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

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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 Mg²⁺. 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.^{3g-k,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 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⁺, Mg²⁺, Ca²⁺ and Ba²⁺ all bind to **1** and induce its folding in a helix; outstanding affinity and selectivity for Mg²⁺ was observed. The hydration sphere of the metals is essential to the binding process to such an extent that, in the case of Mg²⁺, Ca²⁺ and Ba²⁺ 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⁺, Mg²⁺, Ca²⁺ and Ba²⁺ in CDCl₃/CD₃CN (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 with uncomplexed **1** (Fig. 2a and Figs. S6-10 in the

ESI). Saturation was reached at 1 equiv. of metal ion, showing that binding is too strong ($K_a > 10^5 \text{ M}^{-1}$) to be accurately determined by this technique. Complexes with Na⁺, K⁺, Mg²⁺ and Ca²⁺ display six amide NH signals consistent with the conservation of the average C₂ symmetry of the helix. In contrast, the Ba²⁺ complex displays many more signals that span over 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.

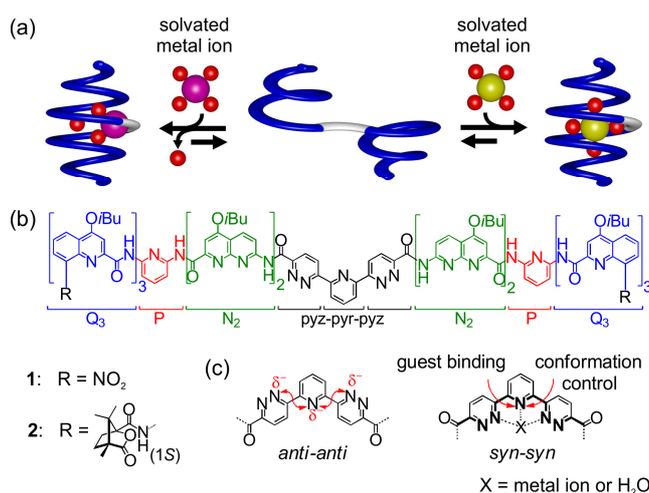


Fig. 1 (a) Schematic representation of metal-induced folding modes of a helical capsule: first-sphere coordination (left) and second-sphere coordination (right). (b) Formula of aromatic oligoamide sequences **1** and **2**. Q, N, P, pyz and pyr stand for 8-amino-2-quinolinecarboxylic acid, 7-amino-1,8-naphthyridine-2-carboxylic 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.

Further titrations were monitored by CD spectroscopy using **2** (0.03 mM) in CDCl₃/CD₃CN (6:4 vol/vol). This sequence is equipped with terminal (1S)-(-)-camphanyl groups (Fig. 1b) that quantitatively induce *P* helicity.⁷ The Q₃PN₂ 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 Figs. S1-5 in the ESI) as the *syn-syn*

