Letter

# A versatile di(8-hydroxyquinoline) building block for supramolecular as well as metallo-supramolecular chemistry†

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**In the solid state the di(8-hydroxyquinoline) derivative 2-$H_2$ forms a hydrogen bonded polymer while with gallium(III) nitrate a cryptate-type triple-stranded *meso*-helicate $[M \subset \{(2)_3Ga_2\}]^+$ is obtained in the presence of the appropriate alkali metal cations as templates. The templates can have a crucial influence on the self-recognition of the ligands, if the complex formation is performed with ligand mixtures.**

Supramolecular aggregates are formed by self-assembly of two or more molecular components. To investigate such processes appropriate building blocks that have the potential to form non-covalent bonds with other species or with themselves must be available.[1] In this respect 8-hydroxyquinoline represents a versatile species.[2] By hydrogen bonding 8-hydroxyquinoline forms a dimer.[3] Deprotonation and complex formation with metal ions leads to metallo-supramolecular species.[4] Additionally, π–π interactions of the electron-rich portion of the aromatic moiety with the corresponding electron-deficient part can influence the "super"-structure that is observed in the solid state.[3]

Recently we described the template-directed self-assembly of triple-stranded helicates from the ethylene-bridged di(8-hydroxyquinoline) ligand **1**-$H_2$ and gallium(III) ions. The di(8-hydroxyquinoline) derivative **1**-$H_2$ itself forms a linear polymer in the solid state by hydrogen bonding.[5] Herein we discuss derivative **2**-$H_2$, which possesses three carbon atoms in the spacer (Fig. 1). We present the solid state "super"-structure of **2**-$H_2$, its coordination chemistry with gallium(III) ions and its ability for template-directed self-recognition in the presence of ligand **1**-$H_2$.

The compound **2**-$H_2$ is prepared in a very simple two-step procedure starting from 8-hydroxyquinoline.[6] In the $^1H$ NMR spectrum of **2**-$H_2$ (DMSO-$d_6$) the signal of the vinylic proton appears at δ 4.66.

**2**-$H_2$ crystallizes in the orthorhombic space group *Pbcn*.‡ The monomeric species **2**-$H_2$ adopts a "V-type" structure with an anti-conformation of the OH and N binding sites. A linear polymeric structure is formed by hydrogen bonding in the solid state. The monomeric units of this polymer are arranged as shown in Fig. 2. Interstrand π–π interactions of the aromatic units lead to a condensed three-dimensional structure.

The derivative **2**-$H_2$ forms with gallium(III) ions, $[Ga(NO_3)_3]$, in methanol an insoluble undefined mixture of neutral coordination compounds of the general formula $[(2)_3Ga_2]_n$ {elemental analysis: $[(2)_3Ga_2] \cdot 11H_2O$}. However, if the reaction is performed in the presence of alkali metal cations (M = K, Rb, Cs) well-defined cryptates $[M \subset \{(2)_3Ga_2\}]^+$ are obtained in a template-directed self-assembly process.§ Characteristic peaks are detected for the cryptates $[M \subset \{(2)_3Ga_2\}]^+$ by positive FAB mass spectrometry (3-NBA as matrix) at $m/z$ = 1199 (M = K), 1245 (M = Rb), and 1293 (M = Cs). In the $^1H$ NMR spectrum (DMSO-$d_6$) of $[K \subset \{(2)_3Ga_2\}]^+$ two doublets are observed at δ 3.57 and 3.18 ($J$ = 16.6 Hz) for the protons in the benzylic position, which become diastereotopic upon complex formation. The signal of the vinylic protons is detected at δ 4.24. The unusual high-field shift of this signal indicates that the protons are located in the anisotropic region of the aromatic units of

