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[9] Crystal data for $[\{Ru_2(O_2CCF_3)_4\}_2(TCNQ)\cdot 3(C_7H_8)]_\infty$ (**1**): $C_{49}H_{28}N_4O_{16}F_{12}Ru_4$, monoclinic, space group $C2/m$, $a = 16.682(3)$, $b = 20.881(4)$, $c = 8.6120(17)$ Å, $\beta = 95.47(3)°$, $V = 2986.2(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.736$ g cm^{-3}, $\mu = 1.10$ mm^{-1}, $F(000) = 1524.00$, $R1$ ($wR2$) = 0.0350 (0.0843) ($I > 2\sigma(I)$), $R1$ ($wR2$) = 0.1536 (0.0961) (all data), GOF = 0.940. Crystal data for $[\{Rh_2(O_2CCF_3)_4\}_2(TCNQ)\cdot 3(C_7H_8)]_\infty$ (**2**): $C_{49}H_{28}N_4O_{16}F_{12}Rh_4$, monoclinic, space group $C2/m$, $a = 16.793(3)$, $b = 20.806(4)$, $c = 8.4450(17)$ Å, $\beta = 95.54(3)°$, $V = 2936.9(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.774$ g cm^{-3}, $\mu = 1.21$ mm^{-1}, $F(000) = 1532.00$, $R1$ ($wR2$) = 0.0471 (0.1202) ($I > 2\sigma(I)$), $R1$ ($wR2$) = 0.0689 (0.1360) (all data), GOF = 0.997. Data were collected on a Bruker SMART CCD diffractometer in the range $1.57 < 2\theta < 28.32$ for **1** and $1.56 < 2\theta < 28.26$ for **2** at 110(2) K with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Of the 18164 and 9188 unique reflections, 3747 and 3548 were unique for **1** and **2**, respectively. The structures were solved by direct methods (SHELXS-97)[26] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[27] The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Full-matrix least-squares refinement was based on 3747 reflections ($I > 2.00\sigma(I)$) for **1** and 3548 reflections ($I > 2.00\sigma(I)$) for **2**. The highest peaks in the final difference map were 1.272 and 1.546 e$^-$ Å^{-3} for **1** and **2**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145608 (**1**) and CCDC-145609 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supramolecular Chemistry of Anionic Cobalt(III) Bis(dicarbollide) and Cyclotriveratrylene in the Solid State and the Gas Phase**

Michaele J. Hardie and Colin L. Raston*

Despite the fundamental role played by anionic species in many natural processes the supramolecular chemistry of anions has been one of the least explored aspects of supramolecular chemistry.[1] While the neutral, isomeric icosahedral carboranes *o*, *m*, *p*-$C_2B_{10}H_{12}$, for instance, are emerging as versatile components in supramolecular systems, forming hydrogen-bonded complexes [2] and host–guest species with a range of host molecules and assemblies,[3–9] studies on the supramolecular chemistry of anionic carboranes, or indeed anionic boranes, are limited. The most significant example of the binding of a borane anion in a supramolecular system is that of the divalent anion $[B_{10}H_{10}]^{2-}$ which forms a host–guest

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[*] Prof. C. L. Raston, Dr. M. J. Hardie
Department of Chemistry
Monash University
Clayton, Melbourne, Victoria 3800 (Australia)
Fax: (+613) 9905-4597
E-mail: c.raston@sci.monash.edu.au

