

# Host–guest complexes of mixed glycol-phenanthroline cryptands: prediction of ion selectivity by quantum chemical calculations IV

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**Abstract** Structures and complex-formation energies, calculated with DFT (B3LYP/LANL2DZp) for the cryptands [2.2.phen] and [2.phen.phen] with endohedrally complexed alkali and alkaline earth metal ions, were utilized to predict their ion selectivity. Both cryptands [2.2.phen] and [2.phen.phen] have a cavity size smaller than [2.2.2], [phen.phen.phen] and [bpy.bpy.bpy], and prefer to bind  $K^+$  and  $Sr^{2+}$ , whereas [2.2.phen] that is larger than [2.phen.phen], has a preference for  $Ba^{2+}$ , and [2.phen.phen] favours  $Na^+$  and  $Ca^{2+}$ . The cryptand flexibility is mainly attributed to the presence of  $CH_2-N_{SP3}\cdots N_{SP3}-CH_2$  groups.

**Keywords** Cation selectivity · Host–guest · DFT

## Introduction

Selective complexation of ions and molecules is a fundamental prerequisite for receptors in biological and technical systems. Therefore, these phenomena have been investigated for many decades [1, 2]. In order to gain deeper understanding in the geometric and electronic requirements necessary for selective complexation, many models with cavities of variable size and structure have been studied experimentally and computationally [3–5]. Examples are

the well-known calixarenes [6, 7], crown ethers [8], cryptands [9, 10], and their inclusion complexes, along with the corresponding metallatopomers, which are easily accessible via self-organization [11].

The synthesis of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane reported by Dietrich, Lehn and Sauvage in 1969, today well known as [2.2.2] (trade name Kryptofix 222), led to a wide range of applications, especially the outstanding property to selectively bind guests, particularly alkali- and alkaline earth metal ions, were immediately recognized and led to many applications, viz. in phase-transfer catalysis [12, 13], studies on Zintl phases [14], selective complexation of radioactive or toxic ions in medicine [15] and elsewhere [16, 17], as chelates for MRI contrast agents [18], and as models for carrier-antibiotics such as Valinomycin and enzyme inhibitors. In contrast, other cryptands with similar topology such as 6,6',6'',6''', 6''',6''''-bis[nitrilotri(methylene)]tris(2,2'-bipyridine) and 2,2', 2'',9,9',9''-bis[nitrilotri(methylene)]tris(1,10-phenanthroline), best abbreviated as [bpy.bpy.bpy] and [phen.phen.phen], were for many years only barely explored. Both were originally designed and synthesized by Lehn et al. with the intention of allowing control over metal-ion binding, as well as for their photophysical and photochemical behaviour via ligand design [19]. In the following years the research was only focused on their photophysics and photochemistry [20]. The lanthanide complexes were found to be efficient luminophores to convert UV light into visible light [21]. These properties can be utilized in fluorescent markers [22, 23], e.g. for detecting or locating nucleic acids [24] or for other labelling techniques [25].

The selective binding of alkali- and alkaline earth metal ions was recently studied by quantum chemical methods [26]. It is surprising that no experimental studies appeared over the last decades, as different cryptand/cryptate or crown ether solvent combinations were investigated

For “Prediction of ion selectivity by quantum chemical calculations III” see, R. Puchta, R. van Eldik. Aust. J. Chem. **60**, 889–897 (2007).

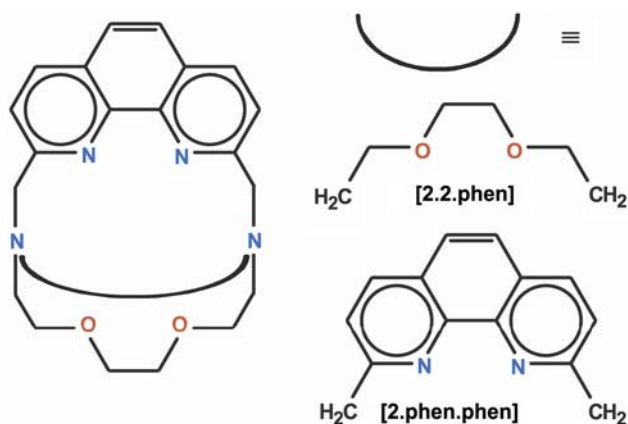
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[27–31] e.g. with respect to their transport properties [32] or ion conductivity, and potential application in batteries and capacitors [33], whereas in parallel alkali- and alkaline earth ion complexes with phenanthroline and bipyridine moieties were also studied [34].

