+) and green (-) lobes represent the signs of the angular part of the AO contributing to a MO.

Table S4: Charge densities (natural charge) on the Li and N centres using the BP86 and B3LYP functionals. Atom numberings of the optimised geometries are given in parentheses.

Centres	Me_6[18]aneN_6 (Conformer **3**)	[Li(Me_6[18]aneN_6)]$^+$
	BP86|B3LYP	BP86|B3LYP
Li	–	0.522|0.546 (Li61)
N1	-0.515|-0.529 (N61)†	-0.548|-0.560 (N62)
N2	-0.512|-0.525 (N62)	-0.544|-0.558 (N63)
N3	-0.503|-0.516 (N63)	-0.529|-0.541 (N64)
N4	-0.515|-0.529 (N64)	-0.548|-0.560 (N65)
N5	-0.512|-0.525 (N65)	-0.544|-0.558 (N66)
N6	-0.503|-0.516 (N66)	-0.529|-0.541 (N67)

† The theoretical labelling is given in parentheses.

Table S5: Charge densities (natural charge) on the M (K and Rb) and N centres obtained using the BP86 and B3LYP functionals.

	BP86		B3LYP	
Centres	M	N	M	N
Me_6[18]aneN_6 (Conformer **4**)	–	-0.493	–	-0.505
[K(Me_6[18]aneN_6)]$^+$	0.734	-0.531	0.742	-0.542
[Rb(Me_6[18]aneN_6)]$^+$	0.934	-0.543	0.929	-0.555

Table S6: Zero-point and BSSE corrected bond dissociation energies† (kJ mol^{-1}) for dissociation of [M(Me_6[18]aneN_6)]$^+$ → M^+ + Me_6[18]aneN_6 (1), M = Li, Na, K, Rb, and Cs, determined using the BP86 and B3LYP functionals.

	(1)	
M	BP86	B3LYP
Li	423.3 (421.5)††	441.4 (437.0)
Na	341.0 (339.2)	362.8 (358.4)
K	264.6 (262.9)	273.4 (269.0)
Rb	209.1 (207.3)	215.0 (210.6)
Cs	151.9 (150.1)	157.3 (152.9)

†The reported values were obtained using the energy of the Me_6[18]aneN_6, structure **4** (see Figure S2); ††The reported values were obtained using the energy of the Me_6[18]aneN_6, structure **3**. (see Figure S2)

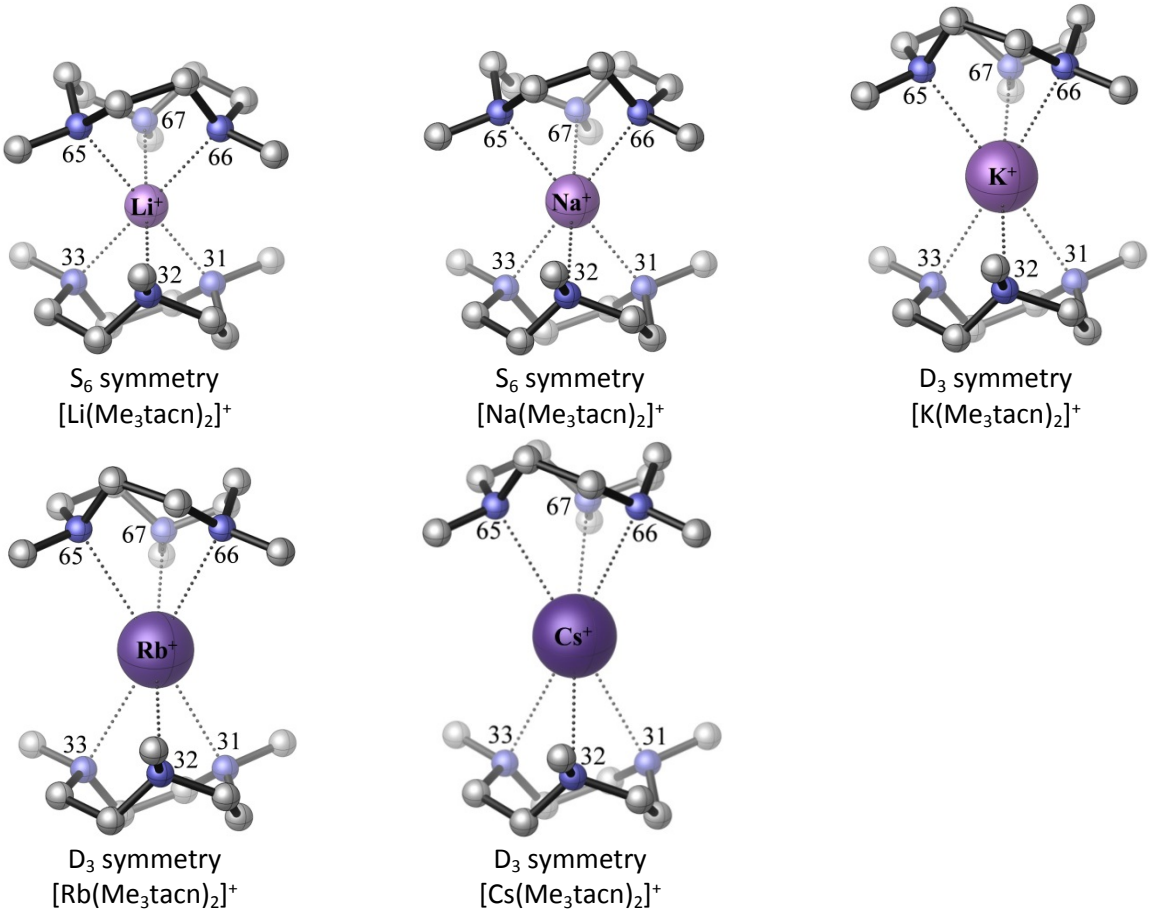


Figure S4: The optimised geometry of the $[M(Me_3tacn)_2]^+$ complexes, where M = Li-Cs, obtained at the BP86/6-311G(d,p) method. The Stuttgart RSC 1997 ECP basis set was used for the Rb and Cs atoms.

Table S7: Comparison of selected experimental and computed bond distances (Å) for the $[M(Me_3tacn)_2]^+$ systems, M = Na (A) and K (B). The N atom numberings of the BP86 and B3LYP optimised geometries are given in brackets.

A

$[Na(Me_3tacn)_2]^+$	Expt	BP86	B3LYP
M-N4 (N31)	2.507(4)	2.611	2.607
M-N5 (N32)	2.600(5)	2.611	2.607
M-N6 (N33)	2.567(5)	2.611	2.607
M-N4^i (N65)	2.507(4)	2.611	2.607
M-N5^i (N66)	2.600(5)	2.611	2.607
M-N6^i (N67)	2.567(5)	2.611	2.607

B

$[K(Me_3tacn)_2]^+$	Expt	BP86	B3LYP
M-N4 (N31)	2.768(6)	2.915	2.911

M-N5 (N32)	2.821(6)	2.915	2.911
M-N6 (N33)	2.808(6)	2.915	2.911
M-N4^{i} (N65)	2.768(6)	2.915	2.911
M-N5^{i} (N66)	2.821(6)	2.915	2.911
M-N6^{i} (N67)	2.808(6)	2.915	2.911

Table S8: Comparison of selected experimental and computed bond angles (°) for the $[M(Me_3tacn)_2]^+$ systems, where M = Na (A) and K (B). The N atom numberings of the BP86 and B3LYP optimised geometries are given in brackets.

