An Expansible Metalla-cryptand as a Component of a Supramolecular Combinatorial Library Formed from Di(8-hydroxyquinoline) Ligands and Gallium(III) or Zinc(II) Ions

Markus Albrecht,*[a] Oliver Blau,[a] and Roland Fröhlich[b]

Abstract: Ethylene-bridged di(8-hydroxyquinoline) ligands **1a–c-H$_2$** can be synthesized in five-step procedures from the corresponding 8-hydroxyquinolines. X-ray structural analysis shows that **1a-H$_2$** in the solid state forms a polymer by hydrogen bonding. When the ligands **1a–c-H$_2$** are mixed with gallium(III) ions, a mixture (supramolecular combinatorial library) is formed of coordination compounds $\{(\mathbf{1a-c})_3Ga_2\}_n$ which by addition of appropriate guests ($M^+ = Na^+$, K^+, NH_4^+, Rb^+) can be transformed quantitatively into a defined metalla-cryptate $[M \subset \{(\mathbf{1a-c})_3Ga_2\}]^+$. Those complexes and the corresponding zinc cryptates $[M' \subset \{(\mathbf{1a})_3Zn_2\}]^-$ ($M'^+ = Li^+$, Na^+, K^+) can also be obtained directly in metal-directed self-assembly processes in the presence of templates. ^{1}H NMR studies and the solid-state structures of $[K/Na \subset \{(\mathbf{1a})_3Ga_2\}]^+$ show that the metalla-cryptand $\{(\mathbf{1a})_3Ga_2\}$ can adjust to the size of the guest present. Thus proton H(2) of the ligand acts as a ^{1}H NMR spectroscopic probe to predict the size of the cryptate in solution.

Keywords: cryptands · gallium · helical structures · host–guest chemistry · zinc

Introduction

Cryptands are polycyclic receptor molecules which are able to bind cations in their interior to form the corresponding cryptates.[1] Metalla-cryptands possess a similar constitution and are formed in metal-directed self-assembly processes. Simple mixing of linear oligodonor ligands with appropriate metal ions can lead to the formation of the cryptand (Figure 1, Path A). This compound can bind a guest species (molecule, ion) to form the corresponding host–guest complex—the metalla-cryptate (Path B).[2–5]

It is also possible for the reaction of the ligands with the metal ions to lead to a mixture (library) of coordination compounds. In this case no selective self-assembly process takes place. However, because of the noncovalent nature of the metal coordination, all the species of this mixture are in dynamic equilibrium. Addition of a guest leads to the removal of the thermodynamically most appropriate receptor and only one metalla-cryptate is formed.[6]

If the guest is present during the self-assembly of the metalla-cryptand (Path C), the cryptate is formed directly in a template-directed self-assembly process.[7]

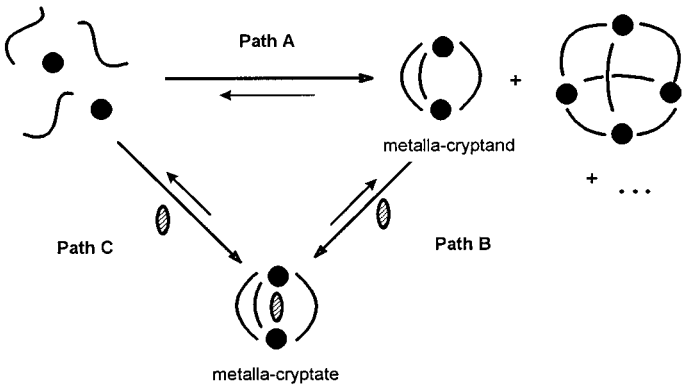

Figure 1. Schematic representation of the reaction pathways which lead to metalla-cryptates. Path A shows the formation of a mixture (supramolecular combinatorial library) of neutral coordination compounds. Addition of a template removes one species from this library in a dynamic process, and forms the thermodynamically most stable metalla-cryptate (Path B). This metalla-cryptate can also be formed directly in a template-directed self-assembly process (Path C).

Lehn et al.[8] and Saalfrank et al.[9] have described systems in which various coordination compounds could be isolated from an undefined solution mixture of complexes by addition of different templates and crystallization of the products.[10, 11]

We have already reported a helicate-type metalla-cryptate $[K \subset \{(\mathbf{1a})_3Ga_2\}]^+$ which self-assembles from three ligands **1a**, two gallium(III) ions, and potassium cations. If no alkali metal cation is present as a template, only an insoluble material, $\{(\mathbf{1a})_3Ga_2\}_n$ (n unknown), is obtained which can be trans-

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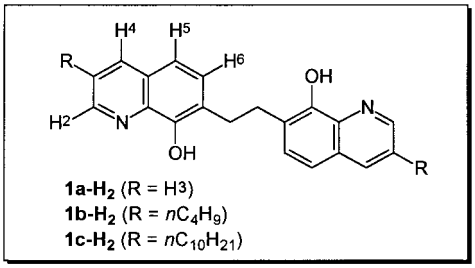
formed into $[K \subset \{(\mathbf{1a})_3Ga_2\}]Cl$ by addition of KCl.[12] To investigate the neutral species $\{\mathbf{1}_3Ga_2\}_n$ we used the 3,3′-di(*n*-butyl)- or -di(*n*-decyl)-substituted di(8-hydroxyquinoline) ligands **1b-H$_2$** or **1c-H$_2$** to form metalla-cryptands/cryptates; we also introduced zinc(II) ions for the template-directed formation of anionic cryptates $M[M \subset \{(\mathbf{1a})_3Zn_2\}]$.

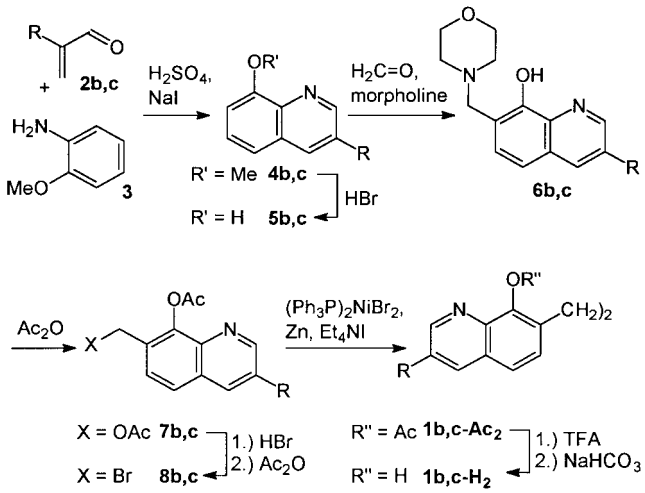
Results and Discussion

Ligand synthesis: The *n*-butyl- and *n*-decyl-substituted derivatives **1b-H$_2$** and **1c-H$_2$** were synthesized by a similar synthetic pathway to that already described for **1a-H$_2$**.[13] However, the alkyl-substituted 8-hydroxyquinolines **5b** and **5c** had to be prepared first (Scheme 1).

The quinoline derivatives **4b** and **4c** are obtained in the Skraup reaction of 2-*n*-butyl- (**2b**) or 2-*n*-decylacrolein (**2c**) with *o*-anisidine (**3**).[14] Cleavage of the methyl ethers affords the hydroxyquinolines **5b** and **5c** which by a Mannich-type reaction with morpholine and formaldehyde lead to the derivatives **6b** and **6c**. Reaction with acetic anhydride removes the morpholine substituents of **6b** and **6c** and the bisacetates **7b** and **7c** are obtained. Reaction with HBr followed by work-up with acetic anhydride transforms the benzylic acetates into the bromides **8b** and **8c**. A mild homocoupling reaction of **8b** and **8c** is performed by a procedure described by Iyoda and Oda with catalytic amounts of $(Ph_3P)_2NiBr_2$ in the presence of zinc and Et_4NI.[15] The ligand precursors **1b-Ac$_2$** and **1c-Ac$_2$** obtained are transformed by acidic hydrolysis of the esters into the ligands **1b-H$_2$** or **1c-H$_2$**, respectively.

Structure of 1a-H$_2$ in the solid state: 8-Hydroxyquinoline is a molecule which by self-recognition forms a dimer in the solid state.[16] Hydrogen bonding between OH groups and nitrogen atoms connects the two monomers and forms a central 10-membered ring. In the case of **1a-H$_2$** this hydrogen bonding cannot occur intramolecularly between the two hydroxyquinoline moieties of the molecule; it has to be intermolecular. The result of the X-ray structure analysis is shown in Figure 2.





Scheme 1.

Figure 2a shows the molecule. In the solid state **1a-H$_2$** forms an infinite linear polymer (Figure 2b).[17] Here a twisted polymeric structure is induced on a supramolecular level by hydrogen bonding between achiral monomers.[18, 19] Neighboring strands can interact in the solid state by $\pi-\pi$ stacking

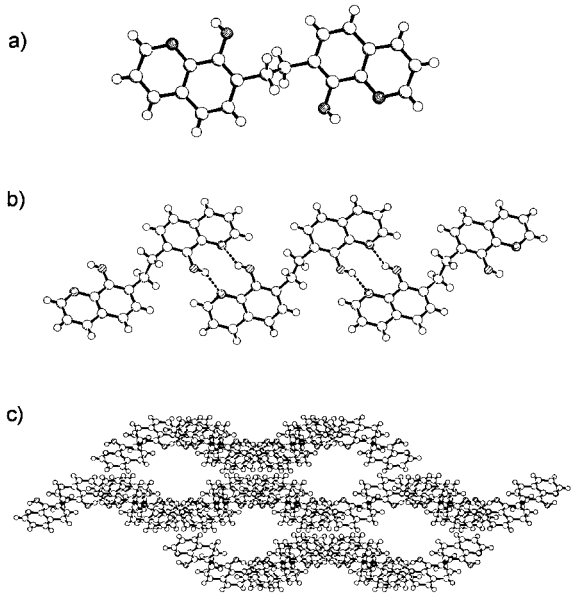


Figure 2. SCHAKAL plot of a) the monomeric ligand **1a-H$_2$**, b) the polymeric chain formed by the ligand, and c) the three-dimensional structure in the solid state.