In this study we extend our previous studies on [bpy.bpy.bpy], [phen.phen.phen] [35], [2.2.2] and its smaller homologues for selective ion complexation, and investigate two hybrid cryptands, formed by a combination of [2.2.2] and [phen.phen.phen]. The resulting cryptands are abbreviated as [2.2.phen] and [2.phen.phen] (see Fig. 1).

As experimental methods investigate systems under real conditions in a whole ensemble of solvent molecules, many successful efforts have been made to simulate cryptands and cryptates together with solvent molecules and in motion, e.g. in the case of [2.2.2] with classical molecular dynamics [36–41] or by Monte-Carlo simulations [42]. In contrast, non-dynamic quantum chemical calculations without solvents focus on only one system and are outstandingly applicable to investigate in detail a molecule or supramolecule in the absence of possibly disturbing side effects. For the alkali- and alkaline earth ion selectivity of [2.2.2], we recently demonstrated [26] the reliability and good correlation of (so called “gas phase”) complex-formation energies with experimental  $\log K_S$  values measured in different solvents [43, 44]. In addition, we successfully applied this approach for [bpy.bpy.bpy] and [phen.phen.phen] [26a]. Therefore, we also calculated complex-formation energies for the alkali- and alkaline earth metal ions here, to determine which ions fit best into [2.2.phen] and [2.phen.phen], investigated how the host responds to the different guest ions, and in addition tested by calculating the NICS [45] values, if the electron delocalization on the aromatic rings is affected by the complexation of cations.



**Fig. 1** Structures of [2.2.phen] and [2.phen.phen]

**Table 1** Calculated (RB3LYP/LANL2DZp) structural data for the metal donor interactions in [M ⊂ 2.2.Phen]<sup>n+</sup> (calculated structures: C<sub>2</sub> symmetry)

	Empty	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Be <sup>2+</sup>	Mg <sup>2+</sup> C <sub>1</sub>	Mg <sup>2+</sup> T.S.	Ca <sup>2+</sup>	Str <sup>2+</sup>	Ba <sup>2+</sup>
M–N <sub>SP2</sub> (Å)	–	2.20	2.73	2.91	2.99	3.11	1.79	2.23/2.24	2.30	2.68	2.79	2.89
M–N <sub>SP3</sub> (Å)	–	2.81	2.85	2.96	3.02	3.09	2.00	2.55/2.72	2.60	2.78	2.87	2.96
M–O (Å)	–	3.14/3.06	2.78/2.84	2.88/2.83	2.94/2.91	3.03/3.01	3.24/3.53	2.30/2.26/3.32/3.41	2.60/2.67	2.69/2.67	2.76/2.74	2.86/2.83
N <sub>SP2</sub> –C...C–N <sub>SP2</sub> (°)	10.3	0.8	2.3	6.7	8.8	11.1	1.8	–2.4	–3.7	–0.73	2.0	5.6
CH <sub>2</sub> –N <sub>SP3</sub> ...N <sub>SP3</sub> –CH <sub>2</sub> (°)	–46.4	–87.1	–75.6	–56.5	–45.7	–35.0	–132.2	–107.7	–114.7	–89.2	–73.6	–55.2
O–C...C–O (°)	74.6	56.9	57.5	61.9	66.7	74.9	49.3	42.9/51.9	47.7	50.6	52.8	56.2
CH <sub>2</sub> –CH <sub>2</sub> –N <sub>SP3</sub> ...N <sub>SP3</sub> –CH <sub>2</sub> –CH <sub>2</sub> (°)	–51.7	–86.5	–78.9	–60.3	–48.8	–37.2	–119.5	–101.0/–107.7	–114.1	–91.8	–76.7	–58.5

## Quantum chemical methods

We performed B3LYP/LANL2DZp hybrid density functional calculations, i.e., with pseudo-potentials on the heavy elements and the valence basis set augmented with polarization functions [46, 47], with no constraints other than symmetry. In addition, the resulting structures were characterized as minima, transition structures, etc., by computation of the vibrational frequencies. The relative energies were corrected for zero point vibrational energies (ZPE). DFT, in particular B3LYP, has been shown to provide accurate geometries, good harmonic vibrational frequencies and is well-suited for NMR [48] and NICS calculations [45]. The GAUSSIAN 03 suite of programs was used [49].