A

$[Na(Me_3tacn)_2]^+$	Expt	BP86	B3LYP
N4 (N31)-M-N5 (N32)	71.2(2)	70.9	71.1
N4 (N31)-M-N6 (N33)	71.1(2)	70.9	71.1
N5 (N32)-M-N6 (N33)	70.5(2)	70.9	71.1
N4^{i} (N65)-M-N5^{i} (N66)	71.2(2)	70.9	71.1
N4^{i} (N65)-M-N6^{i} (N67)	71.1(2)	70.9	71.1
N5^{i} (N66)-M-N6^{i} (N67)	70.5(2)	70.9	71.1
N4 (N31)-M-N4^{i} (N65)	180.0	180.0	180.0
N4 (N31)-M-N5^{i} (N66)	108.8(2)	109.1	108.9
N4 (N31)-M-N6^{i} (N67)	108.9(2)	109.1	108.9
N5 (N32)-M-N4^{i} (N65)	108.8(2)	109.1	108.9
N5 (N32)-M-N5^{i} (N66)	180.0	180.0	180.0
N5 (N32)-M-N6^{i} (N67)	109.5(2)	109.1	108.9
N6 (N33)-M-N4^{i} (N65)	108.9(2)	109.1	108.9
N6 (N33)-M-N5^{i} (N66)	109.5(2)	109.1	108.9
N6 (N33)-M-N6^{i} (N67)	180.0	180.0	180.0

B

$[K(Me_3tacn)_2]^+$	Expt	BP86	B3LYP
N4 (N31)-M-N5 (N32)	64.2(2)	63.0	63.0
N4 (N31)-M-N6 (N33)	64.2(2)	63.0	63.0
N5 (N32)-M-N6 (N33)	63.9(2)	63.0	63.0
N4^{i} (N65)-M-N5^{i} (N66)	64.2(2)	63.0	63.0
N4^{i} (N65)-M-N6^{i} (N67)	64.2(2)	63.0	63.0
N5^{i} (N66)-M-N6^{i} (N67)	63.9(2)	63.0	63.0
N4 (N31)-M-N4^{i} (N65)	179.6(3)	174.8	175.4
N4 (N31)-M-N5^{i} (N66)	116.0(2)	120.2	119.8
N4 (N31)-M-N6^{i} (N67)	115.6(2)	114.2	114.4
N5 (N32)-M-N4^{i} (N65)	116.0(2)	120.2	119.8
N5 (N32)-M-N5^{i} (N66)	117.5(2)	114.2	114.4
N5 (N32)-M-N6^{i} (N67)	178.6(2)	174.8	175.4
N6 (N33)-M-N4^{i} (N65)	115.6(2)	114.2	114.4
N6 (N33)-M-N5^{i} (N66)	178.6(2)	174.8	175.4
N6 (N33)-M-N6^{i} (N67)	114.7(3)	120.2	119.8

$[Na(Me_3tacn)_2]^+$

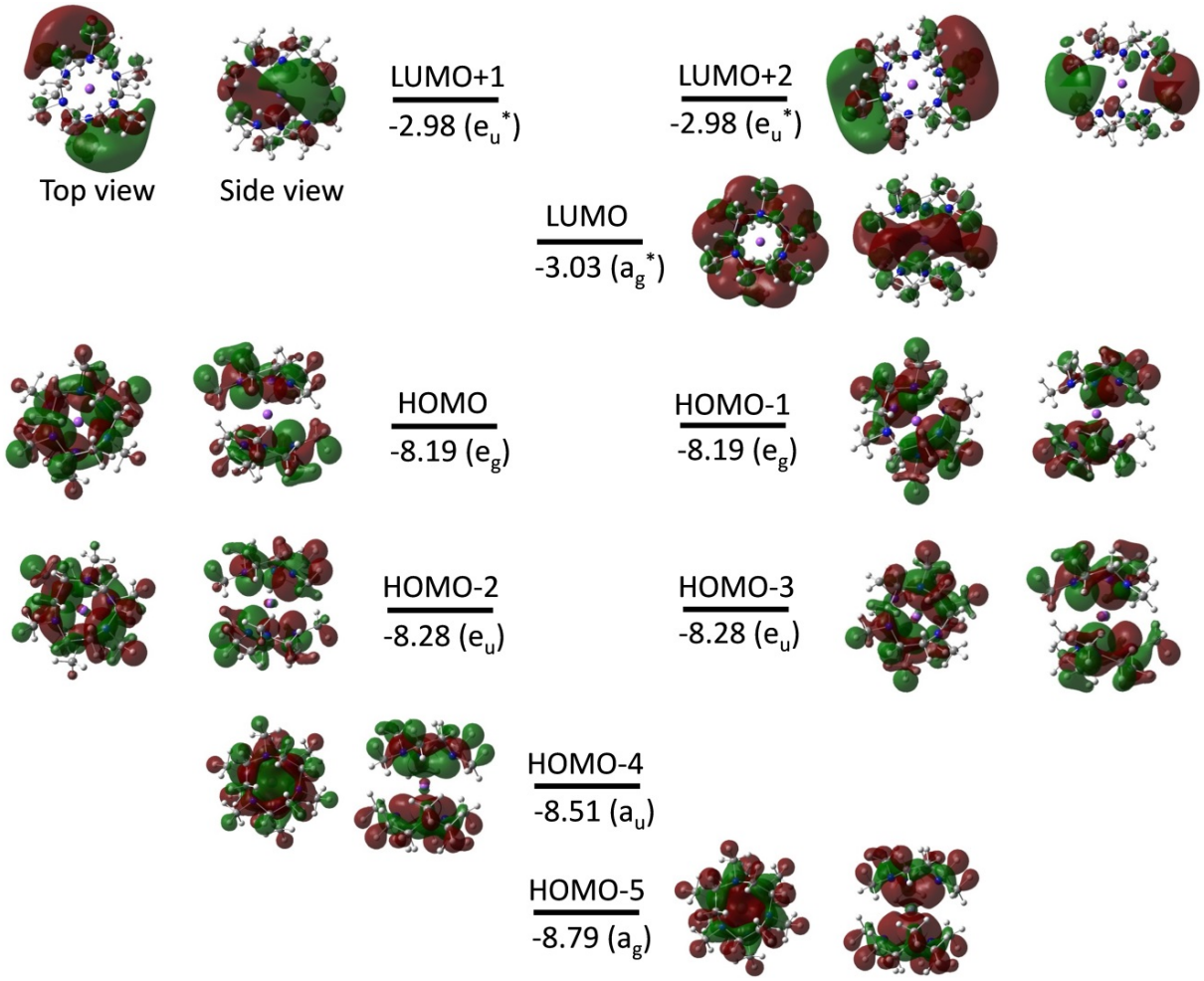


Figure S5: FMOs (isovalue of 0.02 electrons $Bohr^{-3}$) for the $[Na(Me_3tacn)_2]^+$ system obtained using the BP86 functional. The energy and symmetry of the MOs are given in eV and in parentheses, respectively. The dark red (+) and green (-) lobes represent the signs of the angular part of the AO contributing to a MO.

The electronic ground state of the $[Na(Me_3tacn)_2]^+$ system (S_6 symmetry) is ^1A_g.

For the $[Na(Me_3tacn)_2]^+$ system, the HOMOs (HOMO and HOMO-1) are doubly degenerate with e_g symmetry and are mainly localised on the N atoms of the Me_3tacn rings. They are the non-bonding 2p valence orbitals of N atoms.

The HOMO-2 and HOMO-3 (e_u symmetry) are also localised on the N atoms of each Me_3tacn ring and this corresponds to the lone pair (LP) of electrons of the N atoms. An increased contribution (with respect to the HOMO and HOMO-1) of the 3p orbitals of the Na^+ cation can also be observed on the isosurface plots of HOMO-2 and HOMO-3.

The LUMO (a_g* symmetry) is an antibonding molecular orbital which is highly localised on the Na^+ cation, sandwiched between the two Me_3tacn rings. The LUMO also has a small contribution from all the methyl C atoms of the Me_3tacn rings. The sodium contribution corresponds mainly to the 3s orbital of the Na^+ cation and the carbon contribution corresponds to the 3s orbitals of C atoms.

The LUMO+1 and LUMO+2 (e_u* symmetry) are doubly degenerate antibonding molecular orbitals which are mainly localised on the Na^+ cation and correspond to its 3p orbitals. An increased contribution (with respect to the LUMO) of the 3s orbitals of C atoms (21% from each Me_3tacn ring) can also be observed.