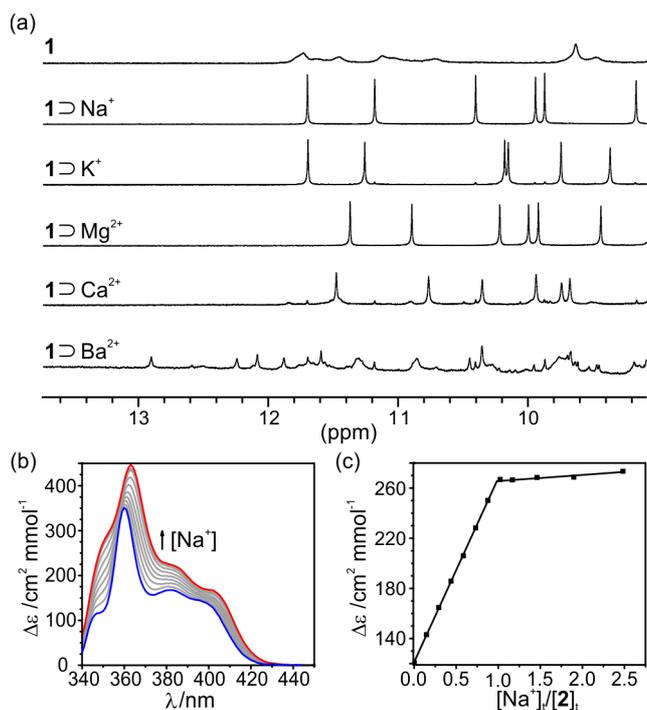


Fig. 2 (a) Excerpts from the 400 MHz ^1H NMR spectra showing the amide resonances of capsule **1** at 1 mM in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (6:4 vol/vol) upon binding metal ions. (b) CD spectra recorded at 298 K for the binding of Na^+ by capsule **2** in $\text{CHCl}_3/\text{MeCN}$ (6:4 vol/vol). $[\mathbf{2}]_{\text{initial}} = 0.030$ mM, $[\text{NaOTf}]_{\text{titrant}} = 0.80$ mM; (c) Plot of $\Delta\epsilon$ vs equiv. of Na^+ at 350 nm. $K_a > 10^7$ M^{-1} .

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 ^1H NMR competition experiments (Figs. S11-13 in the ESI). The results, compiled in Table 1, showed the binding trend $\text{Ba}^{2+} < \text{K}^+ \ll \text{Ca}^{2+} \approx \text{Na}^+ \ll \text{Mg}^{2+}$. Quite remarkably the capsule is extremely selective for Mg^{2+} , displaying a 450 fold selectivity over the second best bound guest Na^+ .

A ^1H NMR competition experiment was set up to better demonstrate selective Mg^{2+} binding (Fig. 3). A sample of sequence **1** was prepared in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (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 1Ca^{2+} and to the coexistence of 1Na^+ and 1Ca^{2+} which have similar stability (Fig. 3c). Finally, Mg^{2+} (1 equiv.) quantitatively displaced all other metal ions to produce 1Mg^{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** ($K^{\text{Mg}}/K^{\text{Ca}} = 740$) 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+} . (Figs. S14 and S15 in the ESI).

Table 1 Thermodynamic data for metal ion binding.

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

^a Determined by competition titration by ^1H NMR (400 MHz) at 298 K and in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (6:4 vol/vol) using capsule **1**; ^b determined by CD at 298 K and in $\text{CHCl}_3/\text{MeCN}$ (6:4 vol/vol) using capsule **2**; ^c from ref. 12; ^d calculated using $d_{\text{ion-water}}$ as the radius of the sphere.

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 1Na^+ , 1K^+ , 1Ca^{2+} and 1Ba^{2+} complexes. Despite the stability of 1Mg^{2+} , crystals were not obtained under these conditions and attempts using different magnesium salts or solvent systems also failed. The crystal structures of 1Na^+ and 1K^+ (Fig. 4a,b), revealed tridentate coordination of the pyz-pyr-pyz unit to the metal ions (see also Figs. S16 and S17 in the ESI). Sodium displays shorter nitrogen-metal distances than potassium (2.586(8), 2.625(8) and 2.701(8) \AA for Na^+ and 2.747(9), 3.031(10) and 3.119(8) \AA 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

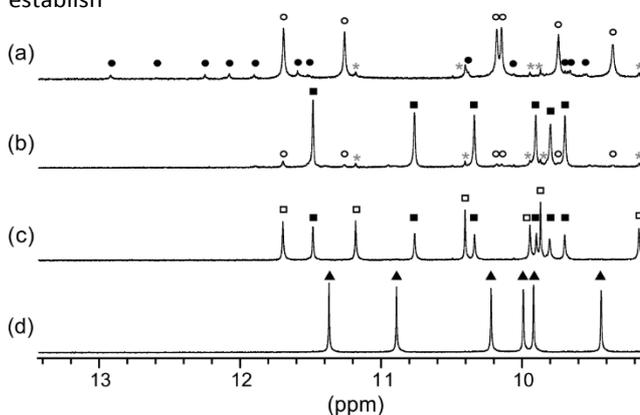


Fig. 3 Part of the ^1H NMR spectrum (400 MHz) at 298 K of a sample of capsule **1** (1 mM) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (6:4 vol/vol) showing the respective amide resonances change upon sequentially adding each metal ion to the same sample: (a) $\text{Ba}(\text{OTf})_2:\text{KOTf}$ 1 equiv. each; (b) plus one equiv. $\text{Ca}(\text{OTf})_2$; (c) plus one equiv. NaOTf (d) plus one equiv. $\text{Mg}(\text{OTf})_2$. Signals of the 1Ba^{2+} , 1K^+ , 1Ca^{2+} , 1Na^+ and 1Mg^{2+} complexes are marked with filled circle, empty circle, filled square, empty square and filled triangle, respectively. Peaks corresponding to the 1Na^+ complex are denoted as grey stars. Note: Peaks corresponding to the 1Na^+ 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.