## Results and discussion

While for [2.2.2] X-ray structures for all alkali- and alkaline earth metal cryptate complexes have been published, no crystal structures are known for [2.2.phen] and [2.phen.phen],

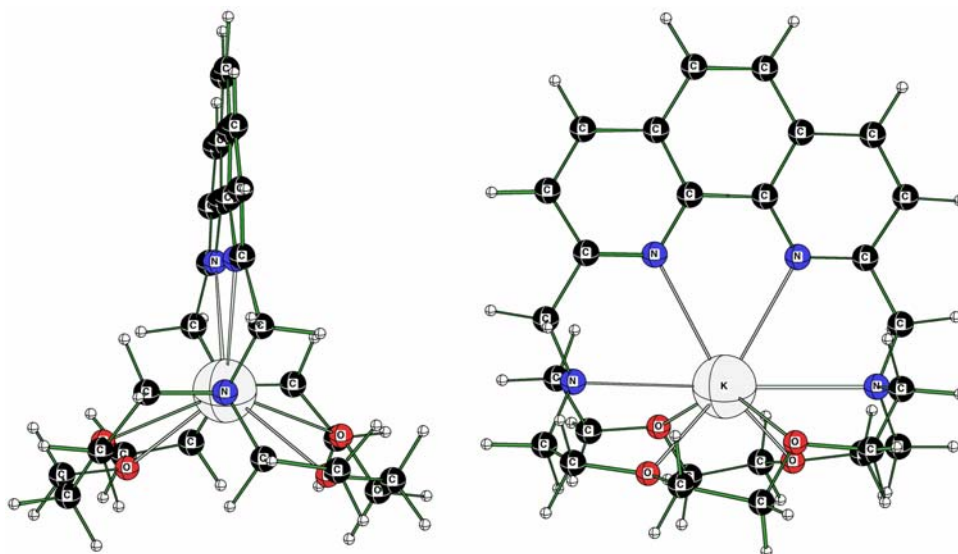
either empty or with endohedrally complexed metal ions. Previous studies showed that the selected method produced good results for related systems [26]. Selected data for the calculated structures (metal–N<sub>SP2</sub>, metal–N<sub>SP3</sub>, metal–O distances and twist angles) are summarized in Tables 1 and 2, and typical structures are shown in Figs. 2 and 3.

In contrast to the *D*<sub>3</sub> symmetric cryptands [2.2.2], [bpy.bpy.bpy] and [phen.phen.phen], [2.2.phen] and [2.phen.phen] show a lower symmetry. Therefore, even small cations like Li<sup>+</sup> and Be<sup>2+</sup> can be successfully inserted into the cavity. Within the *C*<sub>2</sub> symmetry the tiny Be<sup>2+</sup> cations are four times coordinated by nitrogen donors, whereas the oxygen atoms do not contribute to the coordination. As all other ions are coordinated by O- and N-donor atoms, this can be seen as a first indication that Be<sup>2+</sup> could be a special case, probably it is too small. Except for [Mg ⊂ 2.2.phen]<sup>2+</sup>, all structures are local minima on the potential hypersurface. The *C*<sub>2</sub> structure of [Mg ⊂ 2.2.phen]<sup>2+</sup> is a transition state that connects two species 1.2 kcal/mol lower in energy, where the five-fold coordinated metal ion is located beside an imaginary phenanthroline mirror plane, next to one nitrogen bridge head atom.

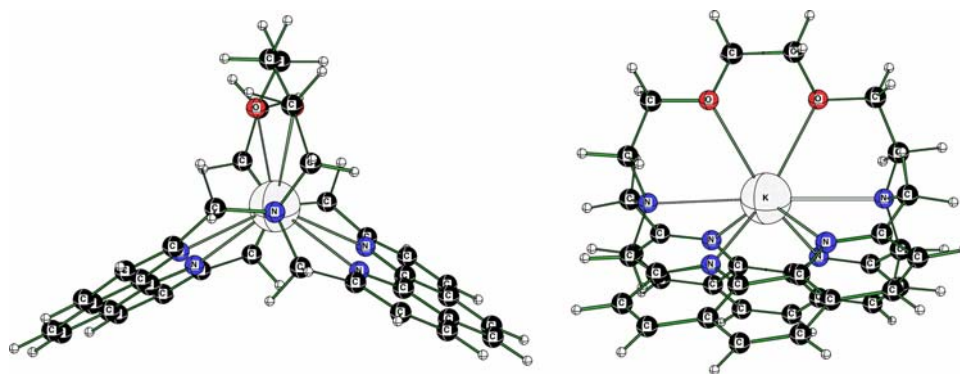
**Table 2** Calculated (RB3LYP/LANL2DZp) structural data for the metal donor interactions in [M ⊂ 2.Phen.Phen]<sup>n+</sup> (calculated structures: *C*<sub>2</sub> symmetry)

