Solubilization of a self-assembled metallocryptand by addition of K^+

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The insoluble self-assembled neutral coordination compound $Ga_2L^1{}_3$ can be solubilized by binding of K^+ if the ligand H_2L^1 with internal oxygen atoms is used.

Helicates are formed in spontaneous self-assembly processes from linear oligo-donor ligands and appropriate metal ions. If nitrogen donors are used, cationic[1] or neutral[2] complexes are obtained, while oxygen donor ligands lead to anionic supramolecular species.[3,4] In recent studies we could show that anionic helicates, which are formed from alkyl-bridged dicatecholate ligands and titanium(iv) ions, are able to bind alkali-metal counter ions in a cryptate-type fashion.[4]

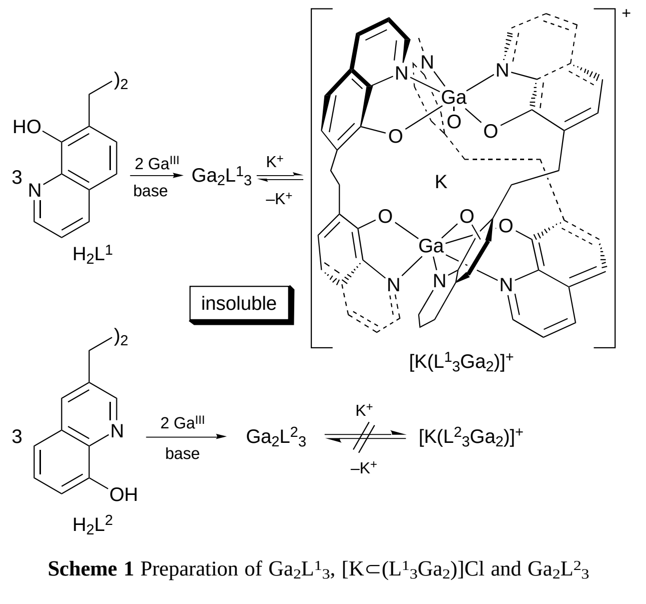
To investigate the cation binding ability of neutral self-assembled metallo-supramolecular hosts[5] we synthesized the ethylene-bridged di(8-hydroxyquinoline) ligands H_2L^1 and H_2L^2.[6] Upon formation of dinuclear triple-stranded complexes with metal ions M^{3+} either a cryptand-type compound $M_2L^1{}_3$ with internal oxygen atoms or a cage molecule $M_2L^2{}_3$ without internal donor atoms should be obtained. The latter is not able to bind alkali-metal cations in its interior.[7]

To prove this hypothesis we performed the reaction of H_2L^1 or H_2L^2 (3 equiv.) with $Ga(NO_3)_3 \cdot H_2O$ (2 equiv.) in the presence of sodium carbonate (3 equiv.) as base in methanol (Scheme 1). Heating overnight afforded yellow solids in quantitative yields. The compounds were insoluble in common solvents but elemental analysis shows the composition $Ga_2L_3 \cdot xH_2O$ (L^1, x = 8; L^2, x = 7).†

If $Ga_2L^1{}_3$ is suspended in $(CD_3)_2SO$ and a large excess of potassium chloride or potassium chlorate is added and the sample is heated to 160 °C, the solution starts to turn yellow. The ^1H NMR spectrum (500 MHz, 296 K, Fig. 1) reveals the signals of the ligating moieties of L^1 at δ 8.67 (dd, *J* 1.0, 8.4 Hz), 7.94 (dd, *J* 1.0, 4.8 Hz), 7.76 (d, *J* 8.4 Hz), 7.62 (dd, *J* 4.8, 8.4 Hz), and 7.31 (d, *J* 8.4 Hz). Resonances of diastereotopic protons of the alkyl spacer at δ 3.08 (m) and 2.69 (m) show the presence of chiral metal complex units. Corresponding ^{13}C NMR signals (125 MHz, 296 K) are observed at δ 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) and 31.0 (CH_2). In accordance with our earlier work on related dinuclear catecholate–titanium systems the compound should adopt the chiral helicate[4] and not the achiral *meso*-helicate[8] structure.