Population analysis of the molecular orbitals (MOs) shows that there is significant transfer of electron density from the lone pairs of the N atoms of the Me_3tacn rings to mainly the empty 3s and 3p orbitals of the Na^+ cation. Several MOs (or group of closely-packed occupied low-lying MOs) account for the cumulative gain of electron density by the empty 3s and 3p orbitals of the Na^+ cation, with HOMO-5 being the orbital with largest Na^+ 3s contribution (10%).

Table S9: Charge analysis (natural charge) on the Na and N centres using the BP86 and B3LYP functionals.

Centres	Na		N	
	BP86	B3LYP	BP86	B3LYP
Me_3tacn	–	–	-0.499	-0.514
$[Na(Me_3tacn)]^+$	+0.867	+0.868	-0.587	-0.598
$[Na(Me_3tacn)_2]^+$	+0.551	+0.569	-0.549	-0.561

The natural charge on the Na^+ centre is much lower than the formal charge of +1, showing a significant electron density transfer from the Me_3tacn ligand framework to the Na^+ centre upon formation of $[Na(Me_3tacn)]^+$. Addition of a second Me_3tacn ligand to form the sandwich $[Na(Me_3tacn)_2]^+$ system results in further decrease. Electron density flows from the σ C–H, σ C–N bonding and N 2p non-bonding orbitals of the Me_3tacn ligands to the 3s and 3p orbitals of the Na^+ cation.

As shown in Table 3, the N atoms on the metal free Me_3tacn ligand have a negative natural charge. Contrary to what is expected, addition of the Na^+ cation to form both the $[Na(Me_3tacn)]^+$ and $[Na(Me_3tacn)_2]^+$ systems results in more negatively charged N atoms, with electron density flowing from the σ C–H and σ C–N bonds on complexation.

Table S10: Charge densities (natural charge) on the K and N centres using the BP86 and B3LYP functionals.

Centres	K		N	
	BP86	B3LYP	BP86	B3LYP
Me_3tacn	–	–	-0.499	-0.514
$[K(Me_3tacn)]^+$	+0.913	+0.917	-0.575	-0.585
$[K(Me_3tacn)_2]^+$	+0.680	+0.689	-0.542	-0.554

Table S11: Zero-point and BSSE corrected bond dissociation energies (kJ mol^{-1}) for dissociation [M(Me_3tacn)]$^+$ → M$^+$ + Me_3tacn (2) and [M(Me_3tacn)$_2$]$^+$ → [M(Me_3tacn)]$^+$ + Me_3tacn (3), M = Li, Na, K, Rb, and Cs, determined using the BP86 and B3LYP functionals.

	(2)		(3)	
M	BP86	B3LYP	BP86	B3LYP
Li	350.4	367.4	63.9	62.3
Na	234.0	246.2	104.5	111.9
K	165.5	168.3	86.5	95.5
Rb	122.0	125.2	77.4	84.1
Cs	96.2	98.1	63.2	68.1

Table S12: Computed bond distances (Å) for the [M(Me_6[18]aneN_6)]$^+$ systems, M = Li–Cs, obtained using the BP86 functional. Me_6[18]aneN_6 is abbreviated as L.

[Li(L)]$^+$	Li	[Na(L)]$^+$	Na	[M(L)]$^+$	K	Rb	[Cs(L)]$^+$	Cs
Li-N62	2.326	Na-N61	2.568	M-N31	2.984	3.062	Cs-N31	3.195
Li-N63	2.428	Na-N62	2.599	M-N32	2.984	3.062	Cs-N32	3.214
Li-N64	2.688	Na-N63	2.672	M-N33	2.984	3.062	Cs-N33	3.195
Li-N65	2.326	Na-N64	2.568	M-N65	2.984	3.062	Cs-N64	3.214
Li-N66	2.428	Na-N65	2.599	M-N66	2.984	3.062	Cs-N65	3.195
Li-N67	2.688	Na-N66	2.672	M-N67	2.984	3.062	Cs-N66	3.214

Table S13: Computed bond distances (Å) for the [M(Me_6[18]aneN_6)]$^+$ systems, where M = Li–Cs, obtained using the B3LYP functional. Me_6[18]aneN_6 is abbreviated as L.

[Li(L)]$^+$	Li	[Na(L)]$^+$	Na	[M(L)]$^+$	K	Rb	[Cs(L)]$^+$	Cs
Li-N62	2.332	Na-N61	2.560	M-N31	2.982	3.058	Cs-N31	3.224
Li-N63	2.418	Na-N62	2.584	M-N32	2.982	3.058	Cs-N32	3.232
Li-N64	2.704	Na-N63	2.656	M-N33	2.982	3.058	Cs-N33	3.224
Li-N65	2.332	Na-N64	2.560	M-N65	2.982	3.058	Cs-N64	3.232
Li-N66	2.418	Na-N65	2.584	M-N66	2.982	3.058	Cs-N65	3.224
Li-N67	2.704	Na-N66	2.656	M-N67	2.982	3.058	Cs-N66	3.232

Table S14: Computed bond distances (Å) for the [M(Me_3tacn)]$^+$ systems, M = Li–Cs, obtained using the BP86 functional.

[M(Me_3tacn)]$^+$	Li	Na	K	Rb	Cs
M-N31	2.029	2.409	2.768	3.006	3.212
M-N32	2.029	2.409	2.768	3.006	3.212
M-N33	2.029	2.409	2.768	3.006	3.212

Table S15: Computed bond distances (Å) for the $[M(Me_3tacn)]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

$[M(Me_3tacn)]^+$	Li	Na	K	Rb	Cs
M-N31	2.009	2.393	2.772	3.008	3.226
M-N32	2.009	2.393	2.772	3.008	3.226
M-N33	2.009	2.393	2.772	3.008	3.226

Table S16: Computed bond distances (Å) for the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the BP86 functional.

$[M(Me_3tacn)_2]^+$	Li	Na	K	Rb	Cs
M-N31	2.460	2.611	2.915	3.120	3.304
M-N32	2.460	2.611	2.915	3.120	3.304
M-N33	2.460	2.611	2.915	3.120	3.304
M-N65	2.460	2.611	2.915	3.120	3.304
M-N66	2.460	2.611	2.915	3.120	3.304
M-N67	2.460	2.611	2.915	3.120	3.304

Table S17: Computed bond distances (Å) for the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

$[M(Me_3tacn)_2]^+$	Li	Na	K	Rb	Cs
M-N31	2.464	2.607	2.911	3.117	3.319
M-N32	2.464	2.607	2.911	3.117	3.319
M-N33	2.464	2.607	2.911	3.117	3.319
M-N65	2.464	2.607	2.911	3.117	3.319
M-N66	2.464	2.607	2.911	3.117	3.319
M-N67	2.464	2.607	2.911	3.117	3.319

Table S18: Computed bond angles (°) for the $[M(Me_6[18]aneN_6)]^+$ systems, M = Li–Cs, obtained using the BP86 functional. $Me_6[18]aneN_6$ is abbreviated as L.