	Empty	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Be <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
M–N <sub>SP2</sub> (Å)	–	2.46/2.37	2.75/2.72	2.86/2.89	2.94/2.97	3.05/3.07	1.92/1.83	2.35/2.28	2.69/2.70	2.77/2.79	2.87/2.89
M–N <sub>SP3</sub> (Å)	–	2.88	2.84	2.91	2.98	3.05	3.01	2.75	2.79	2.85	2.93
M–O (Å)	–	3.41	2.82	2.82	2.87	2.96	4.09	3.25	2.70	2.75	2.93
N <sub>SP2</sub> –C···C–N <sub>SP2</sub> (°)	3.8	–1.02	0.6	3.8	6.4	8.7	–5.2	–3.77	–1.31	0.1	3.7
CH <sub>2</sub> –N <sub>SP3</sub> ··· N <sub>SP3</sub> –CH <sub>2</sub> (°)	–69.4	–90.5	–82.5	–68.4	–58.2	–48.0	–108.1	–104.2	–89.1	–78.5	–64.0
O–C···C–O (°)	72.6	59.0	57.2	61.0	66.5	76.7	57.0	52.7	50.8	52.4	56.1
CH <sub>2</sub> –CH <sub>2</sub> –N <sub>SP3</sub> ··· N <sub>SP3</sub> –CH <sub>2</sub> –CH <sub>2</sub> (°)	–76.6	–88.8	–85.2	–72.1	–62.0	–50.6	–92.9	–100.9	–91.6	–81.5	–67.3

**Fig. 2** Calculated (RB3LYP/LANL2DZp) structure (*C*<sub>2</sub>) for [K ⊂ 2.2.phen]<sup>+</sup>



**Fig. 3** Calculated (RB3LYP/LANL2DZp) structure ( $C_2$ ) of  $[K \subset 2.phen.phen]^+$



**Table 3** Energy contributions to the complexation energy for  $[M \subset 2.2.phen]^{n+}$  (RB3LYP/LANL2DZp)

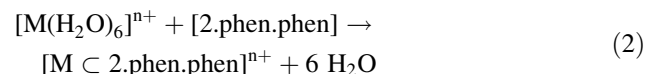
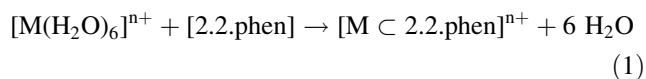
(kcal/mol)	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Be <sup>2+</sup>	Mg <sup>2+</sup> C <sub>1</sub>	Mg <sup>2+</sup> T.S.	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
$\Delta E_{tot}$	10.3	-2.9	-8.8	-2.0	10.7	3.1	-3.0	-1.9	-28.3	-32.4	-31.9
$\Delta ZPE$	-5.7	-5.0	-5.1	-5.3	-4.9	-9.7	-8.9	-8.9	-8.2	-7.9	-6.9
Complexation energy	4.7	-7.9	-13.9	-7.3	5.8	-6.6	-11.9	-10.8	-36.5	-40.3	-38.8

**Table 4** Energy contributions to the complexation energy for  $[M \subset 2.phen.phen]^{n+}$  (RB3LYP/LANL2DZp)

(kcal/mol)	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Be <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
$\Delta E_{tot}$	1.6	-10.4	-12.6	-2.5	15.1	-23.6	-23.6	-45.4	-47.4	-43.2
$\Delta ZPE$	-5.8	-5.4	-5.2	-5.3	-5.0	-11.0	-9.3	-8.3	-8.0	-6.9
Complexation energy	-4.2	-15.8	-17.8	-7.8	10.1	-34.6	-32.9	-53.7	-55.4	-50.1

The main goal of this work was to investigate the selective complexation of alkali- and alkaline earth metal ions by the cryptands [2.2.phen] and [2.phen.phen] in the same manner as in our earlier studies [26], to compare the cavity size [50] and ion selectivity. In principle, it is possible to compare the bond distance between the metal ion and the donor atoms in the cryptate with those computed for a metal ion complexed by solvent molecules such as acetonitrile or ammonia. This method only seems to be valid if the donor atoms coordinating to the metal ions are the same with equal hybridisation in the cryptand and in the solvent, and was