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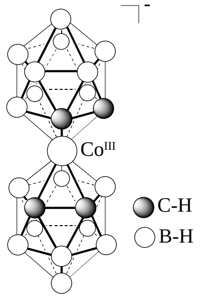
complex with a trimeric mercury–carborane macrocycle.[10] As part of our studies on the binding of large molecules with convex surfaces, including spherical molecules such as carboranes and fullerenes, by curved host molecules we have investigated the host–guest chemistry of the aspherical carborane anion cobalt(III) bis(dicarbollide) $[Co(C_2B_9H_{11})_2]^-$ (**1**) with the rigid bowl-shaped cyclic molecule cyclotriveratrylene (**2**; CTV). The 23 vertex complex **1** is known to be a weakly coordinating anion[11] and herein its use in supramolecular chemistry is established for the first time. CTV forms intracavity host–guest complexes with large spherical main group cage molecules such as fullerenes [8, 12] and *o*-carborane,[7, 8] as well as with cationic organometallic complexes such as $[FeCp(C_6H_5R)]^+$ (Cp = cyclopentadiene).[13] However, small organic molecules are not usually bound as intracavity guests in the solid state, rather they form channel-type structures with intercalated organic molecules situated in spaces created by the homo-assembled CTV packing motif.[14] Recently we demonstrated that CTV can act as a ligand towards Group 1 metals in complexes such as $[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane),[9] where the Na^+, CTV, water, and hydroxide form a coordinate and hydrogen-bonded infinite two-dimensional (2D) array. The normal inclusion properties of CTV within the array are altered with *N,N′*-dimethylformamide (DMF) being complexed as an intracavity guest molecule; DMF does not usually form any type of complex with CTV.[15]



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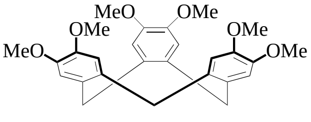

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Mixing equimolar quantities of Na-**1** and CTV in polar organic solvents such as acetonitrile, DMF, or 2,2,2-trifluoroethanol yields a yellow powder, the microanalysis of which is consistent with the formula $[Na(CTV)][Co(C_2B_9H_{11})_2]$. The powder can be recrystallized from very dilute 2,2,2-trifluoroethanol solutions or from more concentrated 2,2,2-trifluoroethanol solutions with a trace of DMF to give orange crystals of $[Na(CTV)][Co(C_2B_9H_{11})_2](CF_3CH_2OH)_{0.25}$ (**3**). The crystals rapidly lose solvent when removed from their mother liquor; their composition and structure were determined from X-ray diffraction data collected at 123(1) K.[16] The structure has several interesting features: a novel two-dimensional sodium–CTV coordination polymer, intracavity host–guest complexation of CF_3CH_2OH molecules by CTV, and the presence of the large organometallic anion **1** within the channels created by the packing of the coordination polymers.

