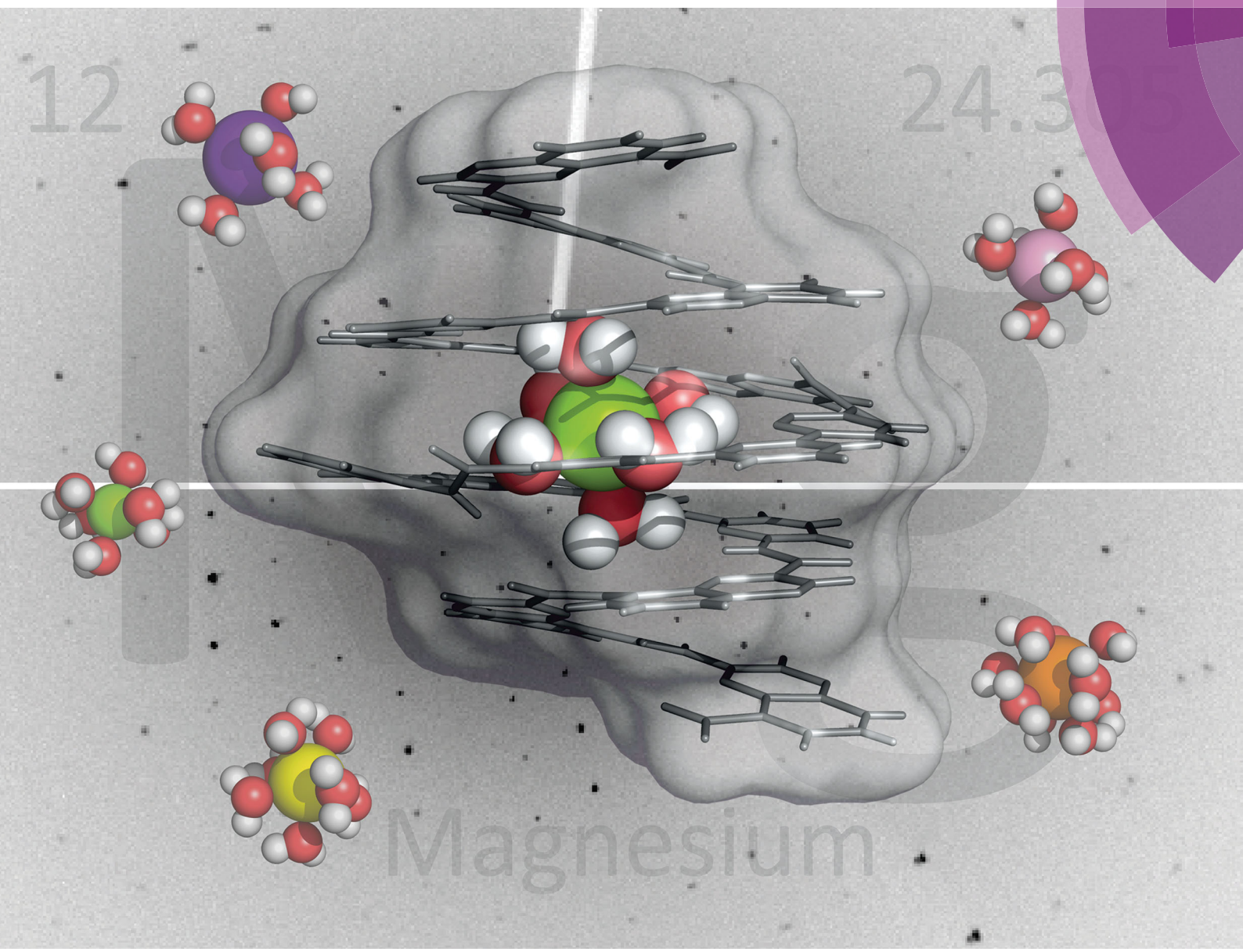
Volume 53 | Number 67 | 28 August 2017 | Pages 9287–9382

ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

Ivan Huc *et al.*

Alkali and alkaline earth metal ion binding by a foldamer capsule: selective recognition of magnesium hydrate

ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2017, 53, 9300

Received 13th July 2017,
Accepted 26th July 2017

DOI: 10.1039/c7cc05422j

rsc.li/chemcomm

Alkali and alkaline earth metal ion binding by a foldamer capsule: selective recognition of magnesium hydrate†

Pedro Mateus, [a] Barbara Wicher, [b] Yann Ferrand [a] and Ivan Huc *[a]

Alkali and alkaline earth metal ion binding by an aromatic oligoamide foldamer was shown to induce its folding into a helical capsule. CD and NMR titrations revealed tight and selective binding of Mg^{2+}. Crystallographic studies demonstrated that, depending on the metal, binding may involve the first or second coordination spheres of the metal hydrates.