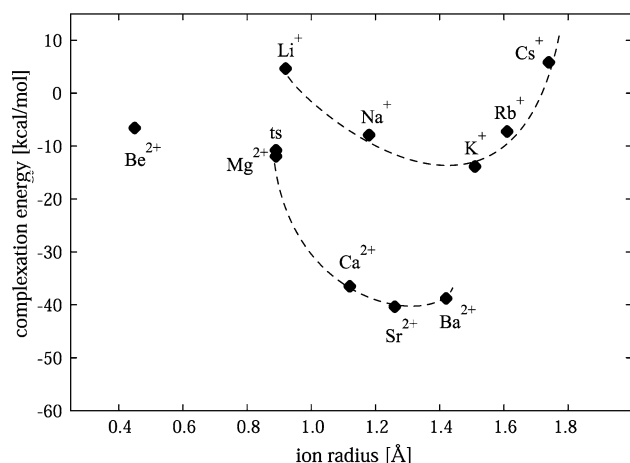
therefore not followed further in this study. Alternatively, the energy of the model reactions (1) and (2) can be evaluated (see Tables 3 and 4). Note that for the sake of consistency, six-fold coordination is adopted for all cations. The lithium [51] and sodium cations prefer four-fold and five-fold coordination, respectively, with additional water molecules hydrogen-bonded in the second coordination sphere instead of coordinated to the cation. However, in the gas phase  $[Li(H_2O)_6]^+$  and  $[Na(H_2O)_6]^+$  are local minima.



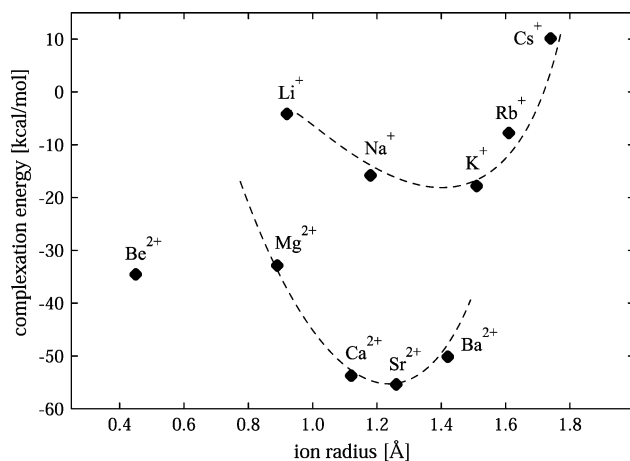
The computed complexation energies, plotted against the ionic radii, show that the most stable endohedral complexes of [2.2.phen] with the alkali ions are formed for K<sup>+</sup> and with the alkaline earth ions for Sr<sup>2+</sup> followed by Ba<sup>2+</sup> (see Fig. 4). Cryptand [2.phen.phen] prefers again to bind K<sup>+</sup> as alkali ion, and Sr<sup>2+</sup> succeeded by Ca<sup>2+</sup> as alkaline earth ions (see Fig. 5). A comparison of the preferred alkaline earth ion selectivity for [2.2.2], [phen.phen.phen], [2.2.phen] and [2.phen.phen] (see Table 5) shows a slight trend in the preferred cation: a decrease in the preferred cation size from [2.2.2] to [phen.phen.phen]. This could be interpreted as a slight decrease in the cavity size. Alkali cations are not very sensitive in this range as the ion radius difference for Na<sup>+</sup> and K<sup>+</sup> is too large. In the case of alkali cations, only [phen.phen.phen] prefers Na<sup>+</sup>.

The positive complexation energies for  $[Cs \subset 2.2.phen]^+$  and  $[Cs \subset 2.phen.phen]^+$  are a clear indication, that the Cs<sup>+</sup> ion is much too large for the cryptands' cavity, while the positive energy value for  $[Li \subset 2.2.phen]^+$  is a sign, that the smallest alkali cation can not be stabilized sufficient. However, all three values fit nicely in the trend.