$[Li(L)]^+$	Li	$[Na(L)]^+$	Na	$[M(L)]^+$	K	Rb	$[Cs(L)]^+$	Cs
N62-Li-N63	78.3	N61-Na-N62	72.7	N31-M-N32	62.0	62.3	N31-Cs-N32	59.7
N62-Li-N64	101.6	N61-Na-N63	105.2	N31-M-N33	118.0	117.7	N31-Cs-N33	118.4
N63-Li-N64	72.9	N62-Na-N63	72.1	N32-M-N33	62.0	62.3	N32-Cs-N33	59.7
N65-Li-N66	78.3	N64-Na-N65	72.7	N65-M-N66	62.0	62.3	N64-Cs-N65	59.7
N65-Li-N67	101.6	N64-Na-N66	105.1	N65-M-N67	118.0	117.7	N64-Cs-N66	104.0
N66-Li-N67	72.9	N65-Na-N66	72.1	N66-M-N67	62.0	62.3	N65-Cs-N66	59.7
N62-Li-N65	174.0	N61-Na-N64	177.1	N31-M-N65	180.0	180.0	N31-Cs-N64	148.2
N62-Li-N66	104.7	N61-Na-N65	108.7	N31-M-N66	118.0	117.7	N31-Cs-N65	118.4
N62-Li-N67	74.7	N61-Na-N66	73.0	N31-M-N67	62.0	62.3	N31-Cs-N66	59.7

N63-Li-N65	104.7	N62-Na-N64	108.7	N32-M-N65	118.0	117.7	N32-Cs-N64	104.0
N63-Li-N66	121.5	N62-Na-N65	127.2	N32-M-N66	180.0	180.0	N32-Cs-N65	148.2
N63-Li-N67	152.1	N62-Na-N66	144.8	N32-M-N67	118.0	117.7	N32-Cs-N66	104.0
N64-Li-N65	74.7	N63-Na-N64	73.0	N33-M-N65	62.0	62.3	N33-Cs-N64	59.7
N64-Li-N66	152.1	N63-Na-N65	144.8	N33-M-N66	118.0	117.7	N33-Cs-N65	118.4
N64-Li-N67	105.8	N63-Na-N66	110.0	N33-M-N67	180.0	180.0	N33-Cs-N66	148.2

Table S19: Computed bond angles (°) for the $[M(Me_6[18]aneN_6)]^+$ systems, where M = Li–Cs, obtained using the B3LYP functional. $Me_6[18]aneN_6$ is abbreviated as L.

$[Li(L)]^+$	Li	$[Na(L)]^+$	Na	$[M(L)]^+$	K	Rb	$[Cs(L)]^+$	Cs
N62-Li-N63	78.4	N61-Na-N62	72.9	N31-M-N32	62.0	62.3	N31-Cs-N32	58.8
N62-Li-N64	101.8	N61-Na-N63	106.2	N31-M-N33	118.0	117.7	N31-Cs-N33	117.0
N63-Li-N64	72.9	N62-Na-N63	72.5	N32-M-N33	62.0	62.3	N32-Cs-N33	58.8
N65-Li-N66	78.4	N64-Na-N65	72.9	N65-M-N66	62.0	62.3	N64-Cs-N65	58.8
N65-Li-N67	101.8	N64-Na-N66	106.2	N65-M-N67	118.0	117.7	N64-Cs-N66	101.2
N66-Li-N67	72.9	N65-Na-N66	72.5	N66-M-N67	62.0	62.3	N65-Cs-N66	58.8
N62-Li-N65	173.6	N61-Na-N64	178.7	N31-M-N65	180.0	180.0	N31-Cs-N64	143.0
N62-Li-N66	104.7	N61-Na-N65	107.7	N31-M-N66	118.0	117.7	N31-Cs-N65	117.0
N62-Li-N67	74.2	N61-Na-N66	73.1	N31-M-N67	62.0	62.3	N31-Cs-N66	58.8
N63-Li-N65	104.7	N62-Na-N64	107.7	N32-M-N65	118.0	117.7	N32-Cs-N64	101.2
N63-Li-N66	122.3	N62-Na-N65	125.8	N32-M-N66	180.0	180.0	N32-Cs-N65	143.0
N63-Li-N67	151.6	N62-Na-N66	145.1	N32-M-N67	118.0	117.7	N32-Cs-N66	101.2
N64-Li-N65	74.2	N63-Na-N64	73.1	N33-M-N65	62.0	62.3	N33-Cs-N64	58.8
N64-Li-N66	151.6	N63-Na-N65	145.1	N33-M-N66	118.0	117.7	N33-Cs-N65	117.0
N64-Li-N67	105.3	N63-Na-N66	110.4	N33-M-N67	180.0	180.0	N33-Cs-N66	143.0

Table S20: Computed bond angles (°) for the $[M(Me_3tacn)]^+$ systems, M = Li–Cs, obtained using the BP86 functional.

$[M(Me_3tacn)]^+$	Li	Na	K	Rb	Cs
N31-M-N32	92.6	78.1	66.6	61.2	56.8
N31-M-N33	92.6	78.1	66.6	61.2	56.8
N32-M-N33	92.6	78.1	66.6	61.2	56.8

Table S21: Computed bond angles (°) for the $[M(Me_3tacn)]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

$[M(Me_3tacn)]^+$	Li	Na	K	Rb	Cs
N31-M-N32	93.4	78.6	66.5	61.0	56.4
N31-M-N33	93.4	78.6	66.5	61.0	56.4
N32-M-N33	93.4	78.6	66.5	61.0	56.4

Table S22: Computed bond angles (°) for the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the BP86 functional.

$[M(Me_3tacn)_2]^+$	Li	Na	K	Rb	Cs
N31-M-N32	75.3	70.9	63.0	58.6	55.0
N31-M-N33	75.3	70.9	63.0	58.6	55.0
N32-M-N33	75.3	70.9	63.0	58.6	55.0
N65-M-N66	75.3	70.9	63.0	58.6	55.0
N65-M-N67	75.3	70.9	63.0	58.6	55.0
N66-M-N67	75.3	70.9	63.0	58.6	55.0
N31-M-N65	180.0	180.0	174.8	174.9	175.6
N31-M-N66	104.7	109.1	120.2	124.5	127.6
N31-M-N67	104.7	109.1	114.2	118.7	122.7
N32-M-N65	104.7	109.1	120.2	124.5	127.6
N32-M-N66	180.0	180.0	114.2	118.7	122.7
N32-M-N67	104.7	109.1	174.8	174.9	175.6
N33-M-N65	104.7	109.1	114.2	118.7	122.7
N33-M-N66	104.7	109.1	174.8	174.9	175.6
N33-M-N67	180.0	180.0	120.2	124.5	127.6

Table S23: Computed bond angles (°) for the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

$[M(Me_3tacn)_2]^+$	Li	Na	K	Rb	Cs
N31-M-N32	75.2	71.1	63.0	58.5	54.6
N31-M-N33	75.2	71.1	63.0	58.5	54.6
N32-M-N33	75.2	71.1	63.0	58.5	54.6
N65-M-N66	75.2	71.1	63.0	58.5	54.6
N65-M-N67	75.2	71.1	63.0	58.5	54.6
N66-M-N67	75.2	71.1	63.0	58.5	54.6
N31-M-N65	180.0	180.0	175.4	173.8	175.8
N31-M-N66	104.8	108.9	119.8	125.3	127.9
N31-M-N67	104.8	108.9	114.4	118.2	123.1
N32-M-N65	104.8	108.9	119.8	125.3	127.9
N32-M-N66	180.0	180.0	114.4	118.2	123.1
N32-M-N67	104.8	108.9	175.4	173.8	175.8
N33-M-N65	104.8	108.9	114.4	118.2	123.1
N33-M-N66	104.8	108.9	175.4	173.8	175.8
N33-M-N67	180.0	180.0	119.8	125.3	127.9

Table S24: Computed charge densities (natural charges) on all the centres of the Me_6[18]aneN_6 structures 3 and 4 (see Figure S2) obtained using the BP86 and B3LYP functionals.