Aromatic helical foldamers and related macrocycles have emerged as versatile bioinspired containers for molecular recognition.[1–5] When foldamer helices possess reduced diameters at both extremities they form capsules that sequester guest molecules and isolate them from the solvent.[5f] In sequences based on aza-aromatic oligoamides, the helix inner wall is composed of numerous hydrogen bond donors and acceptors that may give rise to tight, selective, and diastereoselective binding of polyhydroxylated guests such as monosaccharides,[3k] and organic hydroxy-acids.[3i,j] We have recently introduced sequence **1** (Fig. 1) whose central pyz–pyr–pyz segment was shown to bind to transition metal ions Cu(I), Cu(II) and Ag(I) in such a way that the metal sits on the cavity wall and that part of its coordination sphere remains available to contribute to the recognition of an organic guest.[6] Metal ion binding was also shown to drive helical folding: in the absence of a metal ion, the pyz–pyr–pyz segment exists in an *anti–anti* conformation favoured by repulsion between endocyclic nitrogen atoms (Fig. 1c) that confers the oligomer with an extended conformation in which the two hemi-capsules are not facing each other (Fig. 1a, centre).

Here we report the binding of alkali and alkaline-earth metal ions by sequence **1**. The outer s-electron shell of these metal ions does not promote an affinity of pyridine-based ligands as large as that of transition metals. We nevertheless find that Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+} all bind to **1** and induce its folding in a helix; outstanding affinity and selectivity for Mg^{2+} was observed. The hydration sphere of the metals is essential to the binding process to such an extent that, in the case of Mg^{2+}, Ca^{2+} and Ba^{2+} binding does not involve the pyz–pyr–pyz segment as a first coordination sphere ligand. Instead, the first coordination sphere water molecules undergo second coordination sphere interactions with the capsule that are so strong that they overcome helix folding in the case of barium nona-hydrate, a guest too large to fit in the cavity.

Titrations of **1** (1 mM) with Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+} in $CDCl_3/CD_3CN$ (6 : 4 vol/vol) were monitored by ^1H NMR. In each case, a new set of sharp signals emerged indicating the formation of a metal complex in slow exchange on the NMR timescale

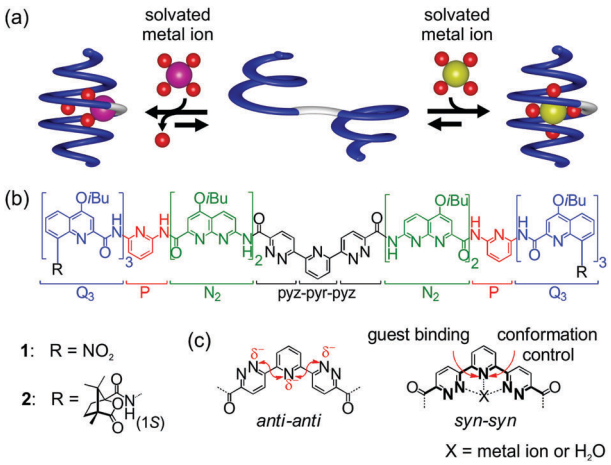


Fig. 1 (a) Schematic representation of metal-induced folding modes of a helical-capsule: first-sphere coordination (left) and second-sphere coordination (right). (b) Formula of aromatic oligoamide sequences **1** and **2**. Q, N, P, pyz and pyr stand for 8-amino-2-quinolinecarboxylic acid, 7-amino-1,8-naphthyridine-2-carboxylic acid, 2,6-diaminopyridine, pyridazine and pyridine monomers, respectively. (c) Preferred conformations of pyz–pyr–pyz in the free form and in the presence of a guest.

[a] *Univ. Bordeaux and CNRS, CBMN (UMR 5248), IECB, 2 rue Robert Escarpit, F-33600 Pessac, France. E-mail: i.huc@iecb.u-bordeaux.fr*

[b] *Department of Chemical Technology of Drugs, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznan, Poland*

† Electronic supplementary information (ESI) available: Synthetic procedures and characterisation of **2** and of the metal complexes of **1**; procedures for titrations and crystallographic experiments. CCDC 1561023 (**1**⊃Na^{2+}), 1561024 (**1**⊃K^+), 1561025 (**1**⊃Ca^{2+}) and 1561026 (**1**⊃Ba^{2+}). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc05422j

