Ni(ii) N4-macrocycle grafted crown ether: caesium cobalt(iii) bis(dicarbollide) coordination polymer

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A mixture of a Ni(TMTAA) grafted crown ether and Cs[Co($C_2B_9H_{11}$)$_2$] in toluene–CH_2Cl_2 affords a 1:1 complex, comprised of layers of infinite two-dimensional polymeric arrays separated by layers of the cobalticarborane anion which themselves form two B–H···Cs$^+$ hydrogen interactions.

The development of multipurpose macrocycles or polytopic co-receptor molecules is an integral part of developments in supramolecular chemistry.[1] The nickel(ii) macrocycle (5,7,12,14-tetramethyldibezo[*b,i*]1,4,8,11-tetraazacyclotetradecine)nickel(ii), [Ni(TMTAA)], is a versatile receptor for neutral globular type molecules, including C_{60}, *o*-carborane, and the phosphorus chalcogenide molecules $P_4(S_3$ or $Se_3)$, as well as disc shaped 18-crown-6, and more.[2] The saddle shaped macrocycle has two divergent curved surfaces (methyl and phenyl lined) which predetermine the supramolecular outcomes. We have recently reported a synthetic procedure which incorporates [Ni(TMTAA)] into crown ethers,[3] effectively forming hybrid macrocyclic receptors that may be regarded as grafted crown ether-type molecules, and have the methyl and phenyl lined surfaces of [Ni(TMTAA)] directed *endo* and *exo* relative to the crown ether cavity. We now report the outcome of complexation studies of one of these novel receptors, **1**, with a caesium salt of the large soft anion, cobalt(iii) bis(di-carbollide), [Co($C_2B_9H_{11}$)$_2$]$^-$. The use of anionic carboranes in supramolecular systems has recently been established, with the use of the weakly coordinating anions carborane [$CB_{11}H_{12}$]$^-$,[4,5] and [Co($C_2B_9H_{11}$)$_2$]$^-$, shown to form complexes with cyclotriveratrylene in both the solid and gas phases[5,6] and also with Ni(TMTAA).[7]

Slow evaporation of a toluene–CH_2Cl_2 solution containing **1** and caesium cobalt(iii) bis(dicarbollide), formed by a metathesis reaction between silver cobalt(iii) bis(dicarbollide)[8] and caesium chloride, in *ca.* 1:1 ratio, affords the complex [**1**][Cs(Co($C_2B_9H_{11}$)$_2$)]·CH_2Cl_2·C_6H_5Me, **2**, in 71% yield, Scheme 1.† The product was analysed by ^{1}H NMR, ESI-MS and microanalysis and its solid state structure established by X-ray diffraction studies.‡

Complex **1** crystallises in the chiral space group $P2_12_12_1$. The asymmetric unit of the complex is comprised of a molecule of **1**, Cs$^+$ and Co($C_2B_9H_{11}$)$_2$$^-$, together with a molecule each of toluene and CH_2Cl_2, Fig. 1. The hexaethyleneoxy ether chain in
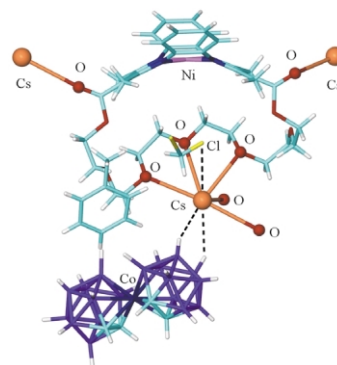

Fig. 1 Cesium coordination sphere in **2**.

2 is folded back upon itself towards one of the benzene rings of the Ni(TMTAA) moiety, as seen previously in the solid state structure of **1**,[3] however, the contortion is not symmetrical. The three central oxygens from the hexaethyleneoxy ether chain bind to the caesium cation, which sits *exo* to the crown ether cavity, together with two hydrogens of the cobalt(iii) bis(di-carbollide) anion which have two close BH···Cs$^+$ contacts (BH···Cs$^+$ (B···Cs$^+$) distance 2.918 (3.817) and 3.299 (3.728) Å). Similar B···Cs distances have been reported previously in a carborane system.[9] Another two oxygens (from carbonyl groups) from two adjacent molecules of **1** complete the caesium coordination sphere. Overall, the caesium ions have a highly unsymmetrical coordination environment. A molecule of CH_2Cl_2 fits snugly into the cavity of the crown ether, with a weak interaction for one of the chlorine atoms with the metal centre (Cl···Cs$^+$ 3.961 Å).