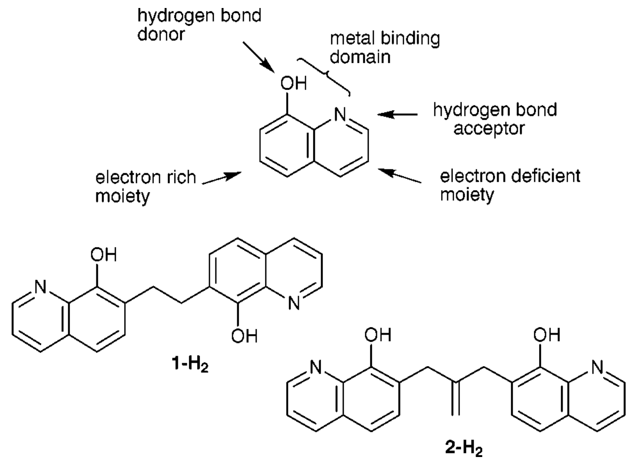


**Fig. 1** Features of the 8-hydroxyquinoline moiety and the ligands **1**-$H_2$ and **2**-$H_2$.

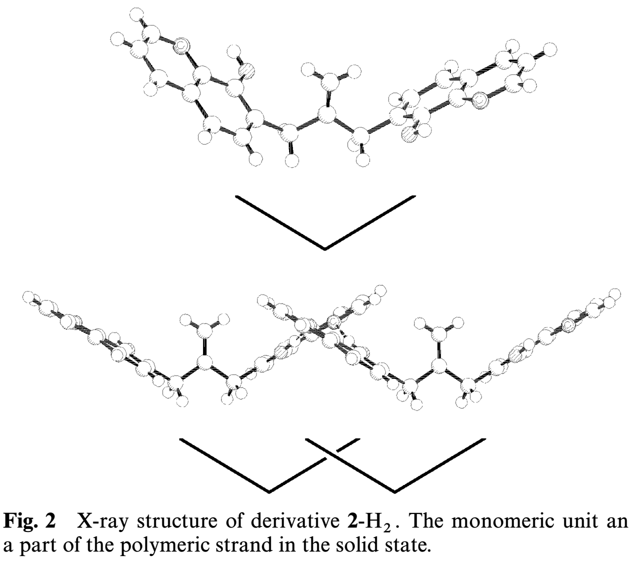
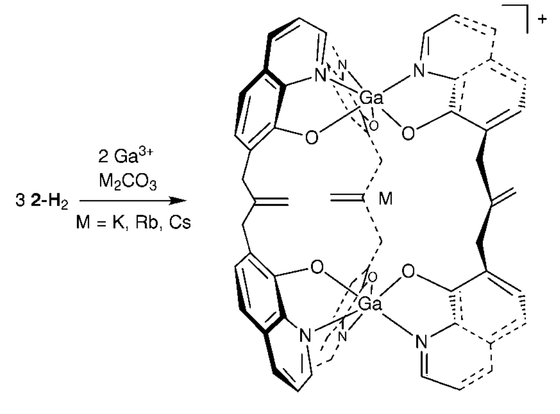


**Fig. 2** X-ray structure of derivative **2**-$H_2$. The monomeric unit and a part of the polymeric strand in the solid state.



$[\text{M}(\mathbf{2})_3\text{Ga}_2]^+$

**Scheme 1** Template-assisted self-assembly of $[\text{M} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$.

$$3\,\mathbf{1}\text{-H}_2 + 3\,\mathbf{2}\text{-H}_2 + 4\,\text{Ga}^{3+} \xrightarrow[-6\,\text{H}^+]{\text{NaCl/CsCl}} [\text{Na}(\mathbf{1})_3\text{Ga}_2]\text{Cl} + [\text{Cs}(\mathbf{2})_3\text{Ga}_2]\text{Cl}$$

**Scheme 2** Template-directed self-recognition of the ligands $\mathbf{1}$-$H_2$ and $\mathbf{2}$-$H_2$ during complex formation.

the ligands **2**. This and the appearance of the signal as a singlet is in accordance with a *meso*-helicate structure as depicted in Scheme 1 and is as would be expected for a triple-stranded dinuclear complex formed from a ligand with an odd number of carbon atoms in the spacer.[10] The NMR spectra of $[\text{M} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$ (M = Rb, Cs) are similar to the one discussed for the potassium compound. The results of preliminary X-ray studies support the structural assignment in solution.[11]

If mixtures of different ligand strands are used for the formation of helicate-type complexes, self-recognition can lead to the exclusive formation of homoleptic coordination compounds. The self-recognition may be controlled by different numbers of metal binding sites or by different spacer lengths.[12] As an alternative we have found an example where the counter ion present influences the homo- or hetero-recognition of ligands during complex formation.[13]

As shown in Scheme 2, reacting a mixture of the two ligands $\mathbf{1}$-$H_2$ (1.5 equiv.) and $\mathbf{2}$-$H_2$ (1.5 equiv.) with two equivalents of gallium(III) nitrate in methanol in the presence of sodium as well as caesium chloride (1 : 1 mixture) gave only the homoleptic complexes $[\text{Na} \subset \{(\mathbf{1})_3\text{Ga}_2\}]^+$ and $[\text{Cs} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$, obtained in a template-directed self-recognition process. No mixing of the ligands is observed. In the $^1$H NMR spectrum (DMSO-$d_6$) signals of the two dinuclear complexes are detected at δ 8.66 (m, 6 H), 7.58–7.56 (m, 12 H), 7.45 (d, $J$ = 8.4 Hz, 6 H), 7.27 (d, $J$ = 8.4 Hz, 6 H), 4.11 (s, 6 H), 3.59 (d, $J$ = 16.9 Hz, 6 H), and 3.14 (d, $J$ = 16.9 Hz, 6 H) for $[\text{Cs} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$ and δ 8.66 (m, 6 H), 7.69 (d, $J$ = 8.4 Hz, 6 H), 7.54 (dd, $J$ = 4.6, 7.9 Hz, 6 H), 7.37 (d, $J$ = 4.6 Hz, 6 H) and 7.31 (d, $J$ = 8.4 Hz, 6 H) for $[\text{Na} \subset \{(\mathbf{1})_3\text{Ga}_2\}]^+$; the signals of the spacer are hidden under the solvent peaks. The positive FAB mass spectrum (3-NBA as matrix) shows the corresponding peaks at $m/z$ = 1105 ($[\text{Na} \subset \{(\mathbf{1})_3\text{Ga}_2\}]^+$) and 1293 ($[\text{Cs} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$).