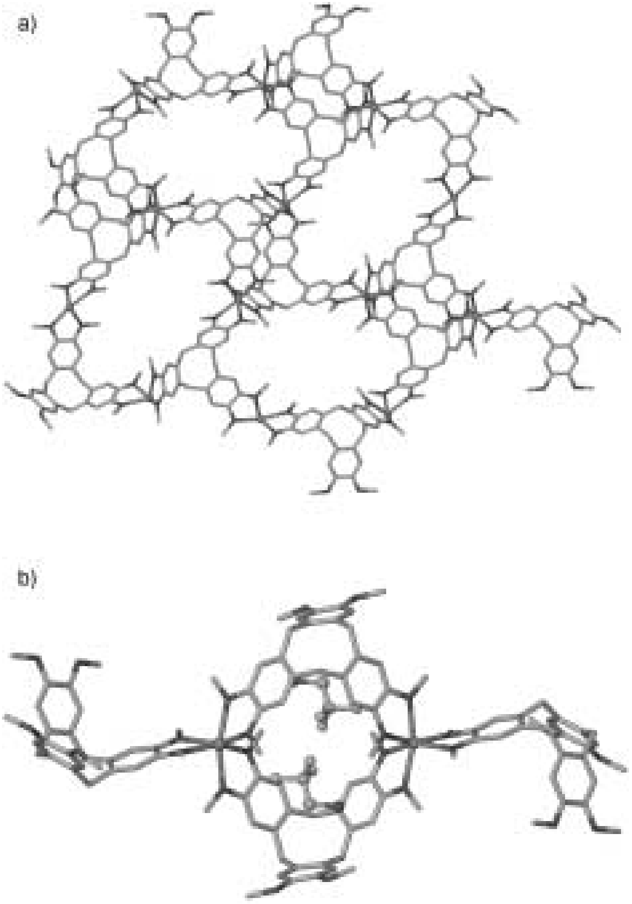

Figure 1. a) Section of the 2D network formed by Na^+ ions and CTV ligands in the complex **3**. The network topology is that of a three-connected 4:8 plane net. b) CTV–CF_3CH_2OH host–guest cavity (see text). Closest F ··· F contact is 2.69 Å, however, each CF_3CH_2OH molecule is estimated to have a 25 % occupancy, giving an approximately 6 % probability of two CF_3CH_2OH guests inhabiting one cavity as shown here and about a 56 % chance of the cavity being empty.

The sodium–cyclotriveratrylene coordination polymer of **3** is shown in Figure 1 a. All the sodium ions and CTV molecules within the polymer are crystallographically equivalent. The Na^+ ion is six coordinate with three chelating CTV ligands having Na–O bond lengths between 2.310(2) and 2.369(2) Å, and is in a highly distorted octahedral environment (*cis* angles range from 67.13(6) (chelate ring) to 110.00(7)°, *trans* angles 152.66(8), 155.81(7), and 160.16(7)°). Adjacent Na^+ centers within the network have opposite configurations, hence the network is not chiral (Figure 1 b). The orientation of the CTV bowls around each Na^+ ion alternates between two up, one down and one up, two down throughout the network. The previous example of CTV acting as a chelating ligand has two CTV molecules around the Na^+ or K^+ centers and in the latter case a coordinate chain is formed.[9] Each CTV molecule is a μ_3 bridging ligand coordinating to three Na^+ ions, thus creating a two-dimensional infinite network where both Na^+ and CTV act as three-connectors. The network topology is described according to classification by Wells as a three-connected 4:8 plane net,[17] which means every node within the net, in this case sodium cations and the centers of the CTV molecules, connects to three others creating tetra-gons and octa-gons as the shortest loops. To the best of our knowledge this is the first time such a network topology has been observed in a coordination polymer; three-connected 2D networks more commonly adopt the (6,3) net which features hexa-gons as the only type of shortest loop.[18] The 4:8 topology is known for the hydrogen-bonded network of caprolactam and the layer structures of LnB_2C_2 (Ln = lanthanide), $BaFeSi_4O_{10}$, and $CaCuSi_4O_{10}$.[17]

The network is not planar, it has two tiers of Na centers and the connections between them are the topological tetra-gons. These tetra-gons form host–guest cavities within the network by virtue of the curved, bowl-like nature of CTV, and because the bowls are in opposite and inward orientations (Figure 1 b). The distance across the cavity, defined by the distance between the centroids of the methylene planes of the CTV molecules, is 11.2 Å. For each CTV molecule there is a guest molecule of CF_3CH_2OH situated with its CH_2 group directly over the center of the CTV bowl (C$\cdots$center of CTV methylene plane 4.33 Å), however the occupancy of the CF_3CH_2OH molecule is estimated at only 25 %[16] and hence the cavities are largely empty. Nevertheless this is a distinctly different host–guest behavior to that usually associated with CTV.