Abstract in German: *Die ethylenverbrückten Di(8-hydroxychinolin)liganden **1a–c-H$_2$** werden ausgehend von den entsprechenden 8-Hydroxychinolinen in fünf Stufen dargestellt. Einkristalluntersuchungen zeigen, daß **1a-H$_2$** im Festkörper durch Wasserstoffbrückenbindungen eine polymere Struktur ausbildet. Reaktion von **1a–c-H$_2$** mit Gallium(III)ionen führt zu einem Gemisch von Koordinationsverbindungen $\{(\mathbf{1a\text{-}c})_3Ga_2\}_n$ (Supramolekulare Verbindungsbibliothek), die durch geeignete Gäste ($M^+ = Na^+, K^+, NH_4^+, Rb^+$) quantitativ in definierte Metallakryptate $[M \subset \{(\mathbf{1a-c})_3Ga_2\}]^+$ überführt werden. Diese Komplexe und entsprechende Zn-Kryptate $[M' \subset \{(\mathbf{1a})_3Zn_2\}]^-$ ($M'^+ = Li^+, Na^+, K^+$) können auch direkt in templatgesteuerten Selbstorganisationsprozessen erhalten werden. ^{1}H-NMR-spektroskopische und Festkörperuntersuchungen von $[K/Na \subset \{(\mathbf{1a})_3Ga_2\}]^+$ zeigen, daß der Metallakryptand $\{(\mathbf{1a})_3Ga_2\}$ seine Größe den vorhandenen Gästen anpassen kann. Das Proton H(2) des Liganden dient dabei als Sonde für die NMR-spektroskopische Untersuchung der Komplexe in Lösung.*

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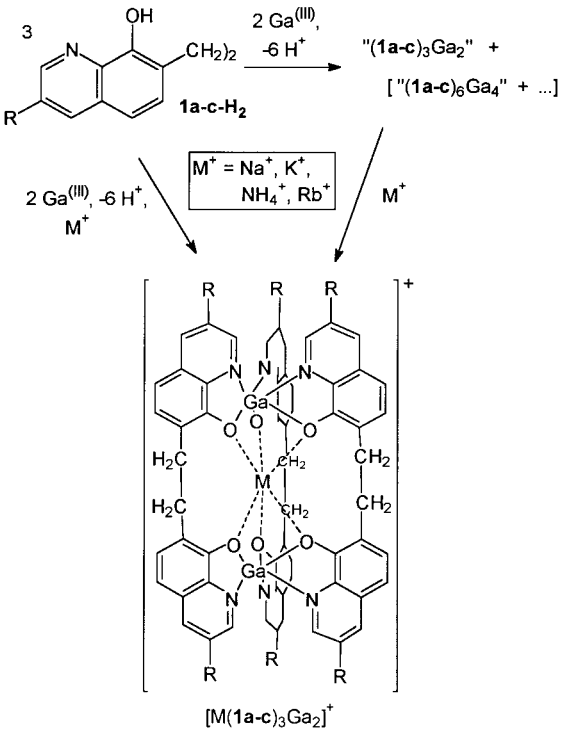
between hydroxyquinoline moieties, forming a two-dimensional network. Stapling of the planes leads to channels in the structure (Figure 2c) which contain dichloromethane molecules as guests.

Coordination studies

Formation and characterization of a supramolecular combinatorial library: Metal complexes of the general type $[(\mathbf{1a,b})_3Ga_2]$ are obtained by reaction of the ligand **1a,b-H$_2$**[20] (3 equiv) with gallium nitrate (2 equiv) in the presence of stoichiometric amounts (3 equiv) of sodium carbonate or cesium carbonate, as base, in methanol (Scheme 2). Overnight a yellow precipitate is formed in 62–99% yield. The solids obtained are insoluble in common organic solvents. Elemental analysis shows the composition of the materials to be $[(\mathbf{1})_3Ga_2]\cdot x\,H_2O$ ($x = 8$ (**1a**), 4 (**1b**)).



Scheme 2.

The $[(\mathbf{1c})_3Ga_2]$ precipitate obtained by mixing **1c-H$_2$** (3 equiv) and gallium nitrate (2 equiv) in methanol is filtered and nitric acid is removed by washing with methanol. The yellow solid is soluble in organic solvents (for example, chloroform, benzene) and can be investigated by spectroscopic methods. However, ^{1}H and ^{13}C NMR spectroscopy of $[(\mathbf{1c})_3Ga_2]$ show only broad undefined signals and indicate the presence of a mixture of various species (isomers or oligomers). MALDI-TOF (2,5-dihydroxybenzoic acid as matrix; Figure 3) and FAB$^+$ mass spectrometry (3-nitrobenzyl alcohol (3-NBA)) reveal that dinuclear (FAB: $m/z = 1947$ $[(\mathbf{1c})_3Ga_2Na]^+$) and tetranuclear gallium complexes (FAB: $m/z = 3848$ $[(\mathbf{1c})_6Ga_4]^+$) are present.[21] Coordination compounds with higher nuclearity are not observed but cannot be ruled out by our experiments. Thus, a mixture of different supramolecular coordination compounds—a supramolecular combinatorial library—is obtained.[6, 7] In comparison, for the defined complex $Na[(\mathbf{1c})_3Ga_2]^+$ only a peak at $m/z = 1947$ can be detected by MALDI-TOF- or FAB$^+$-MS.[22]

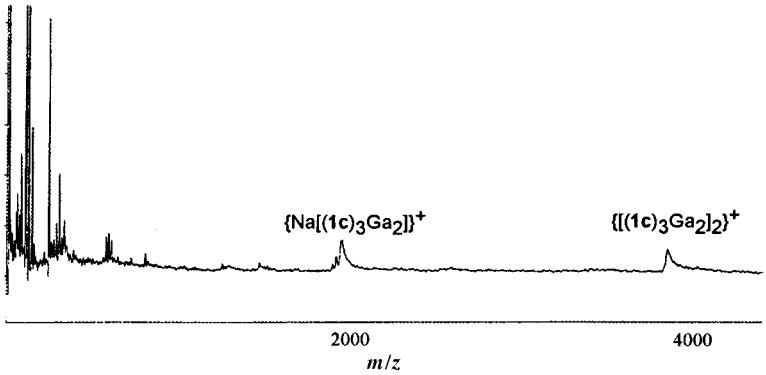


Figure 3. MALDI-TOF-MS (2,5-dihydroxybenzoic acid) of the supramolecular combinatorial library $\{(\mathbf{1c})_3Ga_2\}_n$.

Formation of metalla-cryptates M$[(\mathbf{1a-c})_3Ga_2]^+$: According to Figure 1, Path B, the metalla-cryptates $[M \subset \{(\mathbf{1})_3Ga_2\}]Cl$ are obtained by addition of MCl to the preformed libraries $\{(\mathbf{1})_3Ga_2\}_n$. The complexes $[M \subset \{(\mathbf{1a})_3Ga_2\}]Cl$ (M = Na, K) are soluble in dmso or dmf, whereas $[M \subset \{(\mathbf{1b})_3Ga_2\}]Cl$ (M = Na, K) and $[M \subset \{(\mathbf{1c})_3Ga_2\}]Cl$ (M = Na, K, Rb, NH_4) can be dissolved in $CDCl_3$ or benzene.[23]

Soluble complexes $[M \subset (\mathbf{1a-c})_3Ga_2]Cl$ (**1a**, **1b**: M = Na, K, $\{NH_4\}$; **1c**: M = Na, K, NH_4, Rb) can be obtained on a preparative scale in the template-directed self-assembly of the ligands **1a–c-H$_2$** (3 equiv) with gallium nitrate (2 equiv) in the presence of a large excess of alkali metal chloride in methanol. The corresponding ammonium salt $[(NH_4) \subset (\mathbf{1a})_3Ga_2]OAc$ is obtained by reaction of **1a-H$_2$** with gallium nitrate in the presence of a large excess of ammonium acetate in methanol. The products are precipitated and can be filtered and purified by washing with a small amount of ice–water. The compounds are characterized by NMR spectroscopy and FAB-MS. $[(NH_4) \subset (\mathbf{1a})_3Ga_2]OAc$, which has very low solubility, is characterized only by FAB-MS.

Figure 4 shows the positive FAB-MS spectra of $[M \subset (\mathbf{1a})_3Ga_2]^+$ (M = K, Na, NH_4) in 3-NBA. At high molecular masses ($m/z > 1000$) only signals of the positively charged cryptates can be detected at $m/z = 1121$ ($[K \subset (\mathbf{1a})_3Ga_2]^+$) and 1105 ($[Na \subset (\mathbf{1a})_3Ga_2]^+$), or at 1100 ($[(NH_4) \subset (\mathbf{1a})_3Ga_2]^+$). For the ammonium salt a further peak can be observed at $m/z = 1083$, which corresponds to the protonated complex $[H \subset (\mathbf{1a})_3Ga_2]^+$. Mass spectrometric results similar to those for $[M \subset (\mathbf{1a})_3Ga_2]^+$ (M = K, Na, NH_4) are obtained for the alkyl-substituted derivatives $[M \subset (\mathbf{1b,c})_3Ga_2]^+$ (M = Na, K, $\{NH_4$, Rb$\}$).