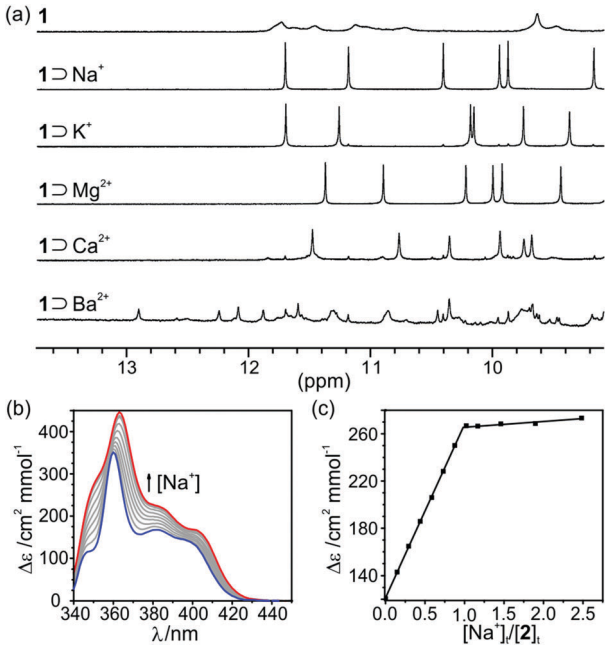


Fig. 2 (a) Excerpts from the 400 MHz ^{1}H NMR spectra showing the amide resonances of capsule **1** at 1 mM in $CDCl_3/CD_3CN$ (6 : 4 vol/vol) upon binding metal ions. (b) CD spectra recorded at 298 K for the binding of Na^+ by capsule **2** in $CHCl_3$/MeCN (6 : 4 vol/vol). $[\mathbf{2}]_{initial}$ = 0.030 mM, $[NaOTf]_{titrant}$ = 0.80 mM; (c) plot of $\Delta\varepsilon$ *vs.* equiv. of Na^+ at 350 nm. $K_a > 10^7$ M^{-1}.

with uncomplexed **1** (Fig. 2a and Fig. S6–S10 in the ESI†). Saturation was reached at 1 equiv. of metal ion, showing that binding is too strong ($K_a > 10^5$ M^{-1}) to be accurately determined by this technique. Complexes with Na^+, K^+, Mg^{2+} and Ca^{2+} display six amide N*H* signals consistent with the conservation of the average C_2 symmetry of the helix. In contrast, the Ba^{2+} complex displays many more signals and these signals span a wider chemical shift range, indicating a loss of symmetry of the complex and the possible coexistence of several binding modes. Signals found at lower fields (>12 ppm) mark weaker ring current effects associated with aromatic stacking and thus a possible perturbation of the helical structure.

Further titrations were monitored by CD spectroscopy using **2** (0.03 mM) in $CDCl_3/CD_3CN$ (6 : 4 vol/vol). This sequence is equipped with terminal (1*S*)-(−)-camphanyl groups (Fig. 1b) that quantitatively induce *P* helicity.[7] The Q_3PN_2 segments of **2** should thus both be *P*-helical regardless of the conformation of the central pyz–pyr–pyz and give rise to a positive CD band in the 350–400 nm region.[8] Yet the *anti–anti* to *syn–syn* conformational change induced by the metal ion was found to be associated with a substantial increase of the molar ellipticity (Fig. 2b, c and Fig. S1–S5 in the ESI†) as the *syn–syn* conformer also contributes to the *P*-helicity. Saturation was again reached near 1 equiv. of guest. It was nevertheless possible to accurately determine K_a values for Ba^{2+} and K^+. For Na^+, Mg^{2+} and Ca^{2+} K_a values are so high that they cannot be calculated directly, but they could be determined in ^{1}H NMR competition experiments (Fig. S11–S13 in the ESI†). The results, compiled in Table 1, showed the binding trend $Ba^{2+} < K^+ \ll Ca^{2+} \approx Na^+ \ll Mg^{2+}$.

Table 1 Thermodynamic data for metal ion binding

	$Na^{+\,a}$	$K^{+\,b}$	$Mg^{2+\,a}$	$Ca^{2+\,a}$	$Ba^{2+\,b}$
$\log K_a$	8.51(5)	6.08(1)	11.16(5)	8.29(5)	5.53(1)
$R_{ion}{}^c$/Å	1.09	1.50	0.76	1.12	1.48
$d_{ion\text{-}water}{}^c$/Å	2.43	2.84	2.10	2.46	2.82
V^d/Å^3	60	96	39	62	93

[a] Determined by competition titration by ^{1}H NMR (400 MHz) at 298 K and in $CDCl_3/CD_3CN$ (6 : 4 vol/vol) using capsule **1**. [b] Determined by CD at 298 K and in $CHCl_3$/MeCN (6 : 4 vol/vol) using capsule **2**. [c] From ref. 12. [d] Calculated using $d_{ion\text{-}water}$ as the radius of the sphere.