The $[Na(CTV)]_\infty$ network has large holes, which are apparent in Figure 1 a, with an approximate cross section of 3.5 × 10.9 Å (measured as the closest H$\cdots$H distances between OMe groups). In the overall crystal lattice, the $[Na(CTV)]_\infty$ networks pack so that these holes are more or less aligned, thus creating methyl-lined channels of roughly circular cross section. One of the three arene faces of each CTV shows a π–π stacking interaction at a separation of 3.6 Å to the centroid of CTV from its adjacent network. This manner of network packing is contrary to close-packing considerations and is therefore likely to arise from templation by the large organometallic ion $[Co(C_2B_9H_{11})_2]^-$ (**1**) which occupies the channels (Figure 2 a). There are two crystallographically distinct types of **1** both of which have their Co core positioned on a center of symmetry and have different staggered arrangements of carborane ligands with C–C$\cdots$C–C torsion angles of −41° and 0°. Reported X-ray structures of **1** are either disordered or have a staggered arrangement.[19] The $[Co(C_2B_9H_{11})_2]^-$ ions within the circular channels, shown in purple in Figures 2 a b, are positioned 4.34 Å apart (B$\cdots$B distance, the corresponding B–H$\cdots$H–B distance is 2.90 Å) and stack in a slightly offset manner. The second type of **1**, shown in orange, run in zigzag chains perpendicular to the first with a closest B$\cdots$B separation of 5.00 Å (the corresponding B–H$\cdots$H–B distance is 3.48 Å). These anions also occupy channels of diamond-like cross section created by the packing of the $[Na(CTV)]_\infty$ networks as is evident in the complete crystal packing diagram of **3** shown in Figure 2 b. The two types of **1** are quite close to one another with a closest C$\cdots$B distance of 3.75 Å (the corresponding C–H$\cdots$H–B distance is 2.40 Å).

Crystals of **3** are soluble in CF_3CH_2OH and thus the coordination polymer breaks up in solution. The electrospray ionization (ESI) mass spectrum of **3** in CF_3CH_2OH reveals a number of singly charged species present in the gas phase. Peaks at *m/z* 1373, 923, and 473 correspond to $[Na(CTV)_3]^+$, $[Na(CTV)_2]^+$, and $[Na(CTV)]^+$ ions, respectively. These species are also present in the mass spectrum obtained from CTV treated with an equimolar amount of NaCl, and run under similar conditions, along with a number of doubly charged clusters including the $[Na_2(CTV)_3]^{2+}$ ion at *m/z* 698. The $[Na(CTV)_3]^+$ ion is only present in trace amounts with $[Na(CTV)_2]^+$ being the predominant species in the gas phase. The ESI mass spectrum of **3** also contains a series of peaks with a different isotope pattern that shows the formation of host–guest complexes in the gas-phase between the sodium–CTV clusters and the ionic **1**. The complexes $[\{Na_2(CTV)_3\}\{Co(C_2B_9H_{11})_2\}]^+$, $[\{Na_2(CTV)_2\}\{Co(C_2B_9H_{11})_2\}]^+$, and $[\{Na_2(CTV)\}\{Co(C_2B_9H_{11})_2\}]^+$ are present at *m/z* 1721, 1270, and 820, respectively, which is consistent with the observation of $[Na_2(CTV)_3]^{2+}$ ions in the spectrum of CTV