Figure 5 shows the aromatic regions of the ^{1}H NMR spectra of **1a-H$_2$**, $[K \subset \{(\mathbf{1a})_3Ga_2\}]Cl$, and $[Na \subset \{(\mathbf{1a})_3Ga_2\}]Cl$ in [D$_6$]DMSO. Upon coordination of the ligand **1a** to gallium(III)

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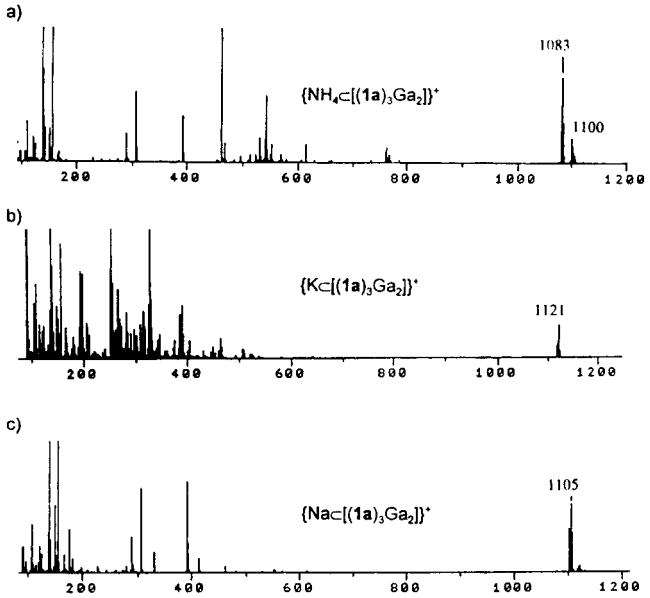


Figure 4. Positive FAB-MS spectra (3-NBA) of a) $[(NH_4) \subset (\mathbf{1a})_3Ga_2^+]$, b) $[K \subset (\mathbf{1a})_3Ga_2^+]$, and c) $[Na \subset (\mathbf{1a})_3Ga_2^+]$.

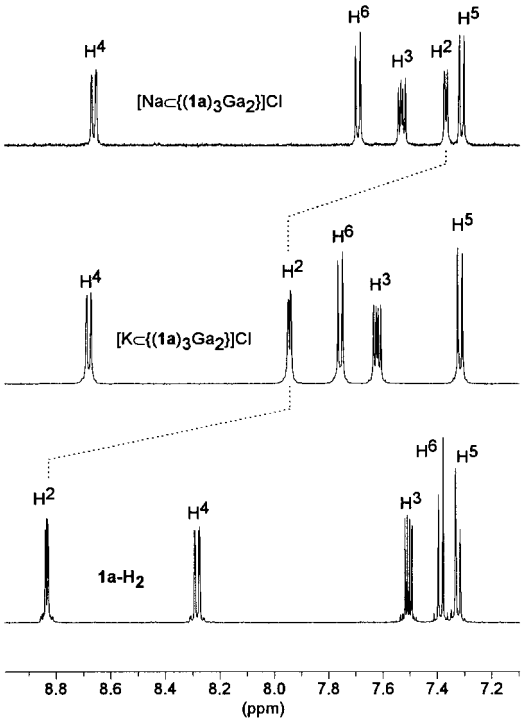


Figure 5. Aromatic regions of the ^{1}H NMR spectra ([D$_6$]DMSO) of **1a-H$_2$**, $[K \subset (\mathbf{1a})_3Ga_2^+]$, and $[Na \subset (\mathbf{1a})_3Ga_2^+]$, showing the high-field shift of H(2) in the gallium complexes.

and formation of the cryptate $[M \subset \{(\mathbf{1a})_3Ga_2\}]Cl$, the signal of proton H(2) ($\delta = 8.82$ in **1a-H$_2$**) is shifted to higher field ($\delta =$ 7.94 (M = K), 7.37 (M = Na)). This shift difference between ligand and complex is due to the spatial position of proton H(2) in the complexes. It is located close to the heteroaromatic portion of a second hydroxyquinolinato unit coordinated to gallium and thus experiences an anisotropic shift. A similar effect was observed earlier for a mononuclear tris(8-hydroxyquinolinato)gallium complex.[24]

For the sodium cryptate $[Na \subset \{(\mathbf{1a})_3Ga_2\}]Cl$ the anisotropic shift is more dramatic than that observed for the corresponding potassium complex. This is surprising because H(2) is located far from the encapsulated alkali metal cation, so it should not be influenced by a change from potassium to sodium. However, because of the difference in size of the alkali metals, the cryptand has to adopt different conformations to make effective binding of the cations possible. Thus the gallium complex moieties act as hinges which enable the expansion (or reduction) of the cavity size of the metalla-cryptand (Figure 6). Upon reduction of the cavity size the ligand units are slightly tilted and proton H(2) is forced closer to the neighboring aromatic system. This leads to a stronger anisotropic shift for H(2) in $[Na \subset \{(\mathbf{1a})_3Ga_2\}]Cl$ than was observed for $[K \subset \{(\mathbf{1a})_3Ga_2\}]Cl$.

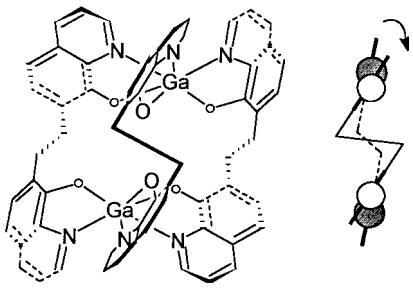


Figure 6. The metalla-cryptand $[(\mathbf{1a})_3Ga_2]$ and a schematic representation of the mechanism of its size-adjustment using the gallium complex units as molecular hinges.

Thus the proton H(2) is an NMR spectroscopic probe which by its NMR chemical shift gives an indication of the size of the stretchable cryptand $[(\mathbf{1a})_3Ga_2]$. If the signal is shifted to low field the cryptand adopts a conformation which enables the encapsulation of relatively large cations, whereas the more compressed cryptand structure leads to a high-field shift of the resonance. NMR spectroscopic results ($CDCl_3$) similar to those for $[M \subset \{\mathbf{1a}_3Ga_2\}]Cl$ were observed for $[M \subset \{(\mathbf{1b})_3Ga_2\}]Cl$ (**1b-H$_2$**: $\delta_{H(2)} = 8.61$; M = K: $\delta_{H(2)} = 7.64$; M = Na: $\delta_{H(2)} = 7.17$).

Solubility problems prevented us from investigating the cryptates $[Rb \subset \{(\mathbf{1a})_3Ga_2\}]^+$ and $[(NH_4) \subset \{(\mathbf{1a})_3Ga_2\}]^+$. Therefore we prepared the more soluble complexes with decyl substituents, $[M \subset \{(\mathbf{1c})_3Ga_2\}]^+$ (M = Na, K, NH_4, Rb). Attempts to obtain analogous cryptates with lithium or cesium cations failed. The Li^+ ion seems to be too small for effective binding in the cavity of the neutral gallium cryptand, whereas the Cs^+ ion is too large.

In the ^{1}H NMR spectra ($CDCl_3$) of $[M \subset \{(\mathbf{1c})_3Ga_2\}]^+$ (M = Na, K, NH_4, Rb) the chemical shift of the signal of proton H(2) follows a similar trend to that observed for the corresponding complexes of ligand **1a** [$\delta_{H(2)} = 8.62$ (ligand **1c-H$_2$**), 7.15 ($[Na \subset \{(\mathbf{1c})_3Ga_2\}]^+$), 7.63 ($[K \subset \{(\mathbf{1c})_3Ga_2\}]^+$), 7.68 ($[(NH_4) \subset \{(\mathbf{1c})_3Ga_2\}]^+$), 7.71 ($[Rb \subset \{(\mathbf{1c})_3Ga_2\}]^+$)]. In the ROESY-NMR spectrum of the cryptate $[(NH_4) \subset \{(\mathbf{1c})_3Ga_2\}]Cl$ in $CDCl_3$, a crosspeak can be observed between the NH_4^+ signal at $\delta = 8.36$ and the resonance of the spacer protons of **1c** at $\delta = 3.27$. This shows that in solution the ammonium cation is bound in the interior of the metalla-cryptand.[23]

As representative examples, the formation of $[M\subset\{(\mathbf{1c})_3Ga_2\}]^+$ by addition of KCl or NaCl to the preformed library $\{(\mathbf{1c})_3Ga_2\}_n$ was followed by ^1H NMR spectroscopy in $CDCl_3$/[D_4]methanol. At room temperature the quantitative transformation of the library of receptors into the defined cryptates takes two weeks.