Preparation of $Ga_2L^1{}_3$ in the presence of a large amount of potassium chloride (70 equiv.) leads to a yellow precipitate from methanol which is soluble in $(CD_3)_2SO$ and gives rise to an NMR spectrum as discussed above. FAB(+) mass spectrometry [Fig. 2, 3-nitrobenzyl alcohol (3-NBA) matrix] confirms that a cationic species $[K(L^1{}_3Ga_2)]^+$ is obtained. At high molar masses exclusively the peak of $[K(L^1{}_3Ga_2)]^+$ can be observed (*m/z* 1121, correct isotopic pattern). An analytically pure sample of $[K(L^1{}_3Ga_2)]Cl \cdot 8H_2O$† was obtained by washing the solid material with a small amount of water. Extracting $[K(L^1{}_3Ga_2)]Cl$ with a large amount of water leads to the removal of KCl to give the insoluble neutral complex $Ga_2L^1{}_3$. Upon heating of $[K(L^1{}_3Ga_2)]Cl$ in $(CD_3)_2SO$ no dynamic behaviour can be observed by NMR spectroscopy up to 430 K indicating a remarkable configurational stability of the complex.[3,8]

$[K(L^1{}_3Ga_2)]Cl$ can be crystallized from dmf–diethyl ether. Preliminary results of an X-ray structure analysis[9] unambiguously show that the complex in the solid state adopts a helical structure and that the K^+ ion is located in the interior of the dinuclear gallium cryptand.



Scheme 1 Preparation of $Ga_2L^1{}_3$, $[K{\subset}(L^1{}_3Ga_2)]Cl$ and $Ga_2L^2{}_3$

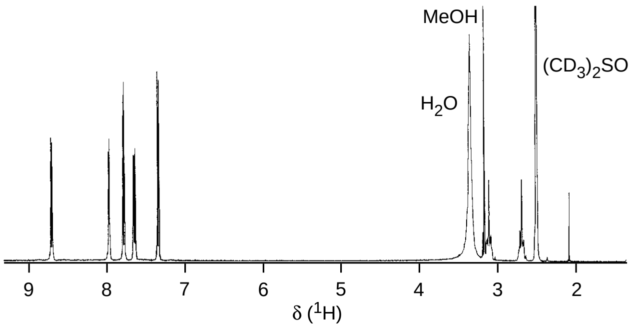


Fig. 1 ^1H NMR spectrum of $[K{\subset}(L^1{}_3Ga_2)]Cl$ in $(CD_3)_2SO$

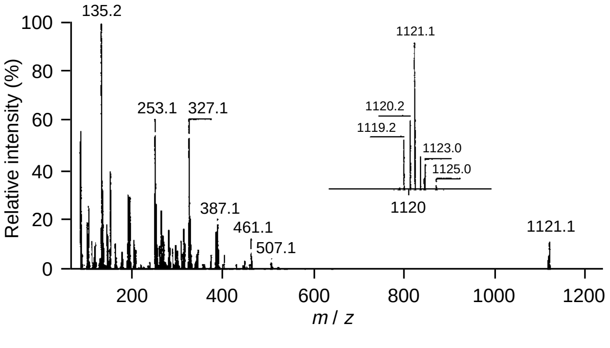


Fig. 2 Positive FAB mass spectrum of $[K{\subset}(L^1Ga_2)]Cl$ (3-NBA matrix)

Due to the lack of internal oxygen donors, $Ga_2L^2{}_3$ is not solubilised by addition of potassium cations and heating to 160 °C. No endohedral complex with the alkaline-metal cation is formed in this case.

To summarise, we introduced a new ligand H_2L^1 for metallo-supramolecular chemistry which upon coordination to Ga^{III} forms the neutral insoluble complex $Ga_2L^1{}_3$. Addition of potassium salts leads to the soluble inclusion compound $[K\subset(L^1{}_3Ga_2)]Cl$. By contrast, no soluble material can be obtained by addition of K^+ to the ligand H_2L^2, which does not possess internal oxygen atoms. Future work will focus on the nature of the insoluble coordination compound $Ga_2L^1{}_3$ and on its behaviour in the presence of different metal cations.

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Footnote

† Anal. Calc. for $C_{60}H_{42}Ga_2N_6O_6\cdot8H_2O$ ($Ga_2L^1{}_3\cdot8H_2O$): C, 58.75; H, 4.77; N, 6.85. Found: C, 58.62; H, 4.38; N, 6.89. Calc. for $C_{60}H_{42}ClGa_2KN_6O_6\cdot8H_2O$ $\{[K(L^1{}_3Ga_2)]Cl\cdot8H_2O\}$: C, 55.39; H, 4.49; N, 6.46. Found: C, 55.11; H, 4.40; N, 6.23. Calc. for $C_{60}H_{42}Ga_2N_6O_6\cdot7H_2O$ ($Ga_2L^2{}_3\cdot7H_2O$): C, 59.63; H, 4.67; N, 6.95. Found: C, 59.80; H, 4.46; N, 6.81%.

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