Quite remarkably the capsule is extremely selective for Mg^{2+}, displaying a 450 fold selectivity over the second best bound guest Na^+.

A ^{1}H NMR competition experiment was set up to better demonstrate selective Mg^{2+} binding (Fig. 3). A sample of sequence **1** was prepared in $CDCl_3/CD_3CN$ (6 : 4 vol/vol) mixture in an NMR tube to which Ba^{2+} and K^+ (1 equiv. each) were added (Fig. 3a). The spectrum then clearly shows preferential binding of K^+ over Ba^{2+}. Upon adding Ca^{2+} (1 equiv.) to the same NMR tube, the spectrum shows that this metal ion displaces Ba^{2+} and most of K^+ (Fig. 3b). The further addition of Na^+ (1 equiv.) led to the disappearance of $\mathbf{1}\supset K^+$ and to the coexistence of $\mathbf{1}\supset Na^+$ and $\mathbf{1}\supset Ca^{2+}$ which have similar stability (Fig. 3c). Finally, Mg^{2+} (1 equiv.) quantitatively displaced all other metal ions to produce $\mathbf{1}\supset Mg^{2+}$ (Fig. 3d).

For most applications, discrimination from Ca^{2+} is the major difficulty in the design of Mg^{2+} ionophores.[9] The selective binding of magnesium over calcium by capsule **1** (K^{Mg}/K^{Ca} = 740) is thus remarkable. Among the numerous examples of Mg^{2+} ionophores reported in the literature,[10] it appears that only one surpasses capsule **1** and does not bind calcium.[11] Also noteworthy is the fact that **1** prefers Mg^{2+} over transition metals Cu^+ and Zn^{2+} (Fig. S14 and S15 in the ESI†).

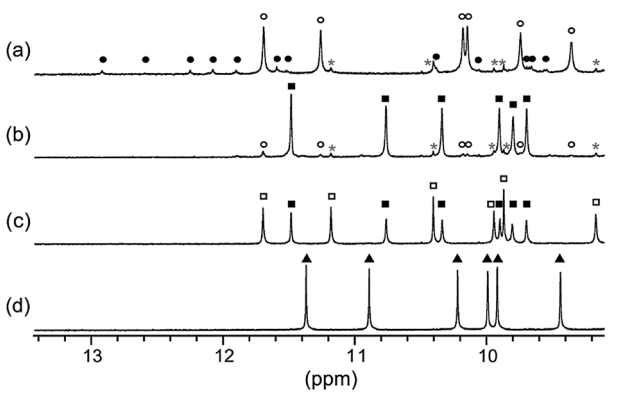


Fig. 3 Part of the ^{1}H NMR spectrum (400 MHz) at 298 K of a sample of capsule **1** (1 mM) in $CDCl_3/CD_3CN$ (6 : 4 vol/vol) showing the respective amide resonances change upon sequentially adding each metal ion to the same sample: (a) Ba(OTf)$_2$:KOTf 1 equiv. each; (b) plus one equiv. Ca(OTf)$_2$; (c) plus one equiv. NaOTf (d) plus one equiv. Mg(OTf)$_2$. Signals of the $\mathbf{1}\supset Ba^{2+}$, $\mathbf{1}\supset K^+$, $\mathbf{1}\supset Ca^{2+}$, $\mathbf{1}\supset Na^+$ and $\mathbf{1}\supset Mg^{2+}$ complexes are marked with filled circle, empty circle, filled square, empty square and filled triangle, respectively. Peaks corresponding to the $\mathbf{1}\supset Na^+$ complex are denoted as grey stars. Note: peaks corresponding to the $\mathbf{1}\supset Na^+$ complex are present in spectra (a) and (b) even though no Na^+ was added, as this metal ion is a well-known, ubiquitous, contaminant of, for instance, glassware.