Molecular structure of $[M\subset\{(\mathbf{1a})_3Ga_2\}]^+$ (M = Na, K) in the solid state: Crystals of $[(dmf)_2K\subset\{(\mathbf{1a})_3Ga_2\}]Cl$ and $[(dmf)_2Na\subset\{(\mathbf{1a})_3Ga_2\}]BF_4$ were obtained from dmf/ether. The complexes crystallize in the trigonal space group $R\bar{3}c$. In the solid state the packing of the $[(dmf)_2M\subset\{(\mathbf{1a})_3Ga_2\}]^+$ ions forms large pores in which the anions are highly disordered. For $[(dmf)_2K\subset\{(\mathbf{1a})_3Ga_2\}]Cl$ only the three highest difference Fourier peaks were assigned to chlorine, summing formally to one atom. However, the strongest remaining peaks of the final difference Fourier calculation were still located in the pores. The BF_4^- ions of $[(dmf)_2Na\subset\{(\mathbf{1a})_3Ga_2\}]BF_4$ could not be localized, but a high residual electron density could be observed in the pores. Similar crystallographic problems in localizing the anions of a triple-stranded helicate have been described by Lehn et al.[8a]

However, the X-ray structural analysis gives an impression of the molecular structures of the cationic cryptates $[M\subset\{(\mathbf{1a})_3Ga_2\}]^+$ (M = Na, K) in the solid state. The two structures are very similar. Figure 7 is a representation of the potassium

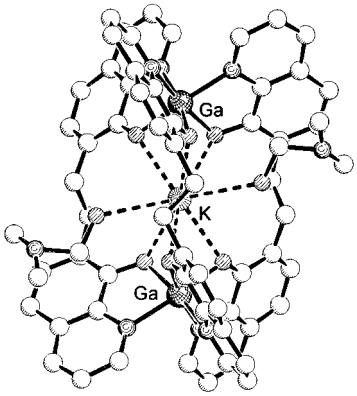
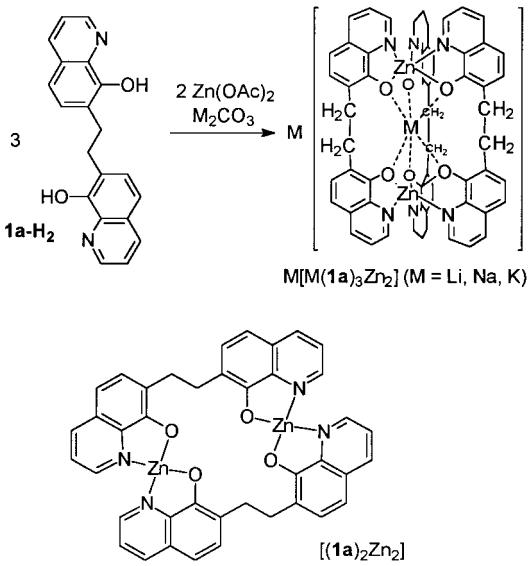


Figure 7. SCHAKAL plot of $[(dmf)_2K\subset(\mathbf{1a})_3Ga_2^+]$ (hydrogen atoms are omitted for clarity).

cryptate. A triple-stranded dinuclear gallium helicate can be observed in which the spacer is orientated in the opposite direction to the helical twist of the helicate.[25] Sodium or potassium ions are encapsulated in the interior of the metallacryptand $\{(\mathbf{1a})_3Ga_2\}$ and are bound to the six internal oxygen atoms of the ligands **1a**.[3, 5] (In addition, two dmf molecules are coordinated to the central alkali metal cation.) The difference between the ionic radii of the sodium and potassium guests[26] means that the cryptand $\{(\mathbf{1a})_3Ga_2\}$ has to adopt different sizes, leading to a gallium–gallium separation of 6.287 Å for $[Na\subset\{(\mathbf{1a})_3Ga_2\}]^+$ and of 6.565 Å for $[K\subset\{(\mathbf{1a})_3Ga_2\}]^+$. The cryptand $\{(\mathbf{1a})_3Ga_2\}$ adjusts to the size of the guest cation present, as in solution, where this adjustment leads to the shift differences which were observed in the ^1H NMR spectra for proton H(2).

Formation of $M[M\subset(\mathbf{1a})_3Zn_2]$ (M = Li, Na, K): The dinuclear zinc complexes $M[M\subset(\mathbf{1a})_3Zn_2]$ (M = Li, Na, K) are prepared by refluxing the ligand **1a-H$_2$** (2 equiv) with zinc acetate (1 equiv) and alkali metal carbonate (M = Li, Na, K) in methanol for 15 h (Scheme 3). The precipitate is collected and washed with a small amount of ice–water. The salts $M[M\subset(\mathbf{1a})_3Zn_2]$ (M = Li, Na, K) are obtained in good yields as yellow solids which are soluble in dmso and can be characterized by ^1H, ^{13}C NMR, FAB-MS, and elemental analysis.



Scheme 3.

The chiral helical structure of the complexes results in two signals in the ^1H NMR spectra for the diastereotopic protons of the spacer (for example, $\delta = 3.36$ and 2.26 for $[K\subset(\mathbf{1a})_3Zn_2]^-$). Again the ^1H NMR chemical shift of proton H(2) of $[M\subset(\mathbf{1a})_3Zn_2]^-$ depends on the alkali metal cation present, indicating inclusion of the ion in the internal cavity. The signal is observed for the potassium compound at $\delta =$ 7.85, for the sodium cryptate at $\delta = 7.27$, and for $[Li\subset(\mathbf{1a})_3Zn_2]^-$ at $\delta = 7.36$. The chemical shift for the proton H(2) of the lithium salt indicates that in this case the binding of the alkali metal cation in the interior of the cryptand is of a different type. The lithium may be bound in the manner observed for an analogous triple-stranded helicate formed from two titanium(IV) ions and three ethylene-bridged di(catechol) ligands.[5b] In the case of the dinuclear zinc cryptate, the formation of the lithium salt is probably due to the negative charge of the host. Thus the binding of lithium in the interior is favored compared with the neutral cryptands $\{(\mathbf{1a-c})_3Ga_2\}$.

If a 1:1 mixture of **1a-H$_2$** and zinc acetate in the presence of potassium carbonate is used for the preparation of dinuclear zinc complexes, a mixture of two different coordination compounds is obtained. One of them can be identified by NMR spectroscopy as $K_2[(\mathbf{1a})_3Zn_2]$. The ^1H NMR spectrum ([D_6]DMSO) of the other shows signals at $\delta = 8.64$ (d, $J =$ 3.0 Hz, 2H), 8.48 (d, $J = 8.4$ Hz, 2H), 7.60 (m, 4H), and 7.06 (d, $J = 8.4$ Hz, 2H) for the aromatic protons. Only one broad

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signal can be observed for the spacer, at $\delta = 3.08$ (4H). Corresponding ^{13}C NMR resonances are observed at $\delta =$ 158.8 (C), 145.7 (CH), 139.2 (CH), 139.1 (C), 131.8 (CH), 128.4 (C), 125.6 (CH), 125.4 (C), 120.7 (CH), and 32.5 (CH_2). The observation of only one NMR signal for the spacer protons indicates that no chiral metal complex units are present. Therefore it is assumed that a planar metalla-crown ether [(**1a**)$_2$Zn$_2$] is formed.[2, 27] A species of this composition can be observed by FAB$^+$ mass spectrometry at $m/z = 761$ ([H(**1a**)$_2$Zn$_2$]$^+$).[28]

Conclusions

By mixing the di(8-hydroxyquinoline) ligands **1** with gallium(III) ions results in the formation of supramolecular (virtual) combinatorial libraries.[6] Since internal oxygen donors are present, the species formed can act as receptors for cationic guest molecules (for example, alkali metal cations). Addition of a guest leads to the most stable host–guest complex and in a dynamic process the most appropriate receptor is removed from the supramolecular combinatorial library to obtain only one defined aggregate.[8] In our case the cryptand is able to adjust to different cationic sizes, using the gallium complex units as molecular hinges.

For the formation of dinuclear zinc helicates, a template-directed self-assembly process takes place in which one of the counterions acts as the template.

Experimental Section

General remarks: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500, AM 400, or WM 250 NMR spectrometer, using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV or FAB$^{+/-}$, 3-NBA matrix) were taken on a Finnigan MAT 90 mass spectrometer. MALDI-TOF spectra (2,5-dihydroxybenzoic acid) were recorded on a Voyager-RP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Solvents were purified by standard methods. Melting points (uncorrected) were determined in Büchi 535 apparatus. Air-sensitive compounds were prepared and handled under argon by Schlenk techniques. Data sets were collected with Enraf Nonius MACH3/CAD4 diffractometers, equipped with sealed-tube/rotating-anode generators. The programs used were: data reduction, MolEN; structure solution, SHELXS-86; structure refinement, SHELXL-93 and SHELXL-97; graphics, SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101924, CCDC-101925, and CCDC-101926. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

3-*n*-Butyl-8-methoxyquinoline (**4b**): A mixture of *o*-anisidine (**3**) (10 g, 81.1 mmol), NaI (122 mg, 0.81 mmol), 2-*n*-butylacrolein (**2b**) (3.76 mL, 28.3 mmol) and concentrated sulfuric acid (16 mL) was heated to 110 °C. More **2b** (15 mL, 113 mmol) was added over a period of 5 h. After one more hour of heating the mixture was cooled, neutralized with aqueous KOH, and extracted with CH_2Cl_2. The organic phase was extracted with hydrochloric acid, neutralized (KOH), and extracted with CH_2Cl_2. Green oil; yield 8.55 g (49 %); ^1H NMR ($CDCl_3$): $\delta = 8.74$ (d, $J = 1.5$ Hz, 1H), 7.81 (d, $J = 1.5$ Hz, 1H), 7.37 (dd, $J = 7.7$, 8.2 Hz, 1H), 7.27 (d, $J = 8.2$ Hz, 1H), 6.92 (d, $J = 7.7$ Hz, 1H), 4.03 (s, 3H), 2.73 (t, $J = 7.7$ Hz, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 155.3$ (C), 150.8 (CH), 138.6 (C), 135.9 (C), 133.9 (CH), 129.3 (C), 126.6 (CH), 119.1 (CH), 106.6 (CH), 55.8 (CH_3), 33.2 (CH_2), 32.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 3311$, 2956, 2929, 1498, 1420, 1333, 1304, 1278, 1199, 752, 718 cm^{-1}; MS (EI): m/z (%): 215 (85) [M^+], 214 (100); HRMS: calcd for $C_{14}H_{17}NO$ 215.1310; found 215.1330.