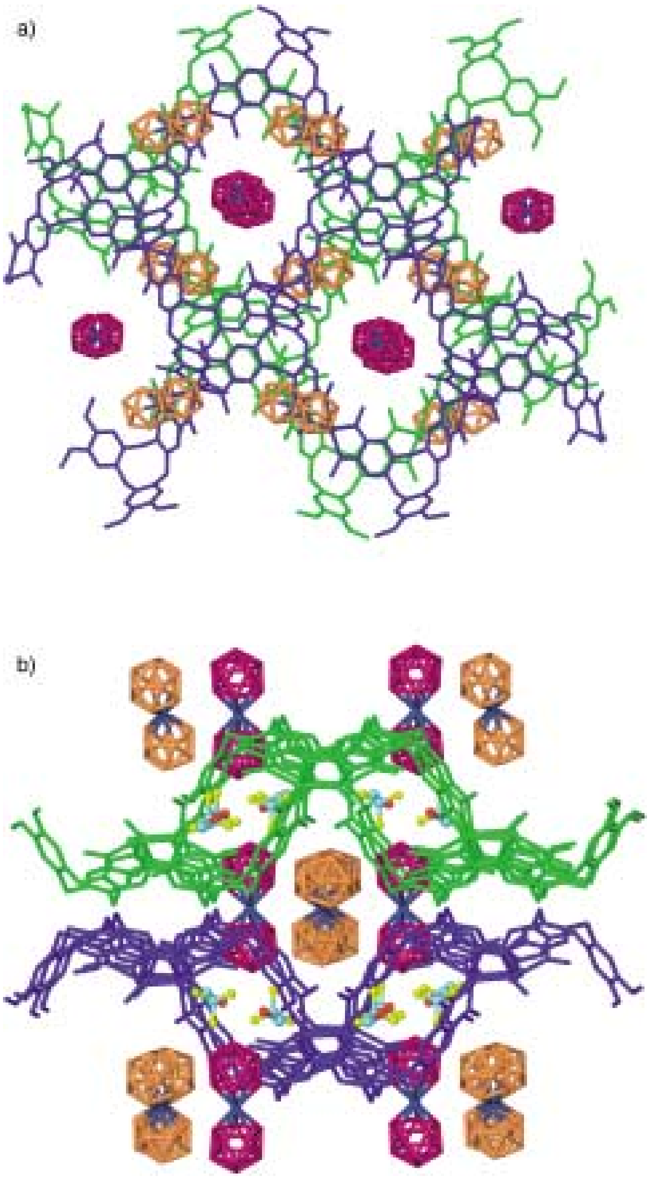

Figure 2. Crystal packing in **3**. a) Packing of two $[Na(CTV)]_\infty$ networks shown in blue and green. The two types of $[Co(C_2B_9H_{11})_2]^-$ ions are highlighted in purple or orange, the C/B positions are not distinguished. Guest CF_3CH_2OH molecules are omitted for clarity; b) crystal packing showing a side-on view of the $[Na(CTV)]_\infty$ networks, highlighting the CF_3CH_2OH-containing cavities within each network and the diamond-like channels created by network packing and occupied by the $[Co(C_2B_9H_{11})_2]^-$ ions shown in orange.

and NaCl. The observed and the calculated isotope pattern for the complex $[\{Na_2(CTV)\}\{Co(C_2B_9H_{11})_2\}]^+$ are shown in Figure 3, and are a convincing match with the observed (820.4687) and calculated (820.4692) m/z values for the major peak. Two cobalt(III) bis(dicarbollide) anions may also be complexed, as evidenced by the small peak at m/z 1617 which corresponds to the complex $[\{Na_3(CTV)_2\}\{Co(C_2B_9H_{11})_2\}_2]^+$. The negative mode ESI mass spectrum of **3** shows only the presence of $[Co(C_2B_9H_{11})_2]^-$ at m/z 324. The use of soft-ionization mass spectrometry to study supramolecular systems has become more prominent in recent years[20] and, while smaller, weakly coordinating anions such as BF_4^- and PF_6^- or small organic anions have been shown to be complexed in the gas phase,[21] the complexation of such a large organometallic anion is particularly noteworthy.