The exceptions in our plots are always the Be<sup>2+</sup> ions. As already mentioned, the beryllium dications are four-fold coordinated by the nitrogen atoms. In the case of



**Fig. 4** RB3LYP/LANL2DZp complexation energies for  $[M \subset 2.2.phen]^{n+}$  according to reaction (1), plotted against the ionic radius of  $M^{n+}$  (dashed line: trend) (for the data see Table 3)



**Fig. 5** RB3LYP/LANL2DZp complexation energies for  $[M \subset 2.phen.phen]^{n+}$  according to reaction (2), plotted against the ionic radius of  $M^{n+}$  (dashed line: trend) (for the data see Table 4)

**Table 5** Preferred ion selectivity in [2.2.2], [2.2.phen], [2.phen.phen] and [phen.phen.phen]

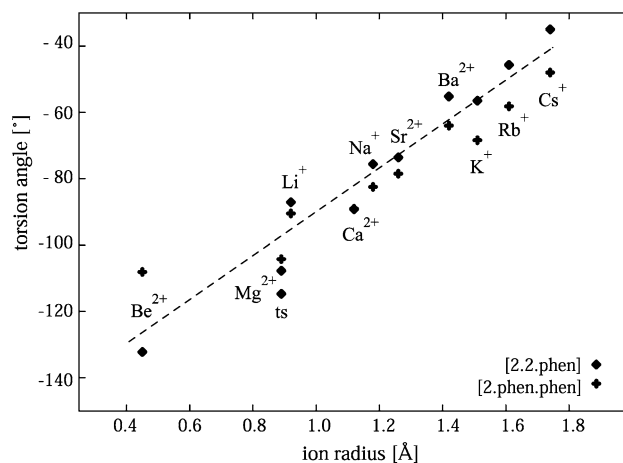
Host	Preferred alkali ion	Preferred alkaline earth ion
[2.2.2]	$K^+$	$Ba^{2+} > Sr^{2+}$
[2.2.phen]	$K^+$	$Sr^{2+} > Ba^{2+}$
[2.phen.phen]	$K^+$	$Sr^{2+} > Ca^{2+}$
[phen.phen.phen]	$Na^+$	$Ca^{2+} > Sr^{2+}$

$[Be \subset 2.2.phen]^{2+}$ , the two phenanthroline and the bridge head nitrogens coordinate, whereas in the case of  $[Be \subset 2.phen.phen]^{2+}$  the four phenanthroline nitrogen atoms coordinate to the metal centre. In  $[Be \subset 2.2.phen]^{2+}$ , an approximate tetrahedral coordination sphere with somewhat elongated bonds compared to  $[Be(pyridine)_4]^{2+}$  (1.75 Å) is formed. The coordination of the  $Be^{2+}$  ion in

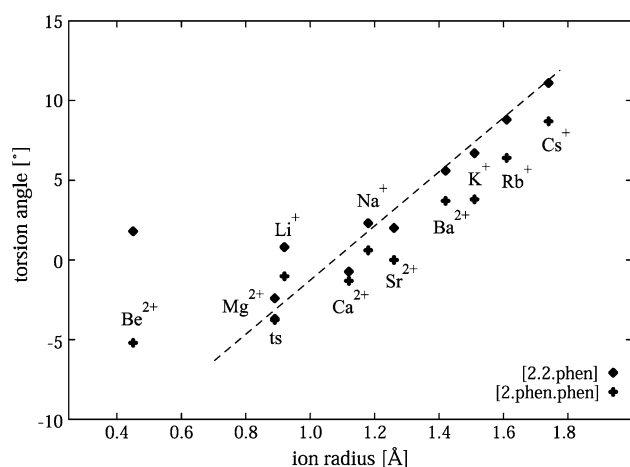
$[Be \subset 2.phen.phen]^{2+}$  is somewhat different. The coordination sphere is best addressed as a distorted tetrahedron. The short (1.83 Å) Be–N-bonds are still bent, while the two longer (1.92 Å) stand linear vis-à-vis. This arrangement is similar to the transition state of the ammonia exchange reaction around  $[Be(NH_3)_4]^{2+}$ . In the transition state the bonds are significant longer and there is a fifth solvent molecule above the ion [52]. In  $[Be \subset 2.2.phen]^{2+}$  this kind of fifth coordination is absent, but the two  $sp^3$  bridge head nitrogen atoms form a kind of second coordination sphere with their lone-pairs. Therefore,  $[Be \subset 2.2.phen]^{2+}$  and  $[Be \subset 2.phen.phen]^{2+}$  can be considered as structures allowing appropriate coordination and even an exaggerated stabilisation in the gas phase, but in solution this structure will surely not be superior to solvated  $Be^{2+}$  and an empty cryptand.