3-*n*-Decyl-8-methoxyquinoline (**4c**): Brown oil; yield: quantitative; ^1H NMR ($CDCl_3$): $\delta = 8.76$ (d, $J = 2.0$ Hz, 1H), 7.85 (d, $J = 2.0$ Hz, 1H), 7.41 (dd, $J = 7.5$, 7.8 Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 1H), 4.06 (s, 3H), 2.77 (t, $J = 7.7$ Hz, 2H), 1.68 (m, 2H), 1.36–1.24 (m, 14H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 155.4$ (C), 150.9 (CH), 138.7 (C), 136.0 (C), 134.0 (CH), 129.3 (C), 126.6 (CH), 119.1 (CH), 106.6 (CH), 55.9 (CH_3), 33.1 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 29.6 ($2 \times CH_2$), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (KBr): $\tilde{\nu} =$ 3000, 2925, 2854, 1572, 1495, 1466, 1380, 1266, 1111, 757 cm^{-1}; MS (EI): m/z (%): 299 (100) [M^+]; HRMS: calcd. for $C_{20}H_{29}NO$ 299.2249; found 299.2238.

3-*n*-Butyl-8-hydroxyquinoline (**5b**): Quinoline **4b** (8.55 g, 39.7 mmol) was refluxed in aqueous HBr (48 %, 60 mL) for 48 h. After neutralization with aqueous KOH the mixture was extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and solvent was removed. Brownish solid; yield: 7.58 g (95 %); m.p.: 68–69 °C; ^1H NMR ($CDCl_3$): $\delta = 8.65$ (s, 1H), 7.91 (s, 1H), 7.49 (t, $J = 7.9$ Hz, 1H), 7.27 (d, $J = 7.9$ Hz, 1H), 7.12 (d, $J = 7.9$ Hz, 1H), 2.80 (t, $J = 7.7$ Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 152.2$ (C), 149.6 (CH), 136.9 (C), 136.3 (C), 134.3 (CH), 128.5 (C), 127.7 (CH), 117.4 (CH), 109.2 (CH), 33.3 (CH_2), 32.9 (CH_2), 22.3 (CH_2), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 3438$, 2956, 2858, 1572, 1495, 1466, 1380, 1267, 1111, 760 cm^{-1}; MS (EI): m/z (%): 201 (100) [M^+]; HRMS: calcd. for $C_{13}H_{15}NO$ 201.1154; found 201.1138; $C_{13}H_{15}NO$: calcd. C 77.58, H 7.51, N 6.96; found C 76.91, H 7.03, N 6.94.

3-*n*-Decyl-8-hydroxyquinoline (**5c**): Brown solid; yield: quantitative; m.p.: 72 °C; ^1H NMR ($CDCl_3$): $\delta = 8.64$ (d, $J = 1.4$ Hz, 1H), 7.90 (d, $J = 1.4$ Hz, 1H), 7.41 (dd, $J = 7.7$, 8.2 Hz, 1H), 7.27 (d, $J = 8.2$ Hz, 1H), 7.12 (d, $J =$ 7.7 Hz, 1H), 2.79 (t, $J = 7.7$ Hz, 2H), 1.70 (m, 2H), 1.39–1.27 (m, 14H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 152.3$ (C), 149.6 (CH), 136.9 (C), 136.3 (C), 134.3 (CH), 128.5 (C), 127.7 (CH), 117.5 (CH), 109.3 (CH), 33.3 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 3290$, 2917, 2850, 1499, 1468, 1277, 1196, 759 cm^{-1}; MS (EI): m/z (%): 285 (100) [M^+]; HRMS: calcd. for $C_{19}H_{27}NO$ 285.2093; found 285.2107; $C_{19}H_{27}NO$: calcd. C 79.95, H 9.53, N 4.91; found C 79.72, H 9.36, N 4.26.

3-*n*-Butyl-8-hydroxy-7-(*N*-morpholinomethyl)quinoline (**6b**): Morpholine (2.81 mL, 32.3 mmol) and 40 % aqueous formaldehyde (4.4 mL, 64.6 mmol) were added to **5b** (6.50 g, 32.3 mmol) in ethanol (85 mL) and the mixture was heated to 40 °C for 15 h. Solvent was removed and the residue was purified by column chromatography (gradient: $CH_2Cl_2 \rightarrow CH_2Cl_2$/methanol, 9:1). Yellow oil; yield: 5.04 g (52 %); ^1H NMR ($CDCl_3$): $\delta = 8.69$ (s, 1H), 7.80 (s, 1H), 7.18 (s, 2H), 3.83 (s, 2H), 3.75 (br, 4H), 2.74 (t, $J = 7.2$ Hz, 2H), 2.59 (br, 4H), 1.65 (m, 2H), 1.36 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 152.7$ (C), 150.6 (CH), 137.6 (C), 135.6 (C), 133.8 (CH), 128.4 (C), 127.9 (CH), 117.1 (CH), 116.5 (C), 66.9 (CH_2), 60.4 (CH_2), 53.1 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 3373$, 2955, 2929, 2855, 1469, 1378, 1290, 1117 cm^{-1}; MS (EI): m/z (%): 300 (1) [M^+], 215 (100); HRMS: calcd. for $C_{18}H_{24}N_2O_2$ 300.1838; found 300.1828.

3-*n*-Decyl-8-hydroxy-7-(*N*-morpholinomethyl)quinoline (**6c**): Brown oil; yield: 52 %; ^1H NMR ($CDCl_3$): $\delta = 8.71$ (d, $J = 2.1$ Hz, 1H), 7.82 (d, $J =$ 2.1 Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 3.85 (s, 2H), 3.77 (t, $J = 4.6$ Hz, 4H), 2.76 (t, $J = 7.7$ Hz, 2H), 2.62 (br, 4H), 1.69 (m, 2H), 1.37–1.25 (m, 14H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 152.7$ (C), 150.6 (CH), 137.7 (C), 135.7 (C), 133.8 (CH), 128.4 (C), 127.9 (CH), 117.1 (CH), 116.5 (C), 66.9 (CH_2), 60.4 (CH_2), 53.1 (CH_2), 33.2 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 3387$, 2925, 2853, 1494, 1469, 1379, 1291, 1118, 865, 721 cm^{-1}; MS (EI): m/z (%): 384 (1) [M^+], 299 (100); HRMS: calcd. for $C_{24}H_{36}N_2O_2$ 384.2777; found 384.2787.

8-Acetoxy-3-*n*-butyl-7-(acetoxymethyl)quinoline (**7b**): A solution of **6b** (5.1 g, 17.0 mmol) in acetic anhydride (20 mL) was refluxed overnight. Volatiles were removed and the remaining oil was dissolved in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). The solvent

was then removed. Brown oil; yield: quantitative (5.36 g); ^{1}H NMR ($CDCl_3$): $\delta = 8.75$ (d, $J = 1.5$ Hz, 1H), 7.88 (d, $J = 1.5$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.54 (d, $J = 8.5$ Hz, 1H), 5.26 (s, 2H) 2.76 (t, $J = 7.6$ Hz, 2H), 2.51 (s, 3H), 2.07 (s, 3H), 1.65 (m, 2H), 1.36 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 170.7$ (C), 169.5 (C), 152.6 (CH), 145.8 (C), 139.5 (C), 136.4 (C), 133.9 (CH), 129.3 (C), 127.3 (CH), 127.2 (C), 125.2 (CH), 61.2 (CH_2), 33.0 (CH_2), 32.8 (CH_2), 22.2 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 13.8 (CH_3); IR (KBr): $\tilde{\nu} = 2959$, 2930, 2859, 1767, 1743, 1650, 1367, 1270, 1235, 1201, 1117 cm^{-1}; MS (EI): m/z (%): 315 (0.2) [M^+], 57 (100); HRMS: calcd. for $C_{18}H_{21}NO_4$ 315.1471; found 315.1459.

8-Acetoxy-3-*n*-decyl-7-(acetoxymethyl)quinoline (7c): Brown oil; yield: quantitative; ^{1}H NMR ($CDCl_3$): $\delta = 8.71$ (s, 1H), 7.84 (s, 1H), 7.59 (d, $J = 8.3$ Hz, 1H), 7.50 (d, $J = 8.3$ Hz, 1H), 5.22 (s, 2H) 2.70 (t, $J = 7.6$ Hz, 2H), 2.46 (s, 3H), 2.03 (s, 3H), 1.62 (m, 2H), 1.26 – 1.20 (m, 14H), 0.81 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 170.5$ (C), 169.2 (C), 152.3 (CH), 145.6 (C), 139.3 (C), 136.2 (C), 133.7 (CH), 129.1 (C), 127.1 (CH), 127.0 (C), 125.0 (CH), 61.0 (CH_2), 32.9 (CH_2), 31.6 (CH_2), 30.7 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 22.4 (CH_2), 20.9 (CH_3), 20.6 (CH_3), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 2926$, 2855, 1769, 1744, 1651, 1366, 1234, 1197 cm^{-1}; MS (EI): m/z (%): 399 (2) [M^+], 357 (100); HRMS: calcd. for $C_{24}H_{33}NO_4$ 399.2410; found 399.2421.