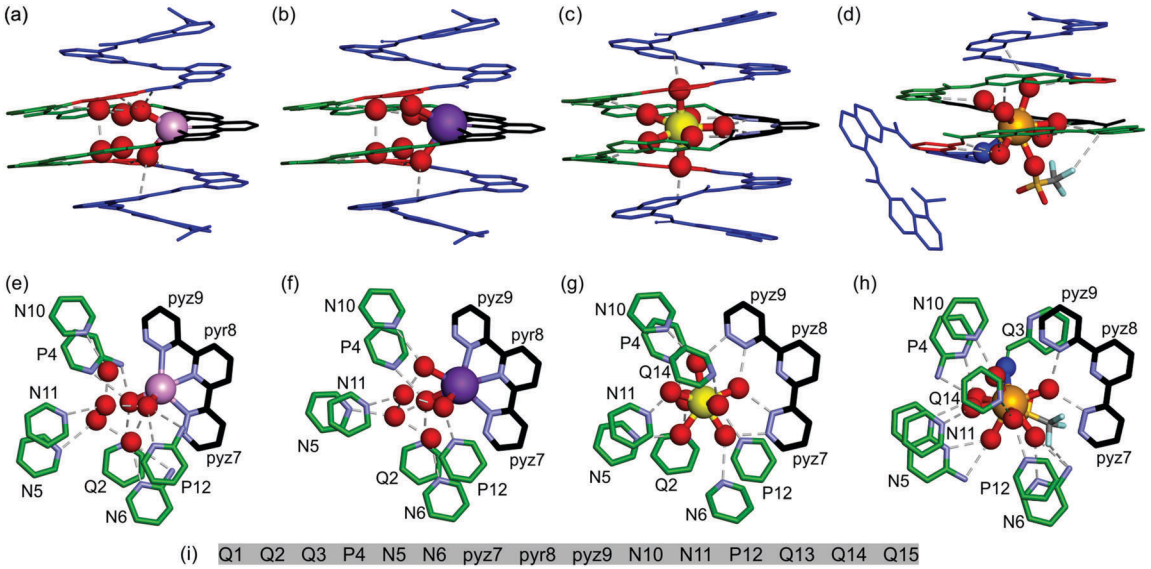


Fig. 4 Solid-state structures of complexes formed between capsule *P*-1 and (a) $[Na(H_2O)_2]^+$; (b) $[K(H_2O)_3]^+$; (c) $[Ca(H_2O)_7]^{2+}$ and (d) $[Ba(H_2O)_7]^{2+}$. Top view of the complexes of *P*-1 with (e) $[Na(H_2O)_2]^+$; (f) $[K(H_2O)_3]^+$; (g) $[Ca(H_2O)_7]^{2+}$ and (h) $[Ba(H_2O)_7]^{2+}$, showing the heterocycles that interact with the metal ions and water molecules. Dashed lines indicate hydrogen bonds. Hydrogen bonding distances can be found in the Tables S3, S6, S9 and S12 (ESI†). (i) Numbering of the units of sequence **1** used in this figure. Isobutoxy side chains and cavity-excluded solvent molecules and counterions are omitted for clarity. The capsule backbone is represented in sticks. Sodium, potassium, calcium and barium atoms are represented in pink, purple, yellow and orange scaled balls, respectively. Oxygen atoms of water molecules are depicted as red balls. Blue ball in (d) and (h) represents a carbonyl oxygen atom.

Crystallographic studies were undertaken to gain further insights into the recognition modes (Fig. 4). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into solutions of the $\mathbf{1}\supset Na^+$, $\mathbf{1}\supset K^+$, $\mathbf{1}\supset Ca^{2+}$ and $\mathbf{1}\supset Ba^{2+}$ complexes. Despite the stability of $\mathbf{1}\supset Mg^{2+}$, crystals were not obtained under these conditions and attempts using different magnesium salts or solvent systems also failed. The crystal structures of $\mathbf{1}\supset Na^+$ and $\mathbf{1}\supset K^+$ (Fig. 4a and b), revealed tridentate coordination of the pyz–pyr–pyz unit to the metal ions (see also Fig. S16 and S17 in the ESI†). Sodium displays shorter nitrogen–metal distances than potassium (2.586(8), 2.625(8) and 2.701(8) Å for Na^+ and 2.747(9), 3.031(10) and 3.119(8) Å for K^+) consistent with its higher association constant. In both cases the metal ions keep part of their water of solvation (two water molecules in the case of Na^+ and three in the case of K^+). These coordinated water molecules establish hydrogen bonds with endocyclic nitrogen atoms of the capsule inner wall, *i.e.* second coordination sphere interactions, contributing to stabilize the complex and the helical structure. Additional water molecules occupy the remaining space and hydrogen bond to both the capsule and the complex. Interestingly, the number and positions of these water molecules are similar for $\mathbf{1}\supset Na^+$ and $\mathbf{1}\supset K^+$.