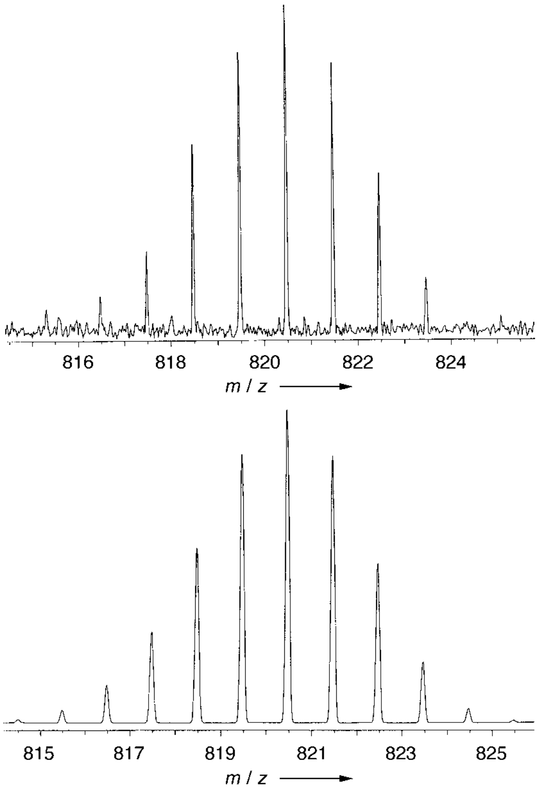

Figure 3. The observed (upper) and calculated (lower) isotope pattern for the host–guest species $[\{Na_2(CTV)\}\{Co(C_2B_9H_{11})_2\}]^+$ from the ESI mass spectrum of **3** in CF_3CH_2OH. The spectrum was run on a Bruker FT mass spectrometer at 65 V.

The solid-state and gas-phase supramolecular behaviors of Na-**1** and CTV are quite distinct. The crystalline complex $[Na(CTV)][Co(C_2B_9H_{11})_2](CF_3CH_2OH)_{0.25}$ features a 2D $[Na(CTV)]_\infty$ coordination polymer with novel topology and layers templated around the counterion **1**. Unusually for CTV, host molecules within the polymer can complex guest solvent molecules, which further supports the argument that the inclusion properties of a known host molecule can be altered by incorporating it into an extended hydrogen-bonded or coordinate network.[8, 9] The $[Na(CTV)]_\infty$ coordination polymer breaks up in solution and $[Na_n(CTV)_m]^{n+}$ clusters are present in the gas phase and can complex one or two molecules of **1**. These findings may prove to form the basis of a general approach to the supramolecular chemistry of metal ion salts of large anions, including reduced fullerenes, in the presence of CTV or indeed related types of rigid, curved receptor molecules.

Experimental Section

Cyclotriveratrylene (20.1 mg, 0.045 mmol) and $Na[Co(C_2B_9H_{11})_2]$ (15.5 mg, 0.045 mmol) were dissolved separately in CF_3CH_2OH and mixed at room temperature to yield $[Na(CTV)][Co(C_2B_9H_{11})_2]$ as a yellow amorphous powder (29.8 mg, 83 %). Elemental analysis calcd for $C_{31}H_{52}B_{18}CoNaO_6$(%): C 46.70, H 6.57; found: C 46.75, H 6.31. Orange prismatic crystals of **3** were grown overnight from dilute solutions of $[Na(CTV)][Co(C_2B_9H_{11})_2]$ in CF_3CH_2OH.

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[16] Crystal data for **3**. Data were collected on a yellow crystal of dimensions 0.38 × 0.18 × 0.10 mm at 123(1) K on an Enraf-Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ radiation. $C_{31.5}H_{53}B_{18}CoF_{0.75}NaO_{6.25}$: $Mr = 822.49$, monoclinic, $C2/c$, $a = 29.9709(4)$, $b = 19.7021(3)$, $c = 19.2700(3)$ Å, $\beta = 129.505(1)$, $V = 8779.5(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.245\ g\,mol^{-1}$, $\mu = 0.445\ mm^{-1}$ (no correction), $\theta_{max} = 28.3°$, 66129 data collected, 10811 unique ($R_{int} = 0.087$), 546 parameters, no restraints, $R_1 = 0.0558$ (7236 data $I > 2\sigma(I)$), $wR_2 = 0.1333$ (all data), $S = 1.040$. The structure was solved by Patterson map and partial structure expansion (SHELXS-97) and refined with a full-matrix least-squares refinement on F^2 (SHELXL-97). Occupancy of the CF_3CH_2OH guest molecule was estimated at 0.25, a more accurate analysis through microanalysis was not possible because the crystals rapidly lost solvent when removed from the mother liquor. The carbon atom positions within the $[Co(C_2B_9H_{11})_2]^-$ ions were assigned by an analysis of anisotropic displacement factors, however, without a neutron diffraction study they should be regarded as tentative. The CF_3CH_2OH guest was refined isotropically otherwise all non-hydrogen atoms were refined anisotropically and all C–H and B–H hydrogen atoms included at calculated positions with a riding refinement. Crystallo-