8-Acetoxy-3-*n*-butyl-7-(bromomethyl)quinoline (8b): HBr (30%) in glacial acetic acid (80 mL) was added to a solution of **7b** (2.0 g, 6.4 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for three days and volatiles were removed. The crude product was purified by column chromatography (hexane/ethyl acetate, 2:1). Colorless oil; yield 1.26 g (59%); ^{1}H NMR ($CDCl_3$): $\delta = 8.78$ (d, $J = 2.0$ Hz, 1H), 7.89 (d, $J = 2.0$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.54 (d, $J = 8.5$ Hz, 1H), 4.63 (s, 2H), 2.78 (t, $J = 7.6$ Hz, 2H), 2.58 (s, 3H), 1.69 (m, 2H), 1.39 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 169.2$ (C), 152.6 (CH), 145.7 (C), 139.5 (C), 136.6 (C), 134.0 (CH), 129.4 (C), 128.7 (C), 127.8 (CH), 125.6 (CH), 33.0 (CH_2), 32.9 (CH_2), 27.2 (CH_2), 22.2 (CH_2), 20.9 (CH_3), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 2957$, 2930, 2871, 2859, 1771, 1468, 1365, 1199, 1170, 1080, 891 cm^{-1}; MS (EI): m/z (%): 335 (1) [M^+], 214 (100); HRMS: calcd. for $C_{16}H_{18}NO_2Br$ 335.0521; found 335.0510.

8-Acetoxy-3-*n*-decyl-7-(bromomethyl)quinoline (8c): Green oil; yield: 36%; ^{1}H NMR ($CDCl_3$): $\delta = 8.77$ (d, $J = 2.1$ Hz, 1H), 7.88 (d, $J = 2.1$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.53 (d, $J = 8.5$ Hz, 1H), 4.63 (s, 2H) 2.77 (t, $J = 7.7$ Hz, 2H), 2.58 (s, 3H), 1.69 (m, 2H), 1.33 – 1.27 (m, 14H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 169.2$ (C), 152.6 (CH), 145.7 (C), 139.6 (C), 136.6 (C), 133.9 (CH), 129.4 (C), 128.7 (C), 127.8 (CH), 125.6 (CH), 33.1 (CH_2), 31.9 (CH_2), 31.0 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 27.2 (CH_2), 22.7 (CH_2), 20.9 (CH_3), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 2925$, 2854, 1772, 1468, 1365, 1195, 1081, 893 cm^{-1}; MS (EI): m/z (%): 419 (0.2) [M^+], 298 (100); HRMS: calcd. for $C_{22}H_{30}NO_2Br$ 419.1460; found 419.1471.

1,2-Bis(8-acetoxy-3-*n*-butylquinolin-7-yl)ethane (1b-Ac$_2$): A suspension of $(Ph_3P)_2NiBr_2$ (67 mg, 0.09 mmol), zinc powder (175 mg, 2.68 mmol), and Et_4NI (459 mg, 1.79 mmol) in anhydrous THF (5 mL) was stirred under argon for 2 h. A solution of the bromide **8b** (300 mg, 0.89 mmol) in THF (6 mL) was added and the mixture was stirred overnight. Filtration and removal of the solvent afforded the crude product which was purified by column chromatography (hexane/ethyl acetate, 2:1). Yellow oil; yield: 96 mg (42%); ^{1}H NMR ($CDCl_3$): $\delta = 8.76$ (d, $J = 2.2$ Hz, 2H), 7.87 (d, $J = 2.2$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 3.09 (s, 4H), 2.78 (t, $J = 7.7$ Hz, 4H), 2.55 (s, 6H), 1.69 (m, 4H), 1.39 (m, 4H), 0.95 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 169.9$ (C), 152.2 (CH), 144.9 (C), 139.7 (C), 135.5 (C), 134.0 (CH), 132.4 (C), 128.3 (CH), 128.1 (C), 125.0 (CH), 33.2 (CH_2), 32.8 (CH_2), 31.0 (CH_2), 22.2 (CH_2), 20.9 (CH_3), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 2956$, 2930, 2859, 1763, 1467, 1365, 1207, 1167, 1079 cm^{-1}; MS (EI): m/z (%): 512 (4) [M^+], 214 (100); HRMS: calcd. for $C_{32}H_{36}N_2O_4$ 512.2675; found 512.2665.

1,2-Bis(8-acetoxy-3-*n*-decylquinolin-7-yl)ethane (1c-Ac$_2$): Yellow solid; yield: 65%; m.p. 93 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.76$ (d, $J = 2.0$ Hz, 2H), 7.87 (d, $J = 2.0$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 3.09 (s, 4H) 2.77 (t, $J = 7.7$ Hz, 4H), 2.56 (s, 6H), 1.70 (m, 4H), 1.34 – 1.27 (m, 28H), 0.89 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 169.9$ (C), 152.3 (CH), 144.9 (C), 139.8 (C), 135.5 (C), 134.0 (CH), 132.4 (C), 128.3 (CH), 128.1 (C), 125.0 (CH), 33.1 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 31.0 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 20.9 (CH_3), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 2955$, 2915, 2849, 1761, 1469, 1366, 1204, 1078, 896 cm^{-1}; MS (EI): m/z (%): 680 (0.3) [M^+], 298 (100); HRMS: calcd. for $C_{44}H_{60}N_2O_4$ 680.4553; found 680.4520; $C_{44}H_{60}N_2O_4 \cdot H_2O$: calcd. C 75.61, H 8.94, N 4.01; found C 75.70, H 8.46, N 3.27.

X-ray structural analysis of 1,2-bis(8-hydroxyquinolin-7-yl)ethane (1a-H$_2$): X-ray quality crystals of **1a-H$_2$** were obtained from a solution of **1a-H$_2$** in dichloromethane by slow evaporation of the solvent. Crystal data for **1a-H$_2$** $\cdot 0.6\,CH_2Cl_2$: formula $C_{20}H_{16}N_2O_2 \cdot 0.6\,CH_2Cl_2$, $M = 367.30$, $0.4 \times 0.3 \times 0.1$ mm^3, $a = 16.009(1)$, $b = 12.560(1)$, $c = 9.008(1)$ Å, $\beta = 96.50(1)°$, $V = 1799.6(3)$ Å^3, $\rho_{calcd} = 1.356$ g cm^{-3}, $\mu = 22.91$ cm^{-1}, empirical absorption correction from ψ scan data ($0.936 \le C \le 0.999$), $Z = 4$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3801 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 1845 independent and 1343 observed reflections [$I \ge 2\sigma(I)$], 134 refined parameters, $R = 0.056$, $wR^2 = 0.164$, max. residual electron density 0.39(-0.27) e Å^{-3}; occupancy of the CH_2Cl_2 determined by refinement, hydrogens calculated and refined as riding atoms.

1,2-Bis(3-*n*-butyl-8-hydroxyquinolin-7-yl)ethane (1b-H$_2$): Trifluoracetic acid (10 drops) were added to a solution of **1b-Ac$_2$** (85 mg, 0.17 mmol) in methanol (10 mL). After 3 days at room temperature volatiles were removed and the residue was dissolved in CH_2Cl_2. The solution was washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$), then the solvent was removed. Yellow solid; yield: 73 mg (quantitative); m.p.: 168 – 171 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.61$ (d, $J = 2.0$ Hz, 2H), 8.28 (br s, 2H), 7.86 (d, $J = 2.0$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 3.24 (s, 4H), 2.79 (t, $J = 7.7$ Hz, 4H), 1.73 – 1.68 (m, 4H), 1.45 – 1.37 (m, 4H), 0.96 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 149.4$ (CH), 149.3 (C), 136.8 (C), 135.3 (C), 134.1 (CH), 130.0 (CH), 126.9 (C), 122.7 (C), 116.6 (CH), 33.4 (CH_2), 33.0 (CH_2), 30.0 (CH_2), 22.3 (CH_2), 13.9 (CH_3); IR (KBr): $\tilde{\nu} = 3284$, 2956, 2927, 2857, 1476, 1413, 1378, 1264, 1233, 1140, 682 cm^{-1}; MS (EI): m/z (%): 428 (21) [M^+], 214 (100); HRMS: calcd. for $C_{28}H_{32}N_2O_2$ 428.2464; found 428.2454; $C_{28}H_{32}N_2O_2 \cdot 0.5\,H_2O$: calcd. C 76.86, H 7.60, N 6.40; found C 76.60, H 7.58, N 5.95.

1,2-Bis(3-*n*-decyl-8-hydroxyquinolin-7-yl)ethane (1c-H$_2$): Colorless solid; yield: quantitative; m.p.: 132 – 134 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.62$ (d, $J = 2.0$ Hz, 2H), 7.87 (d, $J = 2.0$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 2H), 3.25 (s, 4H), 2.78 (t, $J = 7.7$ Hz, 4H), 1.71 (m, 4H), 1.35 – 1.27 (m, 28H), 0.88 (t, $J = 6.9$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 149.3$ (CH), 149.2 (C), 136.7 (C), 135.3 (C), 134.2 (CH), 130.0 (CH), 126.9 (C), 122.8 (C), 116.6 (CH), 33.2 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 30.3 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3); IR (KBr): $\tilde{\nu} = 3287$, 2953, 2918, 2850, 1497, 1476, 1413, 1378, 1264, 1230, 1139, 788, 680 cm^{-1}; MS (EI): m/z (%): 596 (46) [M^+], 298 (100); HRMS: calcd. for $C_{40}H_{56}N_2O_2$ 596.4342; found 596.4326; $C_{40}H_{56}N_2O_2 \cdot 0.5\,H_2O$: calcd. C 79.29, H 9.48, N 4.62; found C 79.53, H 9.16, N 4.05.

[(1a)$_3$Ga$_2$]: 1,2-Bis(8-hydroxyquinolin-7-yl)ethane (**1a-H$_2$**, 20 mg, 0.06 mmol), $Ga(NO_3)_3$ (11 mg, 0.04 mmol), and sodium carbonate (7 mg, 0.06 mmol) in methanol (40 mL) were stirred overnight. The precipitate was filtered and washed with water to remove sodium salts. Yellow hygroscopic solid; yield: 99% (25 mg); IR (KBr): $\tilde{\nu} = 3050$, 2918, 1575, 1502, 1457, 1375, 1316, 1108, 823, 752, 680 cm^{-1}; $C_{60}H_{42}Ga_2N_6O_6 \cdot 8H_2O$: calcd. C 58.75, H 4.77, N 6.85; found C 58.62, H 4.38, N 6.89.