The crystal structure of $\mathbf{1}\supset Ca^{2+}$ (Fig. 4c) showed an encapsulated calcium ion fully surrounded by water molecules. Here the cation is bound through second-sphere coordination only, with the seven water molecules of its hydration shell establishing hydrogen bonds with the capsule. One water molecule was found to hydrogen bond to the pyz–pyr–pyz unit and to occupy the position where metal ions are found when they directly coordinate to nitrogen atoms (see Fig. S18, ESI†). This water presumably stabilizes the *syn–syn* conformation, and contributes to helical folding. In the absence of structure, we can only speculate that Mg^{2+} is bound in a way similar to Ca^{2+}.

The crystal structure of the $\mathbf{1}\supset Ba^{2+}$ complex revealed an unexpected unfolding pattern with one terminal Q_3 cap flipped away from the helix, allowing the Ba^{2+}-triflate ion pair to protrude out of the cavity (Fig. 4d). Capsule opening occurs most likely because the hydrated barium is too voluminous to fit in the closed cavity. The local disruption of the helix to accommodate Ba^{2+} must have a high enthalpic price and illustrates the avidity of the capsule inner wall for these metal hydrates. Nevertheless, the conformational penalty results in weaker binding for Ba^{2+}. As for Ca^{2+}, Ba^{2+} does not directly coordinate to the pyz–pyr–pyz unit but interacts through a water molecule (Fig. S19, ESI†). Binding is thus mostly through second-sphere coordination but for one carbonyl oxygen atom of a Q–P amide bond that coordinates directly to the metal. A triflate completes the first coordination sphere. An anion is found in the crystal lattice, *i.e.* not coordinating the metal, in the structure of the Na^+ and K^+ complexes. For the Ca^{2+} complex, negative charges are borne by water molecules and no triflate is found in the unit cell.

The prime role of second-sphere coordination, *i.e.* hydrogen bonds, to encapsulate Ca^{2+} and Ba^{2+} called for additional experiments to test the stability of these complexes in presence of a solvent that competes for hydrogen bonding. Adding 5% DMSO-d_6 (vol/vol) to the complexes leads to release of Mg^{2+}, Ca^{2+} and Ba^{2+}, while Na^+ and K^+ remain bound even in the presence of 30% DMSO-d_6. This is fully consistent with the binding modes found in the crystal structures. Only when first-sphere coordination to pyz–pyr–pyz is involved does the complex resist the presence of DMSO. In contrast, the binding mode of the metal hydrates of Mg^{2+}, Ca^{2+} and Ba^{2+} resembles that of organic hydroxy acids and of monosaccharides.[3i–k]

This investigation thus expands the scope of molecular recognition by aromatic helical foldamers, in particular with respect to metal binding *via* second-sphere coordination and with respect to the reported high selectivity for magnesium.

This work was supported by the European Union (H2020-MSCA-IF-2015-707071-RAMSES, post-doctoral fellowship to P. M.) and benefited from the facilities and expertise of the Biophysical and Structural Chemistry platform at IECB, CNRS UMS3033, INSERM US001, Bordeaux University, France.

Notes and references

1 Reviews: (*a*) H. Juwarker, J.-m. Suk and K.-S. Jeong, *Chem. Soc. Rev.*, 2009, **38**, 3316; (*b*) I. Saraogia and A. D. Hamilton, *Chem. Soc. Rev.*, 2009, **38**, 1726; (*c*) B.-B. Ni, Q. Yan, Y. Ma and D. Zhao, *Coord. Chem. Rev.*, 2010, **254**, 954; (*d*) K. Yamato, M. Kline and B. Gong, *Chem. Commun.*, 2012, **48**, 12142; (*e*) D.-W. Zhang, X. Zhao and Z.-T. Li, *Acc. Chem. Res.*, 2014, **47**, 1961.

2 For recognition of rod-like guests see: (*a*) A. Tanatani, M. J. Mio and J. S. Moore, *J. Am. Chem. Soc.*, 2001, **123**, 1792; (*b*) T. Nishinaga, A. Tanatani, K. Oh and J. S. Moore, *J. Am. Chem. Soc.*, 2002, **124**, 5934; (*c*) A. Tanatani, T. S. Hughes and J. S. Moore, *Angew. Chem., Int. Ed.*, 2002, **41**, 325; (*d*) Q. Gan, Y. Ferrand, C. Bao, B. Kauffmann, A. Grelard, H. Jiang and I. Huc, *Science*, 2011, **331**, 1172; (*e*) Q. Gan, Y. Ferrand, N. Chandramouli, B. Kauffmann, C. Aube, D. Dubreuil and I. Huc, *J. Am. Chem. Soc.*, 2012, **134**, 15656; (*f*) Q. Gan, X. Wang, B. Kauffmann, F. Rosu, Y. Ferrand and I. Huc, *Nat. Nanotechnol.*, 2017, **12**, 447.