graphic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144465. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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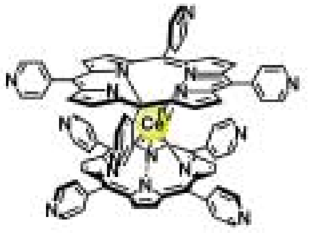
Novel Oligosaccharide Binding to the Cerium(IV) Bis(porphyrinate) Double Decker: Effective Amplification of a Binding Signal through Positive Homotropic Allosterism

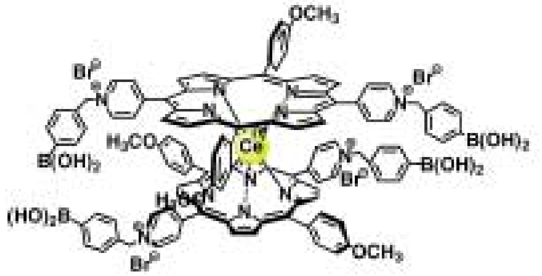
Atsushi Sugasaki, Masato Ikeda, Masayuki Takeuchi, and Seiji Shinkai*

The biomimetic design of allosteric systems is of great significance because they are readily applicable to the efficient regulation of drug release, catalytic reactions, and information transduction.[1] In particular, the positive homotropic allosteric system is useful as a unique tool for amplifying and transforming weak chemical or physical signals into other forms and for constructing novel sensory systems with higher affinity and/or greater selectivity towards analytes. Although there are several examples of artificial heterotropic allosterism in which a substrate and an effector communicate (either positively or negatively) with each other,[1, 2] successful examples of artificial positive homotropic allosterism, however, are very limited.[3–6]

Undoubtedly, the allosteric binding of saccharides that can take place even in aqueous media is essential as a research target in molecular recognition and influential in many related systems: for example, many water-soluble drugs such as vancomycin, ramoplanin, and teicoplanin have a saccharide moiety and the allosteric capture and release of these drugs are of great significance. Previously, we demonstrated that the cerium(IV) bis[tetrakis(4-pyridyl)porphyrinate] double decker (**1**) binds certain dicarboxylic acids in a positive allosteric manner (Hill coefficient 4.0) through hydrogen-bonding interactions to form only the 1:4 complex.[5] In this system the binding of the first dicarboxylic acid to a pair of pyridyl groups through the hydrogen-bonding interaction, although very weak, can suppress the rotation of the two porphyrin planes; as a result, the subsequent binding of the three dicarboxylic acids to the three pairs of aligned pyridyl groups can occur cooperatively. This characteristic double-decker architecture can be used as a scaffold in a system showing positive allosteric binding[6a–c] of saccharides by introducing boronic acid groups, which are known to act as excellent saccharide receptors in aqueous media.[7, 8] By taking these factors into consideration, we designed compound **2** which bears two pairs



1



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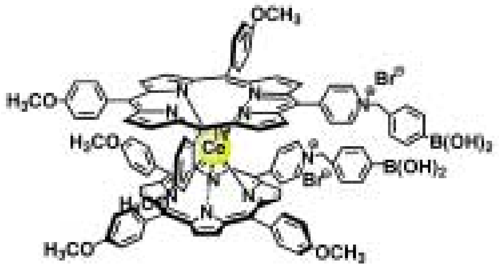

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[*] Prof. S. Shinkai, A. Sugasaki, M. Ikeda, Dr. M. Takeuchi
Department of Chemistry & Biochemistry
Graduate School of Engineering
Kyushu University, Fukuoka 812-8581 (Japan)
Fax: (+81) 92-642-3611
E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

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