	Conformer **4** (planar)			Conformer **3** (puckered)	
Centres	BP86	B3LYP	Centres	BP86	B3LYP
C 1	-0.203	-0.174	C 1	-0.392	-0.356
H 2	0.195	0.183	H 2	0.197	0.186
H 3	0.170	0.158	H 3	0.197	0.186
C 4	-0.398	-0.362	H 4	0.161	0.152
H 5	0.154	0.144	C 5	-0.200	-0.171
H 6	0.206	0.194	H 6	0.217	0.205
H 7	0.206	0.194	H 7	0.164	0.152
C 8	-0.203	-0.174	C 8	-0.205	-0.176
H 9	0.170	0.158	H 9	0.174	0.163
H 10	0.195	0.183	H 10	0.201	0.186
C 11	-0.203	-0.174	C 11	-0.387	-0.351
H 12	0.170	0.158	H 12	0.219	0.207
H 13	0.195	0.183	H 13	0.192	0.181
C 14	-0.398	-0.362	H 14	0.153	0.144
H 15	0.154	0.144	C 15	-0.202	-0.173
H 16	0.206	0.194	H 16	0.172	0.160
H 17	0.206	0.194	H 17	0.197	0.185
C 18	-0.203	-0.174	C 18	-0.201	-0.172
H 19	0.195	0.183	H 19	0.172	0.160
H 20	0.170	0.158	H 20	0.192	0.180
C 21	-0.203	-0.174	C 21	-0.387	-0.353
H 22	0.195	0.183	H 22	0.199	0.188
H 23	0.170	0.158	H 23	0.196	0.185
C 24	-0.398	-0.362	H 24	0.160	0.151
H 25	0.154	0.144	C 25	-0.214	-0.184
H 26	0.206	0.194	H 26	0.159	0.148
H 27	0.206	0.194	H 27	0.222	0.208
C 28	-0.203	-0.174	C 28	-0.198	-0.169
H 29	0.170	0.158	H 29	0.162	0.151
H 30	0.195	0.183	H 30	0.209	0.197
N 31	-0.493	-0.505	C 31	-0.392	-0.356
N 32	-0.493	-0.505	H 32	0.197	0.186
N 33	-0.493	-0.505	H 33	0.197	0.186
C 34	-0.203	-0.174	H 34	0.161	0.152
H 35	0.195	0.183	C 35	-0.200	-0.171
H 36	0.170	0.158	H 36	0.217	0.205
C 37	-0.398	-0.362	H 37	0.164	0.152
H 38	0.154	0.144	C 38	-0.205	-0.176
H 39	0.206	0.194	H 39	0.174	0.163

H	40	0.206	0.194	H	40	0.201	0.186
C	41	-0.203	-0.174	C	41	-0.387	-0.351
H	42	0.170	0.158	H	42	0.153	0.144
H	43	0.195	0.183	H	43	0.219	0.207
C	44	-0.203	-0.174	H	44	0.192	0.181
H	45	0.170	0.158	C	45	-0.202	-0.173
H	46	0.195	0.183	H	46	0.172	0.160
C	47	-0.398	-0.362	H	47	0.197	0.185
H	48	0.154	0.144	C	48	-0.201	-0.172
H	49	0.206	0.194	H	49	0.172	0.160
H	50	0.206	0.194	H	50	0.192	0.180
C	51	-0.203	-0.174	C	51	-0.387	-0.353
H	52	0.195	0.183	H	52	0.160	0.151
H	53	0.170	0.158	H	53	0.199	0.188
C	54	-0.203	-0.174	H	54	0.196	0.185
H	55	0.195	0.183	C	55	-0.214	-0.184
H	56	0.170	0.158	H	56	0.159	0.148
C	57	-0.398	-0.362	H	57	0.222	0.208
H	58	0.154	0.144	C	58	-0.198	-0.169
H	59	0.206	0.194	H	59	0.162	0.151
H	60	0.206	0.194	H	60	0.209	0.197
C	61	-0.203	-0.174	N	61	-0.515	-0.529
H	62	0.170	0.158	N	62	-0.512	-0.525
H	63	0.195	0.183	N	63	-0.503	-0.516
N	64	-0.493	-0.505	N	64	-0.515	-0.529
N	65	-0.493	-0.505	N	65	-0.512	-0.525
N	66	-0.493	-0.505	N	66	-0.503	-0.516

Table S25: Computed charge densities (natural charges) on all the centres of the [M(Me$_6$[18]aneN$_6$)]$^+$ systems, M = Li, K, and Rb, obtained using the BP86 and B3LYP functionals.

Li (Structure **7**)-puckered			K			Rb		
Centres	BP86	B3LYP	Centres	BP86	B3LYP	Centres	BP86	B3LYP
C 1	-0.391	-0.355	C 1	-0.207	-0.178	C 1	-0.209	-0.180
H 2	0.200	0.190	H 2	0.203	0.191	H 2	0.203	0.190
H 3	0.203	0.192	H 3	0.196	0.184	H 3	0.193	0.181
H 4	0.193	0.182	C 4	-0.397	-0.362	C 4	-0.402	-0.368
C 5	-0.201	-0.172	H 5	0.188	0.178	H 5	0.185	0.176
H 6	0.205	0.193	H 6	0.200	0.189	H 6	0.199	0.188
H 7	0.200	0.188	H 7	0.200	0.189	H 7	0.199	0.188
C 8	-0.211	-0.183	C 8	-0.207	-0.178	C 8	-0.209	-0.180
H 9	0.213	0.200	H 9	0.196	0.184	H 9	0.193	0.181
H 10	0.209	0.196	H 10	0.203	0.191	H 10	0.203	0.190
C 11	-0.377	-0.342	C 11	-0.207	-0.178	C 11	-0.209	-0.180

H 12	0.202	0.190	H 12	0.196	0.184	H 12	0.193	0.181
H 13	0.202	0.191	H 13	0.203	0.191	H 13	0.203	0.190
H 14	0.190	0.180	C 14	-0.397	-0.362	C 14	-0.402	-0.368
C 15	-0.201	-0.173	H 15	0.188	0.178	H 15	0.185	0.176
H 16	0.199	0.187	H 16	0.200	0.189	H 16	0.199	0.188
H 17	0.202	0.190	H 17	0.200	0.189	H 17	0.199	0.188
C 18	-0.207	-0.178	C 18	-0.207	-0.178	C 18	-0.209	-0.180
H 19	0.202	0.189	H 19	0.203	0.191	H 19	0.203	0.190
H 20	0.208	0.195	H 20	0.196	0.184	H 20	0.193	0.181
C 21	-0.384	-0.348	C 21	-0.207	-0.178	C 21	-0.209	-0.180
H 22	0.202	0.191	H 22	0.203	0.191	H 22	0.203	0.190
H 23	0.196	0.185	H 23	0.196	0.184	H 23	0.193	0.181
H 24	0.188	0.178	C 24	-0.397	-0.362	C 24	-0.209	-0.180
C 25	-0.208	-0.179	H 25	0.188	0.178	H 25	0.193	0.181
H 26	0.209	0.197	H 26	0.200	0.189	H 26	0.203	0.190
H 27	0.206	0.193	H 27	0.200	0.189	C 27	-0.402	-0.368
C 28	-0.199	-0.171	C 28	-0.207	-0.178	H 28	0.185	0.176
H 29	0.199	0.187	H 29	0.196	0.184	H 29	0.199	0.188
H 30	0.207	0.194	H 30	0.203	0.191	H 30	0.199	0.188
C 31	-0.391	-0.355	N 31	-0.531	-0.542	N 31	-0.543	-0.555
H 32	0.200	0.190	N 32	-0.531	-0.542	N 32	-0.543	-0.555
H 33	0.203	0.192	N 33	-0.531	-0.542	N 33	-0.543	-0.555
H 34	0.193	0.182	K 34	0.734	0.742	Rb 34	0.924	0.929
C 35	-0.201	-0.172	C 35	-0.207	-0.178	C 35	-0.209	-0.180
H 36	0.205	0.193	H 36	0.203	0.191	H 36	0.203	0.190
H 37	0.200	0.188	H 37	0.196	0.184	H 37	0.193	0.181
C 38	-0.211	-0.183	C 38	-0.397	-0.362	C 38	-0.402	-0.368
H 39	0.213	0.200	H 39	0.188	0.178	H 39	0.185	0.176
H 40	0.209	0.196	H 40	0.200	0.189	H 40	0.199	0.188
C 41	-0.377	-0.342	H 41	0.200	0.189	H 41	0.199	0.188
H 42	0.190	0.180	C 42	-0.207	-0.178	C 42	-0.209	-0.180
H 43	0.202	0.190	H 43	0.196	0.184	H 43	0.193	0.181
H 44	0.202	0.191	H 44	0.203	0.191	H 44	0.203	0.190
C 45	-0.201	-0.173	C 45	-0.207	-0.178	C 45	-0.209	-0.180
H 46	0.199	0.187	H 46	0.196	0.184	H 46	0.193	0.181
H 47	0.202	0.190	H 47	0.203	0.191	H 47	0.203	0.190
C 48	-0.207	-0.178	C 48	-0.397	-0.362	C 48	-0.402	-0.368
H 49	0.202	0.189	H 49	0.188	0.178	H 49	0.185	0.176
H 50	0.208	0.195	H 50	0.200	0.189	H 50	0.199	0.188
C 51	-0.384	-0.348	H 51	0.200	0.189	H 51	0.199	0.188
H 52	0.188	0.178	C 52	-0.207	-0.178	C 52	-0.209	-0.180
H 53	0.202	0.191	H 53	0.203	0.191	H 53	0.203	0.190
H 54	0.196	0.185	H 54	0.196	0.184	H 54	0.193	0.181
C 55	-0.208	-0.179	C 55	-0.207	-0.178	C 55	-0.209	-0.180