In our latest contribution on selective ion complexation by {2}-cryptands, we showed that the guest ions contribute differently to the host and its flexibility [26]. An essential pre-requisite for flexibility is a molecular moiety that can undergo twisting and tilting. In the investigated cryptands, there is at least one molecular bar  $C_2H_4-O-C_2H_4-O-C_2H_4$  adjacent to the N bridge head, and one with two pyridine rings in phenanthroline stiffened by a third, weaker aromatic [36d] six-membered ring. The third molecular bar can be formed by the aliphatic di-ether chain in [2.2.phen] or by a phenanthroline moiety in [2.phen.phen]. Descriptors for the twist and tilt of these moieties are the torsion angles such as  $N_{SP2}-C \cdots C-N_{SP2}$  and  $O-C-C-O$ , as well as the  $CH_2-N_{SP3} \cdots N_{SP3}-CH_2$  angle (see Tables 1 and 2).

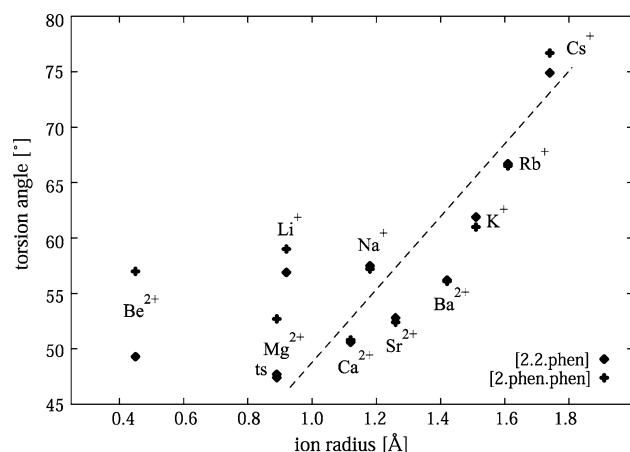
The torsion angles  $CH_2-N_{SP3} \cdots N_{SP3}-CH_2$ ,  $(CH_2-O)CH_2-N_{SP3} \cdots N_{SP3}-CH_2(CH_2-O)$ ,  $N_{SP2}-C \cdots C-N_{SP2}$  and  $O-C-C-O$  show a qualitative linear behaviour that mainly depends on



**Fig. 6** RB3LYP/LANL2DZp torsion angle  $CH_2-N_{SP3} \cdots N_{SP3}-CH_2$  for  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$  plotted against the ionic radius of  $M^{n+}$  (dashed line: trend)



**Fig. 7** RB3LYP/LANL2DZp torsion angle  $N_{SP2}-C\cdots C-N_{SP2}$  for  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$  plotted against the ionic radius of  $M^{n+}$  (dashed line: trend)



**Fig. 8** RB3LYP/LANL2DZp torsion angle  $O-C-C-O$  for  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$  plotted against the ionic radius of  $M^{n+}$  (dashed line: trend)

the ionic size (see Figs. 6–8). Since the torsion angles  $CH_2-N_{SP3}\cdots N_{SP3}-CH_2$  and  $(CH_2-O)CH_2-N_{SP3}\cdots N_{SP3}-CH_2(CH_2-O)$  show almost identical behaviour, we will focus here on the torsion angle  $CH_2-N_{SP3}\cdots N_{SP3}-CH_2$ . This angle covers the

widest range in both host–guest systems;  $[M \subset 2.2.phen]^{n+}$   $100^\circ$  and  $[M \subset 2.phen.phen]^{n+}$   $60^\circ$  (see Fig. 6). This is a clear indication that the twist angle between the  $CH_2$ -group and the  $N_{sp3}$ -bridge head is most important for the adjustment of the host to the guest. Throughout the series, all cryptates show the same stereochemistry, easily derivable from the algebraic sign, here minus and therefore  $\lambda$ . For the series of angles  $N_{SP2}-C\cdots C-N_{SP2}$  and  $O-C-C-O$ , the differences are much smaller. The value of  $N_{SP2}-C\cdots C-N_{SP2}$  is in the range of  $12^\circ$ , whereas  $O-C-C-O$  is around  $26^\circ$  in  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$ .