3 Neutral guest recognition: (*a*) V. Berl, M. J. Krische, I. Huc, J.-M. Lehn and M. Schmutz, *Chem. – Eur. J.*, 2000, **6**, 1938; (*b*) J.-L. Hou, X.-B. Shao, G.-J. Chen, Y.-X. Zhou, X.-K. Jiang and Z.-T. Li, *J. Am. Chem. Soc.*, 2004, **126**, 12386; (*c*) M. Inouye, M. Waki and H. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 2022; (*d*) H. Abe, H. Machiguchi, S. Matsumoto and M. Inouye, *J. Org. Chem.*, 2008, **73**, 4650; (*e*) C. Li, G.-T. Wang, H.-P. Yi, X.-K. Jiang, Z.-T. Li and R.-X. Wang, *Org. Lett.*, 2007, **9**, 1797; (*f*) M. Waki, H. Abe and M. Inouye, *Angew. Chem., Int. Ed.*, 2007, **46**, 3059; (*g*) C. Bao, B. Kauffmann, Q. Gan, K. Srinivas, H. Jiang and I. Huc, *Angew. Chem., Int. Ed.*, 2008, **47**, 4153; (*h*) J. Garric, J.-M. Léger and I. Huc, *Angew. Chem., Int. Ed.*, 2005, **44**, 1954; (*i*) Y. Ferrand, A. M. Kendhale, B. Kauffmann, A. Grélard, C. Marie, V. Blot, M. Pipelier, D. Dubreuil and I. Huc, *J. Am. Chem. Soc.*, 2010, **132**, 7858; (*j*) G. Lautrette, B. Wicher, B. Kauffmann, Y. Ferrand and I. Huc, *J. Am. Chem. Soc.*, 2016, **138**, 10314; (*k*) N. Chandramouli, Y. Ferrand, G. Lautrette, B. Kauffmann, C. D. Mackereth, M. Laguerre, D. Dubreuil and I. Huc, *Nat. Chem.*, 2015, **7**, 334; (*l*) H. Q. Zhao, S. Sheng, Y. H. Hong and H. Q. Zeng, *J. Am. Chem. Soc.*, 2014, **136**, 14270; (*m*) H.-G. Jeon, J. Y. Jung, P. Kang, M.-G. Choi and K.-S. Jeong, *J. Am. Chem. Soc.*, 2016, **138**, 92.

4 Cation recognition: (*a*) R. B. Prince, T. Okada and J. S. Moore, *Angew. Chem., Int. Ed.*, 1999, **38**, 233; (*b*) A. Petitjean, L. A. Cuccia, J.-M. Lehn, H. Nierengarten and M. Schmutz, *Angew. Chem., Int. Ed.*, 2002, **41**, 1195; (*c*) Y. Zhao and Z. Zhong, *J. Am. Chem. Soc.*, 2006, **128**, 9988; (*d*) Z. Zhong and Y. Zhao, *Org. Lett.*, 2007, **9**, 2891; (*e*) K. Yamato, L. H. Yuan, W. Feng, A. J. Helsel, A. R. Sanford, J. Zhu, J. G. Deng, X. C. Zeng and B. Gong, *Org. Biomol. Chem.*, 2009, **7**, 3643; (*f*) J.-m. Suk, V. R. Naidu, X. Liu, M. S. Lah and K.-S. Jeong, *J. Am. Chem. Soc.*, 2011, **133**, 13938; (*g*) J. Shen, C. Ren and H. Zeng, *J. Am. Chem. Soc.*, 2017, **139**, 5387.

5 Anion recognition: (*a*) K.-J. Chang, B.-N. Kang, M.-H. Lee and K.-S. Jeong, *J. Am. Chem. Soc.*, 2005, **127**, 12214; (*b*) R. M. Meudtner and S. Hecht, *Angew. Chem., Int. Ed.*, 2008, **47**, 4926; (*c*) H. Juwarker, J. M. Lenhardt, D. M. Pham and S. L. Craig, *Angew. Chem., Int. Ed.*, 2008, **47**, 3740; (*d*) Y. Hua and A. H. Flood, *J. Am. Chem. Soc.*, 2010, **132**, 12838; (*e*) Y. Wang, F. Bie and H. Jiang, *Org. Lett.*, 2010, **12**, 3630; (*f*) Y. Hua, Y. Liu, C.-H. Chen and A. H. Flood, *J. Am. Chem. Soc.*, 2013, **135**, 14401; (*g*) A. L. Connor, T. Hu, C. S. F. Detchou, R. Liu, S. V. S. R. K. Pulavarti, T. Szyperski, Z. Lu and B. Gong, *Chem. Commun.*, 2016, **52**, 9905.