H 56	0.209	0.197	H 56	0.203	0.191	H 56	0.203	0.190
H 57	0.206	0.193	H 57	0.196	0.184	H 57	0.193	0.181
C 58	-0.199	-0.171	C 58	-0.397	-0.362	C 58	-0.209	-0.180
H 59	0.199	0.187	H 59	0.188	0.178	H 59	0.193	0.181
H 60	0.207	0.194	H 60	0.200	0.189	H 60	0.203	0.190
Li 61	0.522	0.546	H 61	0.200	0.189	C 61	-0.402	-0.368
N 62	-0.548	-0.560	C 62	-0.207	-0.178	H 62	0.185	0.176
N 63	-0.544	-0.558	H 63	0.196	0.184	H 63	0.199	0.188
N 64	-0.529	-0.541	H 64	0.203	0.191	H 64	0.199	0.188
N 65	-0.548	-0.560	N 65	-0.531	-0.542	N 65	-0.543	-0.555
N 66	-0.544	-0.558	N 66	-0.531	-0.542	N 66	-0.543	-0.555
N 67	-0.529	-0.541	N 67	-0.531	-0.542	N 67	-0.543	-0.555

Table S26: Computed charge densities (natural charges) on all the centres of the $[M(Me_6[18]aneN_6)]^+$ systems, M = Na and Cs, obtained using the BP86 and B3LYP functionals.

Na (Structure **1**)-puckered			Cs		
Centres	BP86	B3LYP	Centres	BP86	B3LYP
C 1	-0.391	-0.357	C 1	-0.208	-0.180
H 2	0.202	0.191	H 2	0.204	0.192
H 3	0.202	0.191	H 3	0.193	0.181
H 4	0.189	0.179	C 4	-0.404	-0.370
C 5	-0.196	-0.167	H 5	0.188	0.179
H 6	0.201	0.188	H 6	0.197	0.185
H 7	0.196	0.184	H 7	0.197	0.185
C 8	-0.212	-0.183	C 8	-0.208	-0.180
H 9	0.214	0.201	H 9	0.193	0.181
H 10	0.208	0.195	H 10	0.204	0.192
C 11	-0.376	-0.340	C 11	-0.211	-0.182
H 12	0.201	0.190	H 12	0.192	0.179
H 13	0.202	0.190	H 13	0.199	0.186
H 14	0.188	0.178	C 14	-0.402	-0.368
C 15	-0.200	-0.172	H 15	0.182	0.172
H 16	0.198	0.186	H 16	0.200	0.188
H 17	0.205	0.192	H 17	0.200	0.188
C 18	-0.207	-0.178	C 18	-0.211	-0.182
H 19	0.201	0.188	H 19	0.199	0.186
H 20	0.209	0.196	H 20	0.192	0.179
C 21	-0.384	-0.347	C 21	-0.208	-0.180
H 22	0.202	0.191	H 22	0.204	0.192
H 23	0.198	0.187	H 23	0.193	0.181
H 24	0.188	0.178	C 24	-0.404	-0.370
C 25	-0.207	-0.178	H 25	0.188	0.179
H 26	0.203	0.192	H 26	0.197	0.185

H	27	0.207	0.195	H	27	0.197	0.185
C	28	-0.199	-0.171	C	28	-0.208	-0.180
H	29	0.200	0.188	H	29	0.193	0.181
H	30	0.207	0.194	H	30	0.204	0.192
C	31	-0.391	-0.357	N	31	-0.540	-0.551
H	32	0.202	0.191	N	32	-0.534	-0.544
H	33	0.202	0.191	N	33	-0.540	-0.551
H	34	0.189	0.179	C	34	-0.211	-0.182
C	35	-0.196	-0.167	H	35	0.199	0.186
H	36	0.201	0.188	H	36	0.192	0.179
H	37	0.196	0.184	C	37	-0.402	-0.368
C	38	-0.212	-0.183	H	38	0.182	0.172
H	39	0.214	0.201	H	39	0.200	0.188
H	40	0.208	0.195	H	40	0.200	0.188
C	41	-0.376	-0.340	C	41	-0.211	-0.182
H	42	0.188	0.178	H	42	0.192	0.179
H	43	0.201	0.190	H	43	0.199	0.186
H	44	0.202	0.190	C	44	-0.208	-0.180
C	45	-0.200	-0.172	H	45	0.193	0.181
H	46	0.198	0.186	H	46	0.204	0.192
H	47	0.205	0.192	C	47	-0.404	-0.370
C	48	-0.207	-0.178	H	48	0.188	0.179
H	49	0.201	0.188	H	49	0.197	0.185
H	50	0.209	0.196	H	50	0.197	0.185
C	51	-0.384	-0.347	C	51	-0.208	-0.180
H	52	0.188	0.178	H	52	0.204	0.192
H	53	0.202	0.191	H	53	0.193	0.181
H	54	0.198	0.187	C	54	-0.211	-0.182
C	55	-0.207	-0.178	H	55	0.199	0.186
H	56	0.203	0.192	H	56	0.192	0.179
H	57	0.207	0.195	C	57	-0.402	-0.368
C	58	-0.199	-0.171	H	58	0.182	0.172
H	59	0.200	0.188	H	59	0.200	0.188
H	60	0.207	0.194	H	60	0.200	0.188
N	61	-0.542	-0.554	C	61	-0.211	-0.182
N	62	-0.547	-0.560	H	62	0.192	0.179
N	63	-0.540	-0.554	H	63	0.199	0.186
N	64	-0.542	-0.554	N	64	-0.534	-0.544
N	65	-0.547	-0.560	N	65	-0.540	-0.551
N	66	-0.540	-0.554	N	66	-0.534	-0.544
Na	67	0.563	0.574	Cs	67	0.936	0.944

Table S27: Computed charge densities (natural charges) on all the centres of the $[M(Me_3tacn)]^+$ systems, M = Li–Cs, obtained using the BP86 functional.