[(1b)$_3$Ga$_2$]: Yellow hygroscopic solid; yield: 62% IR (KBr): $\tilde{\nu} = 3420$, 2955, 2929, 2859, 1580, 1461, 1404, 1375, 1104, 758 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1419 [(**1b**)$_3$Ga$_2$H$^+$]; $C_{84}H_{90}Ga_2N_6O_6 \cdot 4H_2O$: calcd. C 67.66, H 6.62, N 5.64; found C 67.37, H 5.92, N 5.45.

[(1c)$_3$Ga$_2$]: Yellow hygroscopic solid; yield: 97%; IR (KBr): $\tilde{\nu} = 3406$, 2924, 2853, 1580, 1493, 1461, 1374, 1098, 757, 687 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1923 [(**1c**)$_3$Ga$_2$H$^+$], 1947 [(**1c**)$_3$Ga$_2$Na$^+$]; 3848 [(**1c**)$_6$Ga$_4^+$]; $C_{120}H_{162}Ga_2N_6O_6 \cdot 6H_2O$: calcd C 70.92, H 8.63, N 4.14; found C 70.80, H 8.32, N 3.92.

General procedure for the preparation of cryptates [M $\subset$ (1)$_3$Ga$_2$]Cl: Ligand **1a-H$_2$** (20 mg, 0.06 mmol) (or **1b-H$_2$** or **1c-H$_2$**), $Ga(NO_3)_3 \cdot 9H_2O$ (10.5 mg, 0.04 mmol) and a large excess of MCl (M = Na, K; ca. 150 mg) in methanol (40 mL) were refluxed for 15 h. The cryptate was filtered and washed with ice – water (4 mL).

[Na $\subset$ (1a)$_3$Ga$_2$]Cl: Yellow hygroscopic solid; yield: 49%; ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.66$ (d, $J = 7.9$ Hz, 6H), 7.69 (d, $J = 8.4$ Hz, 6H), 7.54 (dd, $J = 4.6$, 7.9 Hz, 6H), 7.37, (d, $J = 4.6$ Hz, 6H), 7.31 (d, $J = 8.4$ Hz, 6H), 2.63 – 2.61 (m, 6H), one multiplet of the spacer hidden under the water peak (COSY); ^{13}C NMR ([D$_6$]DMSO): $\delta = 153.9$ (C), 143.8 (CH), 141.0

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(CH), 136.1 (C), 131.7 (CH), 128.0 (C), 126.7 (C), 121.4 (CH), 112.2 (CH), 30.6 (CH_2); ^{23}Na NMR ([D$_6$]DMSO): $\delta = 1.2$; IR (KBr): $\tilde{\nu} = 3402$, 3050, 2917, 2853, 1574, 1503, 1459, 1376, 1316, 1112, 825, 754, 682 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1105 [Na $\subset$ (**1a**)$_3$Ga$_2^+$]; $C_{60}H_{42}Ga_2N_6O_6NaCl \cdot 5H_2O$: calcd. C 58.54, H 4.26, N 6.83; found C 58.90, H 4.13, N 6.47.

[Na $\subset$ (1a)$_3$Ga$_2$]BF$_4$: This shows the same ^{1}H NMR signals as the corresponding chloride; $C_{60}H_{42}Ga_2N_6O_6NaBF_4 \cdot 2.5H_2O$: calcd. C 58.24, H 3.83, N 6.79; found C 58.41, H 4.17, N 6.24.

X-ray structural analysis of [(dmf)$_2$Na $\subset$ (1a)$_3$Ga$_2$]BF$_4$: X-ray quality crystals were obtained from dmf/ether. Formula $C_{66}H_{56}N_8O_8BF_4NaGa_2$, $M = 1338.43$, $0.2 \times 0.1 \times 0.05$ mm^3, $a = 25.279(4)$, $c = 52.000(9)$ Å, $\gamma = 120°$, $V = 28778(8)$ Å^3, $\rho_{calcd} = 1.390$ g cm^{-3}, $\mu = 9.22$ cm^{-1}, $Z = 18$, trigonal, space group $R\bar{3}c$ (no. 167), $\lambda = 0.71073$ Å, $T = 223$ K, ω scans, 8961 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.43$ Å^{-1}, 2987 independent and 1618 observed reflections [$I \geq 2\sigma(I)$], 176 refined parameters, $R = 0.136$, $wR^2 = 0.340$, max. residual electron density 3.85(−1.32) e Å^{-3}; Ga refined anisotropically but all other atoms only isotropically, displacement parameter of Na indicates movement inside the cavity, BF_4 could not be found, highest remaining electron density in the pores, hydrogen atoms calculated and refined as riding atoms.

[K $\subset$ (1a)$_3$Ga$_2$]Cl: Yellow hygroscopic solid; yield: 53%; ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.67$ (dd, $J = 1.0$, 8.4 Hz, 6H), 7.94 (dd, $J = 1.0$, 4.8 Hz, 6H), 7.76 (d, $J = 8.4$ Hz, 6H), 7.62 (dd, $J = 4.8$, 8.4 Hz, 6H), 7.31 (d, $J = 8.4$ Hz, 6H), 3.09–3.07 (m, 6H), 2.70–2.68 (m, 6H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 153.5$ (C), 144.8 (CH), 141.2 (CH), 136.1 (C), 132.0 (CH), 128.2 (C), 125.7 (C), 121.7 (CH), 112.5 (CH), 31.0 (CH_2); IR (KBr): $\tilde{\nu} = 3402$, 3052, 2937, 2858, 1578, 1503, 1461, 1377, 1317, 1107, 826, 732, 680 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1121 [K $\subset$ (**5**)$_3$Ga$_2^+$]; $C_{60}H_{42}Ga_2N_6O_6KCl \cdot 8H_2O$: calcd C 55.39, H 4.49, N 6.46; found C 55.11, H 4.40, N 6.23. [K $\subset$ (**1a**)$_3$Ga$_2$]Cl could also be obtained by heating [(**1a**)$_3$Ga$_2$] in the presence of an excess of KCl in [D$_6$]DMSO.

X-ray structural analysis of [(dmf)$_2$K $\subset$ (1a)$_3$Ga$_2$]Cl: X-ray quality crystals were obtained from DMF/ether. Formula $C_{66}H_{56}N_8O_8ClKGa_2$, $M = 1303.18$, $0.4 \times 0.3 \times 0.1$ mm^3, $a = 25.427(5)$, $c = 51.693(9)$ Å, $\gamma = 120°$, $V = 28944(9)$ Å^3, $\rho_{calcd} = 1.346$ g cm^{-3}, $\mu = 10.04$ cm^{-1}, $Z = 18$, trigonal, space group $R\bar{3}c$ (no. 167), $\lambda = 0.71073$ Å, $T = 223$ K, ω scans, 12646 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.49$ Å^{-1}, 4213 independent and 1522 observed reflections [$I \geq 2\sigma(I)$], 365 refined parameters, $R = 0.096$, $wR^2 = 0.247$, max. residual electron density 1.40(−0.66) e Å^{-3}; displacement parameter of K indicates movement inside the cavity, chlorine assigned to the three highest peaks of the difference Fourier summing to one atom, refined isotropically, the strongest remaining peaks of the final difference Fourier calculation are located in the pores, atoms of the DMF molecule refined with common isotropic displacement parameter, hydrogen atoms calculated and refined as riding atoms.

[Na $\subset$ (1b)$_3$Ga$_2$]Cl: Yellow hygroscopic solid; yield: 73%; ^{1}H NMR ($CDCl_3$): $\delta = 8.22$ (d, $J = 1.6$ Hz, 6H), 7.63 (d, $J = 8.3$ Hz, 6H), 7.17 (d, $J = 8.3$ Hz, 6H), 6.87 (d, $J = 1.6$ Hz, 6H), 3.45–3.39 (m, 6H), 2.68–2.52 (m, 18H), 1.52–1.43 (m, 12H), 1.23–1.13 (m, 12H), 0.87–0.84 (m, 18H); IR (KBr): $\tilde{\nu} = 3431$, 2956, 2928, 2859, 1580, 1490, 1465, 1396, 1377, 1341, 1098, 756, 691 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1443 [Na $\subset$ (**1b**)$_3$Ga$_2^+$]; $C_{84}H_{90}Ga_2N_6O_6NaCl \cdot 8H_2O$: calcd.C 62.21, H 6.59, N 5.18; found C 61.93, H 5.58, N 5.22.

[K $\subset$ (1b)$_3$Ga$_2$]Cl: Yellow hygroscopic solid; yield: 66%; ^{1}H NMR ($CDCl_3$): $\delta = 8.21$ (s, 6H), 7.64 (d, $J = 8.4$ Hz, 6H), 7.45 (s, 6H), 7.15 (d, $J = 8.4$ Hz, 6H), 3.33–3.29 (m, 6H), 2.73–2.62 (m, 18H), 1.29–1.25 (m, 12H), 0.95–0.87 (m, 18H); IR (KBr): $\tilde{\nu} = 3435$, 3046, 2955, 2929, 2858, 1464, 1395, 1376, 1347, 756, 691 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1457 [K $\subset$ (**1b**)$_3$Ga$_2^+$]; $C_{84}H_{90}Ga_2N_6O_6KCl \cdot 3H_2O$: calcd. C 65.19, H 6.25, N 5.43; found C 64.99, H 6.33, N 5.66.