The small tilting in the phenanthroline moiety described by  $N_{SP2}-C\cdots C-N_{SP2}$  is easy to understand since the polycyclic hetero-aromatic system is inflexible. Again a very similar linear trend is found for both cryptate families (see Fig. 7). The main exceptions are  $[Be \subset 2.2.phen]^{2+}$  and  $[Be \subset 2.phen.phen]^{2+}$ . The  $Be^{2+}$  ion as the smallest ion that shows the above-described unusual coordination patterns, does not need to twist the chelating group as much as one would expect from the extrapolation of the other values. To a smaller extent the same behaviour is seen in  $[Li \subset 2.phen.phen]^+$ , as  $Li^+$  is also coordinated to the almost planar phenanthroline moieties. The consequence of the preferred binding of smaller ions such as  $Be^{2+}$ ,  $Li^+$  and  $Mg^{2+}$  by the phenanthroline nitrogens in both cryptands (see Tables 1 and 2), is again reflected in the  $O-C-C-O$  twist angle (see Fig. 8). As  $Be^{2+}$ ,  $Li^+$  and  $[Mg \subset 2.phen.phen]^{2+}$  do not significantly coordinate to the ether oxygen atoms (see Tables 1 and 2), they also do not affect these groups. Following this, there is a tendency for a qualitative linear increase observed for  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$ . Here the stereochemistry, again derivable from the algebraic sign, is in all cases positive and therefore  $\delta$ .

Lehn et al. [19] designed cryptands with aromatic moieties to utilize their photochemical and photophysical properties. The application of NICS calculations allows to investigate if there is an influence on the aromaticity of the three phenanthroline rings when cations are endohedrally complexed. A comparison between the cryptands and the complexes  $[M \subset 2.2.phen]^{n+}$  and  $[M \subset 2.phen.phen]^{n+}$

**Table 6** Calculated (RB3LYP/LANL2DZp) NICS data for  $[M \subset 2.2.phen]^{n+}$

	Empty	$Li^+$	$Na^+$	$K^+$	$Rb^+$	$Cs^+$	$Be^{2+}$	$Mg^{2+} C_1$	$Mg^{2+} T.S.$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$
<i>Pyridine moiety</i>												
NICS(0)	-7.02	-6.72	-5.77	-6.98	-7.10	-7.22	-6.20	-6.25, -6.55	-6.50	-6.74	-6.83	-7.06
NICS(1)	-9.60	-9.57	-7.98	-9.59	-9.55	-10.53	-9.52	-8.44, -9.35	-9.87	-9.70	-9.56	-9.54
<i>Benzene moiety</i>												
NICS(0)	-5.16	-5.97	-6.85	-5.76	-5.72	-5.64	-6.20	-6.28	-6.24	-6.32	-6.41	-6.44
NICS(1)	-7.52	-8.09	-9.66	-7.95	-7.88	-7.85	-8.41	-7.66	-8.37	-8.42	-8.46	-8.45

**Table 7** Calculated (RB3LYP/LANL2DZp) NICS data for [M C 2.phen.phen]<sup>nt</sup>

	Empty	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Be <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
<i>Pyridine moiety</i>											
NICS(0)	-6.76	-6.61	-6.68	-7.01	-7.16	-7.33	-6.14	-6.44	-6.77	-6.85	-7.09
NICS(1)	-9.85	-9.53	-9.47	-9.63	-9.59	-9.61	-11.12	-10.21	-9.69	-9.57	-9.54
<i>Benzene moiety</i>											
NICS(0)	-5.07	-5.83	-5.63	-5.59	-5.50	-5.44	-7.07	-6.43	-6.27	-6.25	-6.23
NICS(1)	-7.54	-8.47	-7.85	-7.75	-7.65	-7.63	-11.08	-9.21	-8.34	-8.27	-8.22

shows no significant differences. As documented in the literature [45] and in accordance with Clars' concept [53], the results show that the pyridine ring has a higher NICS value, and a better cyclic electron delocalization, than the benzene moiety (see Tables 6 and 7).

## Conclusions

According to our DFT-calculations, [2.2.phen] and [2.phen.phen] have somewhat smaller cavities than [2.2.2]. The investigated cryptands prefer to bind Sr<sup>2+</sup> and Ba<sup>2+</sup> or Ca<sup>2+</sup> as alkaline earth metal ions. The slight difference in the alkaline earth ion selectivity is an indication of a decreasing cavity size from [2.2.phen] to [2.phen.phen]. The preferred alkali metal ion is K<sup>+</sup>. The main part of the cage flexibility, important for selective host binding, comes from the CH<sub>2</sub>-N<sub>SP3</sub>...N<sub>SP3</sub>-CH<sub>2</sub> motive. The stereo-arrangement of this molecular motive fixed at the bridge head nitrogen, is in all investigated host-guest systems identical and does not change depending on the size of the guest ion. According to our NICS calculations, the complexed cations show no significant influence on the aromaticity of the phenanthroline moiety.

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