Here the self-recognition of the ligands during the formation of the dinuclear gallium complexes is controlled by the size of the templates that are present (sodium *versus* caesium). The relatively small sodium cation preferably binds in the interior of the small metalla-cryptand $[(\mathbf{1})_3\text{Ga}_2]$ while the larger caesium cation is encapsulated by $[(\mathbf{2})_3\text{Ga}_2]$.

In summary, we have shown that the di(8-hydroxyquinoline) derivative $\mathbf{2}$-$H_2$ in the solid state forms a hydrogen-bonded polymer. Metal-directed self-assembly in the presence of gallium(III) ions and appropriate alkali metal cation templates affords dinuclear triple-stranded *meso*-helicates $[\text{M} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$. Performing the self-assembly with a mixture of ligands $\mathbf{1}$-$H_2$ and $\mathbf{2}$-$H_2$ and a 1 : 1 mixture of sodium and caesium chloride leads to the exclusive formation of the homoleptic complexes $[\text{Na} \subset \{(\mathbf{1})_3\text{Ga}_2\}]^+$ and $[\text{Cs} \subset \{(\mathbf{2})_3\text{Ga}_2\}]^+$. The presented results show that derivatives like $\mathbf{2}$-$H_2$ possess a high potential as building blocks for supramolecular as well as metallo-supramolecular chemistry.

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## Notes and references

† Dedicated to Professor Gerhard Schröder on the occasion of his 70th birthday.

‡ X-Ray structural analysis of $\mathbf{2}$-$H_2$ : $C_{22}H_{18}N_2O_2$, $M = 342.38$, orthorhombic, $a = 10.366(1)$, $b = 11.528(1)$, $c = 14.350(1)$ Å, $U = 1714.8(3)$ Å$^3$, space group $Pbcn$, $\mu(\text{MoK}\alpha) = 0.086$ mm$^{-1}$, $Z = 4$, $D_c = 1.326$ g cm$^{-3}$, $F(000) = 720$, $T = 173(2)$ K. Data were recorded with a Nonius Kappa CCD diffractometer, using 200 frames, each frame covering a 1° oscillation with an exposure time of 2 × 15 seconds. 2046 collected reflections, 2046 unique reflections [1660 $I > 2\sigma(I)$] were used for refinement. The data were processed with Denzo $L_p$ correction. Structure solution by direct methods and refinement on $F^2$.[7–9] The hydrogen atoms were calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and were refined as riding atoms. The final $R$ values were $R = 0.0426$, $wR^2 = 0.1040$ [$I > 2\sigma(I)$], $R = 0.0564$, $wR^2 = 0.1117$ (all data) for 120 parameters. A final difference map displayed no electron density higher than 0.21 e Å$^{-3}$.

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§ Ligand $\mathbf{2}$-$H_2$ was synthesized as described in the literature.[6] Preparation of $[\text{K} \subset \{(\mathbf{2})_3\text{Ga}_2\}]\text{Cl}$: $\mathbf{2}$-$H_2$ (25 mg, 0.07 mmol) and $\text{Ga(NO}_3)_3 \cdot \text{H}_2\text{O}$ (11.2 mg, 0.05 mmol) are refluxed in methanol (10 ml) in the presence of KCl (50 mg) for 15 h. The precipitate is collected and washed with ice water. Yield: 25.0 mg (74%); $^1$H NMR (DMSO-$d_6$): δ 8.65 (dd, $J$ = 1.2, 8.3 Hz, 6 H), 7.54 (dd, $J$ = 4.8, 8.3 Hz, 6 H), 7.44 (m, 12 H), 7.26 (d, $J$ = 8.4 Hz, 6 H), 4.24 (s, 6 H), 3.57 (d, $J$ = 16.6 Hz, 6 H), 3.18 (d, $J$ = 16.6 Hz, 6 H); $^{13}$C NMR (DMSO-$d_6$): δ 155.0 (C), 148.1 (C), 143.8 (CH), 140.9 (CH), 136.1 (C), 132.9 (CH), 128.3 (C), 123.2 (C), 121.6 (CH), 111.9 (CH), 107.5 ($CH_2$), 37.1 ($CH_2$); positive FAB MS (3-NBA): $m/z$ = 1199 [M − Cl]$^+$; anal. calc. for $C_{66}H_{48}ClGa_2KN_6O_6 \cdot 9H_2O$: C 56.73, H 4.76, N 6.01; found: C 56.37, H 4.23, N 6.07%.

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