Centres	Me_3tacn	$[Li(Me_3tacn)]^+$	$[Na(Me_3tacn)]^+$	Centres	$[K(Me_3tacn)]^+$	$[Rb(Me_3tacn)]^+$	$[Cs(Me_3tacn)]^+$
C 1	-0.378	-0.386	-0.387	C 1	-0.391	-0.393	-0.394
H 2	0.196	0.209	0.203	H 2	0.198	0.194	0.192
H 3	0.194	0.210	0.206	H 3	0.203	0.201	0.199
H 4	0.156	0.198	0.194	H 4	0.193	0.190	0.189
C 5	-0.210	-0.216	-0.218	C 5	-0.217	-0.218	-0.218
H 6	0.188	0.227	0.224	H 6	0.219	0.216	0.215
H 7	0.190	0.208	0.205	H 7	0.203	0.201	0.200
C 8	-0.191	-0.205	-0.204	C 8	-0.202	-0.204	-0.203
H 9	0.160	0.211	0.204	H 9	0.199	0.194	0.192
H 10	0.196	0.213	0.205	H 10	0.199	0.194	0.192
C 11	-0.210	-0.216	-0.218	C 11	-0.391	-0.393	-0.394
H 12	0.190	0.208	0.205	H 12	0.198	0.194	0.192
H 13	0.188	0.227	0.224	H 13	0.203	0.201	0.199
C 14	-0.378	-0.386	-0.387	H 14	0.193	0.190	0.189
H 15	0.194	0.210	0.206	C 15	-0.217	-0.218	-0.218
H 16	0.156	0.198	0.194	H 16	0.219	0.216	0.215
H 17	0.196	0.209	0.203	H 17	0.203	0.201	0.200
C 18	-0.191	-0.205	-0.204	C 18	-0.202	-0.204	-0.203
H 19	0.160	0.211	0.204	H 19	0.199	0.194	0.192
H 20	0.196	0.213	0.205	H 20	0.199	0.194	0.192
C 21	-0.378	-0.386	-0.387	C 21	-0.391	-0.393	-0.394
H 22	0.156	0.198	0.194	H 22	0.198	0.194	0.192
H 23	0.196	0.209	0.203	H 23	0.203	0.201	0.199
H 24	0.194	0.210	0.206	H 24	0.193	0.190	0.189
C 25	-0.210	-0.216	-0.218	C 25	-0.217	-0.218	-0.218
H 26	0.188	0.227	0.224	H 26	0.203	0.201	0.200
H 27	0.190	0.208	0.205	H 27	0.219	0.216	0.215
C 28	-0.191	-0.205	-0.204	C 28	-0.202	-0.204	-0.203
H 29	0.160	0.211	0.204	H 29	0.199	0.194	0.192
H 30	0.196	0.213	0.205	H 30	0.199	0.194	0.192
N...31	-0.499	-0.604	-0.587	N...31	-0.575	-0.564	-0.556
N...32	-0.499	-0.604	-0.587	N...32	-0.575	-0.564	-0.556
N...33	-0.499	-0.604	-0.587	N...33	-0.575	-0.564	-0.556
M...34		0.806	0.867	M...34	0.913	0.969	0.977

Table S28: Computed charge densities (natural charges) on all the centres of the $[M(Me_3tacn)]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

Centres	Me_3tacn	$[Li(Me_3tacn)]^+$	$[Na(Me_3tacn)]^+$	Centres	$[K(Me_3tacn)]^+$	$[Rb(Me_3tacn)]^+$	$[Cs(Me_3tacn)]^+$
C 1	-0.343	-0.352	-0.353	C 1	-0.357	-0.359	-0.359
H 2	0.185	0.199	0.193	H 2	0.187	0.183	0.180
H 3	0.183	0.199	0.195	H 3	0.192	0.189	0.188
H 4	0.147	0.189	0.184	H 4	0.183	0.181	0.180
C 5	-0.181	-0.189	-0.190	C 5	-0.189	-0.190	-0.189
H 6	0.175	0.215	0.211	H 6	0.206	0.203	0.201
H 7	0.178	0.196	0.193	H 7	0.191	0.189	0.189
C 8	-0.163	-0.177	-0.176	C 8	-0.174	-0.176	-0.174
H 9	0.149	0.199	0.192	H 9	0.187	0.182	0.179
H 10	0.183	0.201	0.193	H 10	0.186	0.181	0.179
C 11	-0.181	-0.189	-0.190	C 11	-0.357	-0.359	-0.359
H 12	0.178	0.196	0.193	H 12	0.187	0.183	0.180
H 13	0.175	0.215	0.211	H 13	0.192	0.189	0.188
C 14	-0.343	-0.352	-0.353	H 14	0.183	0.181	0.180
H 15	0.183	0.199	0.195	C 15	-0.189	-0.190	-0.189
H 16	0.147	0.189	0.184	H 16	0.206	0.203	0.201
H 17	0.185	0.199	0.193	H 17	0.191	0.189	0.189
C 18	-0.163	-0.177	-0.176	C 18	-0.174	-0.176	-0.174
H 19	0.149	0.199	0.192	H 19	0.187	0.182	0.179
H 20	0.183	0.201	0.193	H 20	0.186	0.181	0.179
C 21	-0.343	-0.352	-0.353	C 21	-0.357	-0.359	-0.359
H 22	0.147	0.189	0.184	H 22	0.187	0.183	0.180
H 23	0.185	0.199	0.193	H 23	0.192	0.189	0.188
H 24	0.183	0.199	0.195	H 24	0.183	0.181	0.180
C 25	-0.181	-0.189	-0.190	C 25	-0.189	-0.190	-0.189
H 26	0.175	0.215	0.211	H 26	0.191	0.189	0.189
H 27	0.178	0.196	0.193	H 27	0.206	0.203	0.201
C 28	-0.163	-0.177	-0.176	C 28	-0.174	-0.176	-0.174
H 29	0.149	0.199	0.192	H 29	0.186	0.181	0.179
H 30	0.183	0.201	0.193	H 30	0.187	0.182	0.179
N...31	-0.514	-0.614	-0.598	N...31	-0.585	-0.575	-0.566
N...32	-0.514	-0.614	-0.598	N...32	-0.585	-0.575	-0.566
N...33	-0.514	-0.614	-0.598	N...33	-0.585	-0.575	-0.566
M...34		0.804	0.868	M...34	0.917	0.973	0.981

Table S29: Computed charge densities (natural charges) on all the centres of the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the BP86 functional.

Centres	$[Li(Me_3tacn)_2]^+$	$[Na(Me_3tacn)_2]^+$	Centres	$[K(Me_3tacn)_2]^+$	$[Rb(Me_3tacn)_2]^+$	$[Cs(Me_3tacn)_2]^+$
C 1	-0.379	-0.378	C 1	-0.383	-0.389	-0.390
H 2	0.199	0.199	H 2	0.201	0.199	0.198
H 3	0.200	0.201	H 3	0.195	0.193	0.191
H 4	0.190	0.188	H 4	0.186	0.184	0.184
C 5	-0.212	-0.213	C 5	-0.214	-0.216	-0.216
H 6	0.218	0.217	H 6	0.214	0.212	0.211
H 7	0.203	0.203	H 7	0.201	0.199	0.199
C 8	-0.198	-0.194	C 8	-0.196	-0.201	-0.201
H 9	0.197	0.195	H 9	0.192	0.188	0.187
H 10	0.208	0.205	H 10	0.199	0.195	0.193
C 11	-0.212	-0.213	C 11	-0.383	-0.389	-0.390
H 12	0.203	0.203	H 12	0.201	0.199	0.198
H 13	0.218	0.217	H 13	0.195	0.193	0.191
C 14	-0.379	-0.378	H 14	0.186	0.184	0.184
H 15	0.200	0.201	C 15	-0.214	-0.216	-0.216
H 16	0.190	0.188	H 16	0.201	0.199	0.199
H 17	0.199	0.199	H 17	0.214	0.212	0.211
C 18	-0.198	-0.194	C 18	-0.196	-0.201	-0.201
H 19	0.197	0.195	H 19	0.199	0.195	0.193
H 20	0.208	0.205	H 20	0.192	0.188	0.187
C 21	-0.379	-0.378	C 21	-0.383	-0.389	-0.390
H 22	0.190	0.188	H 22	0.186	0.184	0.184
H 23	0.199	0.199	H 23	0.201	0.199	0.198
H 24	0.200	0.201	H 24	0.195	0.193	0.191
C 25	-0.212	-0.213	C 25	-0.214	-0.216	-0.216
H 26	0.218	0.217	H 26	0.201	0.199	0.199
H 27	0.203	0.203	H 27	0.214	0.212	0.211
C 28	-0.198	-0.194	C 28	-0.196	-0.201	-0.201
H 29	0.197	0.195	H 29	0.199	0.195	0.193
H 30	0.208	0.205	H 30	0.192	0.188	0.187
N...31	-0.544	-0.549	N...31	-0.542	-0.550	-0.544
N...32	-0.544	-0.549	N...32	-0.542	-0.550	-0.544
N...33	-0.544	-0.549	N...33	-0.542	-0.550	-0.544
M...34	0.513	0.551	M...34	0.680	0.908	0.936
C 35	-0.379	-0.378	C 35	-0.383	-0.389	-0.390
H 36	0.199	0.199	H 36	0.201	0.199	0.198
H 37	0.200	0.201	H 37	0.195	0.193	0.191
H 38	0.190	0.188	H 38	0.186	0.184	0.184
C 39	-0.212	-0.213	C 39	-0.214	-0.216	-0.216