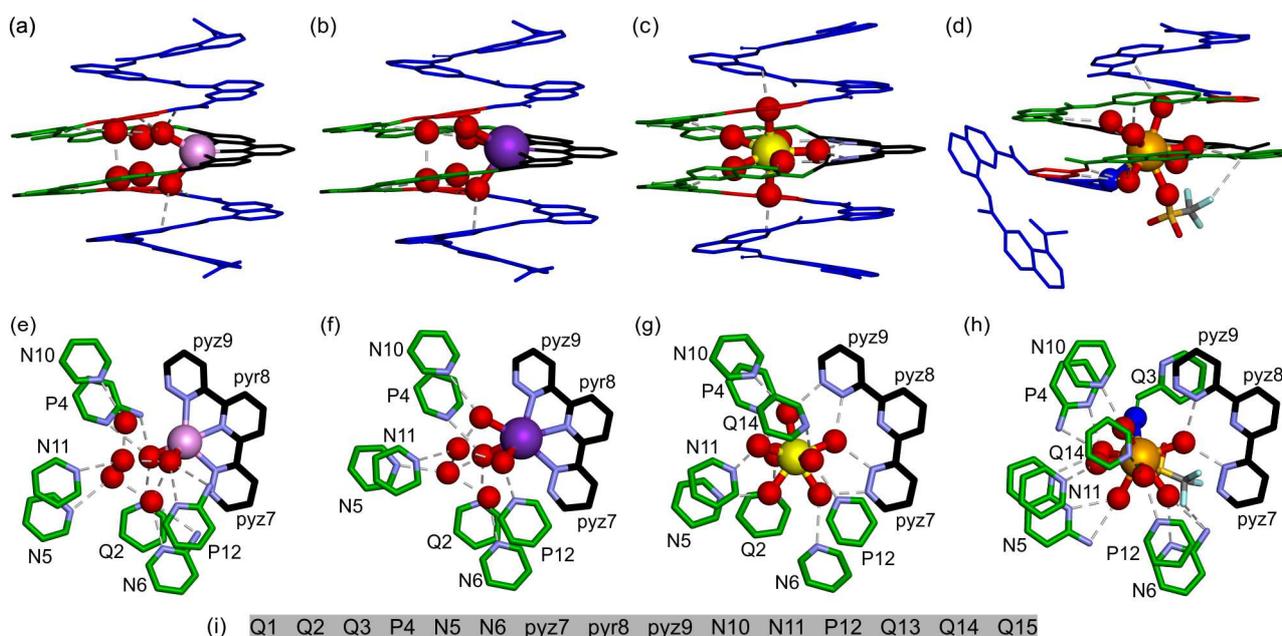


Fig. 4 Solid-state structures of complexes formed between capsule **P-1** and (a) $[\text{Na}(\text{H}_2\text{O})_2]^+$; (b) $[\text{K}(\text{H}_2\text{O})_3]^+$; (c) $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$ and (d) $[\text{Ba}(\text{H}_2\text{O})_7]^{2+}$. Top view of the complexes of **P-1** with (e) $[\text{Na}(\text{H}_2\text{O})_2]^+$; (f) $[\text{K}(\text{H}_2\text{O})_3]^+$; (g) $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$ and (h) $[\text{Ba}(\text{H}_2\text{O})_7]^{2+}$, 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 Supplementary Tables S3, S6, S9 and S12. (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.

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 1DNa^+ and 1DK^+ .

The crystal structure of 1DCa^{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). 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 way similar to Ca^{2+} .

The crystal structure of the 1DBa^{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). 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. It is the only

anion observed coordinating the metal ion among all four structures, indicating that in most cases, negative charges are borne by water molecules.

The prime role of second-sphere coordination, i.e. hydrogen bonds, to encapsulate Ca^{2+} and Ba^{2+} called for additional experiments to tests 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.

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