6 M. Horeau, G. Lautrette, B. Wicher, V. Blot, J. Lebreton, M. Pipelier, D. Dubreuil, Y. Ferrand and I. Huc, *Angew. Chem., Int. Ed.*, 2017, **56**, 6823.

7 A. M. Kendhale, L. Poniman, Z. Dong, K. Laxmi-Reddy, B. Kauffmann, Y. Ferrand and I. Huc, *J. Org. Chem.*, 2011, **76**, 195.

8 Y. Ferrand, N. Chandramouli, A. M. Kendhale, C. Aube, B. Kauffmann, A. Grélard, M. Laguerre, D. Dubreuil and I. Huc, *J. Am. Chem. Soc.*, 2012, **134**, 11282.

9 (*a*) P. Bühlmann, E. Pretsch and E. Bakker, *Chem. Rev.*, 1998, **98**, 1593; (*b*) G. R. C. Hamilton, S. K. Sahoo, S. Kamila, N. Singh, N. Kaur, B. W. Hylanda and J. F. Callan, *Chem. Soc. Rev.*, 2015, **44**, 4415.

10 (*a*) A. V. Bordunov, J. S. Bradshaw, X. X. Zhang, N. K. Dalley, X. Kou and R. M. Izatt, *Inorg. Chem.*, 1996, **35**, 7229; (*b*) Y. Suzuki, H. Komatsu, T. Ikeda, N. Saito, S. Araki, D. Citterio, H. Hisamoto, Y. Kitamura, T. Kubota, J. Nakagawa, K. Oka and K. Suzuki, *Anal. Chem.*, 2002, **74**, 1423; (*c*) T. Shoda, K. Kikuchi, H. Kojima, Y. Urano, H. Komatsu, K. Suzuki and T. Nagano, *Analyst*, 2003, **128**, 719; (*d*) Q.-Z. Yang, L.-Z. Wu, H. Zhang, B. Chen, Z.-X. Wu, L.-P. Zhang and C.-H. Tung, *Inorg. Chem.*, 2004, **43**, 5195; (*e*) H. Komatsu, N. Iwasawa, D. Citterio, Y. Suzuki, T. Kubota, K. Tokuno, Y. Kitamura, K. Oka and K. Suzuki, *J. Am. Chem. Soc.*, 2004, **126**, 16353; (*f*) G. Farruggia, S. Iotti, L. Prodi, M. Montalti, Ne. Zaccheroni, P. B. Savage, V. Trapani, P. Sale and F. I. Wolf, *J. Am. Chem. Soc.*, 2006, **128**, 344; (*g*) H. M. Kim, P. R. Yang, M. S. Seo, J.-S. Yi, J. H. Hong, S.-J. Jeon, Y.-G. Ko, K. J. Lee and B. R. Cho, *J. Org. Chem.*, 2007, **72**, 2088; (*h*) J. Kim, T. Morozumi and H. Nakamura, *Org. Lett.*, 2007, **9**, 4419; (*i*) H. Hama, T. Morozumi and H. Nakamura, *Tetrahedron Lett.*, 2007, **48**, 1859; (*j*) D. Ray and P. K. Bharadwaj, *Inorg. Chem.*, 2008, **47**, 2252; (*k*) M. Ishida, Y. Naruta and F. Tani, *Angew. Chem., Int. Ed.*, 2010, **49**, 91; (*l*) Y. Ma, H. Liu, S. Liua and R. Yang, *Analyst*, 2012, **137**, 2313; (*m*) R. Alam, T. Mistri, A. Katarkar, K. Chaudhuri, S. K. Mandal, A. R. Khuda-Bukhsh, K. K. Dasa and M. Ali, *Analyst*, 2014, **139**, 4022; (*n*) P. S. Hariharan and S. P. Anthony, *RSC Adv.*, 2014, **4**, 41565; (*o*) A. Pandey, A. Kumar, S. Vishwakarma and K. K. Upadhyay, *RSC Adv.*, 2016, **6**, 6724.

11 S. Watanabe, S. Ikishima, T. Matsuo and K. Yoshida, *J. Am. Chem. Soc.*, 2001, **123**, 8402.

12 I. Persson, *Pure Appl. Chem.*, 2010, **82**, 1901.