H 40	0.218	0.217	H 40	0.214	0.212	0.211
H 41	0.203	0.203	H 41	0.201	0.199	0.199
C 42	-0.198	-0.194	C 42	-0.196	-0.201	-0.201
H 43	0.197	0.195	H 43	0.192	0.188	0.187
H 44	0.208	0.205	H 44	0.199	0.195	0.193
C 45	-0.212	-0.213	C 45	-0.383	-0.389	-0.390
H 46	0.203	0.203	H 46	0.201	0.199	0.198
H 47	0.218	0.217	H 47	0.195	0.193	0.191
C 48	-0.379	-0.378	H 48	0.186	0.184	0.184
H 49	0.200	0.201	C 49	-0.214	-0.216	-0.216
H 50	0.190	0.188	H 50	0.201	0.199	0.199
H 51	0.199	0.199	H 51	0.214	0.212	0.211
C 52	-0.198	-0.194	C 52	-0.196	-0.201	-0.201
H 53	0.197	0.195	H 53	0.199	0.195	0.193
H 54	0.208	0.205	H 54	0.192	0.188	0.187
C 55	-0.379	-0.378	C 55	-0.383	-0.389	-0.390
H 56	0.190	0.188	H 56	0.186	0.184	0.184
H 57	0.199	0.199	H 57	0.201	0.199	0.198
H 58	0.200	0.201	H 58	0.195	0.193	0.191
C 59	-0.212	-0.213	C 59	-0.214	-0.216	-0.216
H 60	0.218	0.217	H 60	0.201	0.199	0.199
H 61	0.203	0.203	H 61	0.214	0.212	0.211
C 62	-0.198	-0.194	C 62	-0.196	-0.201	-0.201
H 63	0.197	0.195	H 63	0.199	0.195	0.193
H 64	0.208	0.205	H 64	0.192	0.188	0.187
N...65	-0.544	-0.549	N...65	-0.542	-0.550	-0.544
N...66	-0.544	-0.549	N...66	-0.542	-0.550	-0.544
N...67	-0.544	-0.549	N...67	-0.542	-0.550	-0.544

Table S30: Computed charge densities (natural charges) on all the centres of the $[M(Me_3tacn)_2]^+$ systems, M = Li–Cs, obtained using the B3LYP functional.

Centres	$[Li(Me_3tacn)_2]^+$	$[Na(Me_3tacn)_2]^+$	Centres	$[K(Me_3tacn)_2]^+$	$[Rb(Me_3tacn)_2]^+$	$[Cs(Me_3tacn)_2]^+$
C 1	-0.343	-0.342	C 1	-0.348	-0.355	-0.356
H 2	0.187	0.188	H 2	0.190	0.188	0.187
H 3	0.189	0.189	H 3	0.184	0.181	0.180
H 4	0.179	0.178	H 4	0.177	0.175	0.175
C 5	-0.184	-0.185	C 5	-0.186	-0.188	-0.188
H 6	0.205	0.204	H 6	0.201	0.199	0.197
H 7	0.191	0.191	H 7	0.189	0.188	0.187
C 8	-0.169	-0.165	C 8	-0.168	-0.172	-0.172
H 9	0.184	0.183	H 9	0.180	0.176	0.175
H 10	0.195	0.192	H 10	0.186	0.182	0.180
C 11	-0.184	-0.185	C 11	-0.348	-0.355	-0.355
H 12	0.191	0.191	H 12	0.190	0.188	0.187
H 13	0.205	0.204	H 13	0.184	0.181	0.180
C 14	-0.343	-0.342	H 14	0.177	0.175	0.175
H 15	0.189	0.189	C 15	-0.186	-0.188	-0.188
H 16	0.179	0.178	H 16	0.189	0.188	0.187
H 17	0.187	0.188	H 17	0.201	0.199	0.197
C 18	-0.169	-0.165	C 18	-0.168	-0.172	-0.172
H 19	0.184	0.183	H 19	0.186	0.182	0.180
H 20	0.195	0.192	H 20	0.180	0.176	0.175
C 21	-0.343	-0.342	C 21	-0.348	-0.355	-0.356
H 22	0.179	0.178	H 22	0.177	0.175	0.175
H 23	0.187	0.188	H 23	0.190	0.188	0.187
H 24	0.189	0.189	H 24	0.184	0.181	0.180
C 25	-0.184	-0.185	C 25	-0.186	-0.188	-0.188
H 26	0.205	0.204	H 26	0.189	0.188	0.187
H 27	0.191	0.191	H 27	0.201	0.199	0.197
C 28	-0.169	-0.165	C 28	-0.168	-0.172	-0.172
H 29	0.184	0.183	H 29	0.186	0.182	0.180
H 30	0.195	0.192	H 30	0.180	0.176	0.175
N...31	-0.557	-0.561	N...31	-0.554	-0.561	-0.555
N...32	-0.557	-0.561	N...32	-0.554	-0.561	-0.555
N...33	-0.557	-0.561	N...33	-0.554	-0.561	-0.555
M...34	0.537	0.569	M...34	0.689	0.914	0.940
C 35	-0.343	-0.342	C 35	-0.348	-0.355	-0.355
H 36	0.187	0.188	H 36	0.190	0.188	0.187
H 37	0.189	0.189	H 37	0.184	0.181	0.180
H 38	0.179	0.178	H 38	0.177	0.175	0.175
C 39	-0.184	-0.185	C 39	-0.186	-0.188	-0.188

H 40	0.205	0.204	H 40	0.201	0.199	0.197
H 41	0.191	0.191	H 41	0.189	0.188	0.187
C 42	-0.169	-0.165	C 42	-0.168	-0.172	-0.172
H 43	0.184	0.183	H 43	0.180	0.176	0.175
H 44	0.195	0.192	H 44	0.186	0.182	0.180
C 45	-0.184	-0.185	C 45	-0.348	-0.355	-0.356
H 46	0.191	0.191	H 46	0.190	0.188	0.187
H 47	0.205	0.204	H 47	0.184	0.181	0.180
C 48	-0.343	-0.342	H 48	0.177	0.175	0.175
H 49	0.189	0.189	C 49	-0.186	-0.188	-0.188
H 50	0.179	0.178	H 50	0.189	0.188	0.187
H 51	0.187	0.188	H 51	0.201	0.199	0.197
C 52	-0.169	-0.165	C 52	-0.168	-0.172	-0.172
H 53	0.184	0.183	H 53	0.186	0.182	0.180
H 54	0.195	0.192	H 54	0.180	0.176	0.175
C 55	-0.343	-0.342	C 55	-0.348	-0.355	-0.356
H 56	0.179	0.178	H 56	0.177	0.175	0.175
H 57	0.187	0.188	H 57	0.190	0.188	0.187
H 58	0.189	0.189	H 58	0.184	0.181	0.180
C 59	-0.184	-0.185	C 59	-0.186	-0.188	-0.188
H 60	0.205	0.204	H 60	0.189	0.188	0.187
H 61	0.191	0.191	H 61	0.201	0.199	0.197
C 62	-0.169	-0.165	C 62	-0.168	-0.172	-0.172
H 63	0.184	0.183	H 63	0.186	0.182	0.180
H 64	0.195	0.192	H 64	0.180	0.176	0.175
N...65	-0.557	-0.561	N...65	-0.554	-0.561	-0.555
N...66	-0.557	-0.561	N...66	-0.554	-0.561	-0.555
N...67	-0.557	-0.561	N...67	-0.554	-0.561	-0.555

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