[Na $\subset$ (1c)$_3$Ga$_2$]Cl: Yellow hygroscopic solid; yield: 44%; ^{1}H NMR ($CDCl_3$): $\delta = 8.19$ (s, 6H), 7.62 (d, $J = 8.4$ Hz, 6H), 7.15 (d, $J = 8.4$ Hz, 6H), 6.87 (s, 6H), 3.45–3.39 (m, 6H), 2.66–2.61 (m, 6H), 2.59–2.56 (m, 12H), 1.58 (m, 12H), 1.47 (m, 12H), 1.31–1.18 (m, 72H), 0.89 (m, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 154.0$ (C), 143.2 (CH), 139.5 (CH), 136.1 (C), 134.8 (C), 132.6 (CH), 128.5 (C), 127.1 (C), 112.2 (CH), 32.8 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 31.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2, double intensity), 28.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (KBr): $\tilde{\nu} = 3052$, 3018, 2925, 2853, 1466, 1396, 1375, 1098, 756 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1945 [Na $\subset$ (**1c**)$_3$Ga$_2^+$]; $C_{120}H_{162}Ga_2N_6O_6NaCl \cdot 3H_2O$: calcd. C 70.77, H 4.13, N 8.31; found C 70.51, H 4.17, N 8.12.

[K $\subset$ (1c)$_3$Ga$_2$]Cl: Yellow solid; yield: 39%; ^{1}H NMR ($CDCl_3$): $\delta = 8.19$ (s, 6H), 7.63 (d, $J = 8.4$ Hz, 6H), 7.43 (s, 6H), 7.13 (d, $J = 8.4$ Hz, 6H), 3.30 (m, 6H), 2.66 (m, 18H), 1.59–1.55 (m, 24H), 1.31–1.21 (m, 72H), 0.89 (m, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 154.1$ (C), 143.7 (CH), 139.5 (CH), 136.2 (C), 135.1 (C), 132.7 (CH), 128.8 (C), 125.7 (C), 111.9 (CH), 32.9 (CH_2), 32.0 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (KBr): $\tilde{\nu} = 3052$, 3018, 2925, 2853, 1466, 1396, 1375, 1098, 756 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1961 [K $\subset$ (**1c**)$_3$Ga$_2^+$]; $C_{120}H_{162}Ga_2N_6O_6KCl \cdot 6CH_2Cl_2$: calcd. C 60.34, H 6.99, N 3.35; found C 61.14, H 6.69, N 3.48.

[(NH$_4$) $\subset$ (1c)$_3$Ga$_2$]Cl: Yellow solid; yield: 39%; ^{1}H NMR ($CDCl_3$): $\delta = 8.36$ (br, 4H), 8.20 (s, 6H), 7.68 (s, 6H), 7.64 (d, $J = 8.4$ Hz, 6H), 7.14 (d, $J = 8.4$ Hz, 6H), 3.29–3.27 (m, 6H), 2.71 (m, 18H), 1.61 (m, 24H), 1.29–1.25 (m, 72H), 0.90 (t, $J = 7.0$ Hz, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 158.8$ (C), 144.1 (CH), 139.3 (CH), 136.3 (C), 135.3 (C), 132.6 (CH), 128.8 (C), 125.3 (C), 112.0 (CH), 32.8 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (KBr): $\tilde{\nu} = 3439$, 2924, 2853, 1465, 1395, 1376, 1097 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1923 [H $\subset$ (**1c**)$_3$Ga$_2^+$]; $C_{120}H_{166}Ga_2N_7O_6Cl \cdot 6CH_2Cl_2$: calcd. C 60.85, H 7.21, N 3.94; found C 59.97, H 6.89, N 3.98.

[Rb $\subset$ (1c)$_3$Ga$_2$]Cl: Yellow hygroscopic solid contaminated with the corresponding potassium cryptate; ^{1}H NMR ($CDCl_3$): $\delta = 8.18$ (s, 6H), 7.71 (s, 6H), 7.63 (d, $J = 8.2$ Hz, 6H), 7.12 (d, $J = 8.2$ Hz, 6H), 3.23 (m, 6H), 2.71 (m, 18H), 1.58 (m, 24H), 1.28 (m, 72H), 0.88 (t, $J = 6.9$ Hz, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 154.2$ (C), 144.1 (CH), 139.3 (CH), 136.4 (C), 135.3 (C), 132.7 (CH), 128.9 (C), 125.0 (C), 111.8 (CH), 32.9 (CH_2), 32.0 (CH_2), 31.6 (CH_2), 31.0 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (KBr): $\tilde{\nu} = 3410$, 2924, 2853, 1582, 1491, 1465, 1394, 1377, 1097 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 2007 [Rb $\subset$ (**1c**)$_3$Ga$_2^+$].

[(NH$_4$) $\subset$ (1a)$_3$Ga$_2$]OAc: Ligand **1a-H$_2$** (20 mg, 0.06 mmol), $Ga(NO_3)_3$ (10.5 mg, 0.04 mmol) and a large excess of ammonium actate (150 mg) in methanol (40 mL) were refluxed for 15 h. The cryptate was filtered and washed with cold water (4 mL). Yellow hygroscopic solid; yield: 54% (14 mg, 0.01 mmol); IR (KBr): $\tilde{\nu} = 3566$, 3050, 1574, 1502, 1459, 1376, 1315, 1108, 825, 681 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1100 [(NH$_4$) $\subset$ (**1a**)$_3$Ga$_2^+$]; $C_{62}H_{49}Ga_2N_7O_8 \cdot 6H_2O$: calcd C 58.75, H 4.85, N 7.73; found C 58.77, H 4.75, N 7.00.

General procedure for the preparation of cryptates M$_2$[(1a)$_3$Zn$_2$]: Ligand **1a-H$_2$** (20 mg, 0.06 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (6.8 mg, 0.03 mmol), and M_2CO_3 (M = Li, Na, K, 0.06 mmol) in methanol (40 mL) were refluxed for 15 h. The precipitate was filtered and washed with ice–water (4 mL).

Li$_2$[(1a)$_3$Zn$_2$]: Yellow hygroscopic solid; yield: 94%; ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.22$ (dd, $J = 1.5$, 8.3 Hz, 6H), 7.41 (d, $J = 8.0$ Hz, 6H), 7.36 (dd, $J = 1.5$, 4.4 Hz, 6H), 7.25, (dd, $J = 4.4$, 8.3 Hz, 6H), 6.77 (d, $J = 8.0$ Hz, 6H), signals of the spacer hidden under solvent peaks; IR (KBr): $\tilde{\nu} = 3044$, 1565, 1503, 1454, 1389, 1372, 1309, 1105, 826, 685 cm^{-1}; FAB$^-$-MS (3-NBA): m/z: 1081 [Li(**1a**)$_3$Zn$_2^-$]; $C_{60}H_{42}Li_2N_6O_6Zn_2 \cdot 3H_2O$: calcd. C 63.12, H 4.24, N 7.36; found C 62.91, H 4.49, N 7.19.

Na$_2$[(1a)$_3$Zn$_2$]: Yellow hygroscopic solid; yield: 70%; ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.23$ (d, $J = 8.3$ Hz, 6H), 7.42 (d, $J = 8.0$ Hz, 6H), 7.27 (br, 6H), 7.25, (dd, $J = 4.4$, 8.2 Hz, 6H), 6.79 (d, $J = 8.0$ Hz, 6H), signals of the spacer hidden under solvent peaks; ^{13}C NMR ([D$_6$]DMSO): $\delta = 160.9$ (C), 142.4 (CH), 140.0 (C), 137.8 (CH), 131.0 (CH), 128.8 (C), 125.9 (C), 119.6 (CH), 106.7 (CH), 32.6 (CH_2); IR (KBr): $\tilde{\nu} = 3415$, 3019, 2921, 2857, 1562, 1503, 1456, 1389, 1370, 1103, 823, 688 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1077 [H$_3$(**1a**)$_3$Zn$_2^+$], 1144 [Na$_3$(**1a**)$_3$Zn$_2^+$]; $C_{60}H_{42}Na_2N_6O_6Zn_2 \cdot 8H_2O$: calcd. C 57.02, H 4.63, N 6.65; found C 57.00, H 4.76, N 6.38.

K$_2$[(1a)$_3$Zn$_2$]: Yellow hygroscopic solid; yield: 85%; ^{1}H NMR ([D$_6$]DMSO): $\delta = 8.22$ (d, $J = 7.7$ Hz, 6H), 7.85 (d, $J = 3.7$ Hz, 6H), 7.47 (d, $J = 8.1$ Hz, 6H), 7.31, (dd, $J = 3.7$, 7.7 Hz, 6H), 6.77 (d, $J = 8.1$ Hz, 6H), 3.36 (m, 6H), 2.26 (m, 6H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 161.0$ (C), 143.2 (CH), 140.1 (C), 137.8 (CH), 131.4 (CH), 129.1 (C), 125.0 (C), 120.0 (CH), 106.6 (CH), 32.7 (CH_2); IR (KBr): $\tilde{\nu} = 3394$, 1561, 1503, 1454, 1390, 1368, 1103, 822, 804, 688 cm^{-1}; FAB$^+$-MS (3-NBA): m/z: 1077 [H$_3$(**1a**)$_3$Zn$_2^+$]; FAB$^-$-MS (3-NBA): m/z: 1113 [K(**1a**)$_3$Zn$_2^-$]; $C_{60}H_{42}K_2N_6O_6Zn_2 \cdot 9H_2O$: calcd. C 54.84, H 4.60, N 6.40; found C 55.19, H 4.97, N 5.63.

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