The extended structure of complex **2** is shown in Figs. 2–4. The metal ion–oxygen centres coordination form 2D sheets in the *ab* plane with **1**.Cs$^+$ moieties linked through Cs$^+$···$O_{carbonyl}$ interactions. These 2D sheets are interposed with layers of cobalt(iii) bis(dicarbollide) anions, themselves weakly interacting with the metal centres, as well as toluene molecules,
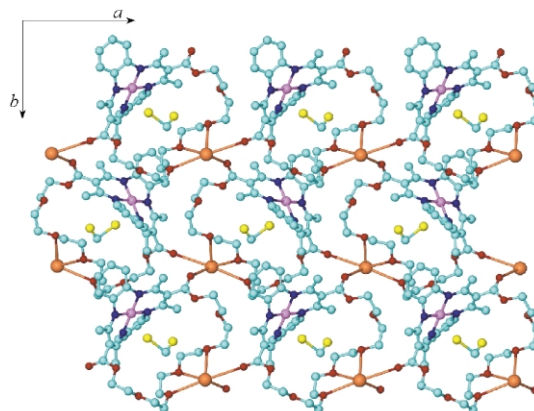
$$Cs^+(Co(C_2B_9H_{11})_2)^- + \mathbf{1} \xrightarrow[\text{slow evaporation}]{CH_2Cl_2(acetone)/toluene} [\mathbf{1}][Cs(Co(C_2B_9H_{11})_2)][CH_2Cl_2][toluene]$$

2

Co($C_2B_9H_{11}$)$_2^-$

Scheme 1

Fig. 2 Infinite two-dimensional coordination polymer formed between **1** and Cs$^+$; hydrogens, toluene molecules and cobalt(iii) bis(dicarbollide) anions have been ommitted for clarity.
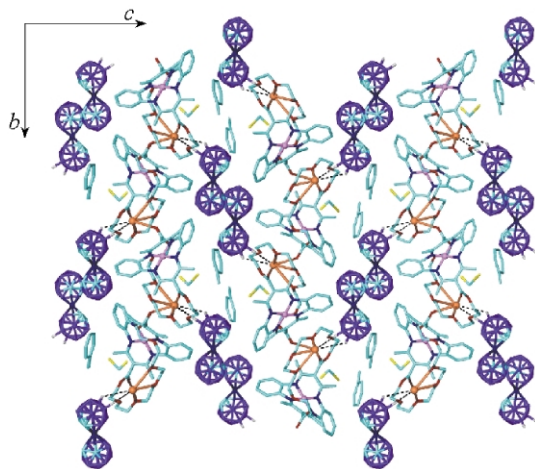
Fig. 3 Layers of the 2-D polymeric arrays running in parallel opposite directions; BH⋯Cs⁺ contacts are shown as dashed lines, and all other hydrogen atoms have been ommitted for clarity.

Fig. 3. There is a helical arrangement of B–H⋯H–C interactions between adjacent cobalt(III) bis(dicarbollide) anions, H⋯H 2.077 and 2.425 Å, Fig. 4. These distances are consistent with those previously observed for non-classical dihydrogen bonds between cobalt(III) bis(dicarbollide) anions in supramolecular arrays.[5,6] Part of the hexaethyleneoxy ether chain resides in the phenyl lined curved face of a Ni(TMTAA) moiety in an adjacent molecule of **1**. Its contortion is such that it presents a complementarity of curvature between the two surfaces.

Studies have also shown interaction in solution. The binding of caesium to the hexaethyleneoxy ether oxygens is observed in the ¹H NMR spectrum by six resonances corresponding to six distinct CH_2 environments. These peaks are shifted considerably when compared to the spectrum of the free ligand,[3] where the six central hexaethyleneoxy ether CH_2 environments are quite similar and their resonances overlap. The spectrum also indicates symmetrical binding of the caesium cation within the crown cavity, molecular modelling showing that the cavity is large enough to accommodate the ion. The ESI mass spectrum shows peaks at m/z 867.15 and 1601.41 corresponding to the
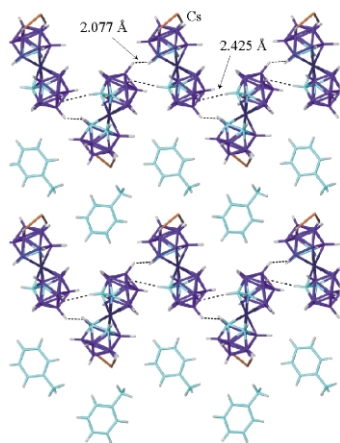

Fig. 4 C-H⋯H–B interplay between the cobalt(III) bis(dicarbollide) anions.

singly charged species **1**.Cs⁺ and **1**₂.Cs⁺ respectively, present in the gas phase.

The synthesis of novel supramolecular receptors takes into account the specific task which they are to perform. However the exact outcome of any complexation experiment can be unpredictable. The result described herein is an example of the successful application of a purpose built receptor; that is, the complexation of an alkali metal cation, forming a novel supramolecular complex.

Notes and references

† Ag[Co(C₂B₉H₁₁)₂] was prepared from commercially available Na-[Co(C₂B₉H₁₁)₂] using the literature procedure.[8]

Cs[Co(C₂B₉H₁₁)₂]: to a solution of silver cobalt(III) bis(dicarbollide) (30 mg, 69.5 μmol) in methanol (5 ml) was added a solution of CsCl (20 mg, 118.8 μmol) in methanol (5 ml). The mixture was filtered, concentrated *in vacuo*, the residue extracted with acetone, filtered and the solvent removed *in vacuo* affording orange crystalline solid in quantitative yield.

[**1**][Cs(C₂B₉H₁₁)₂][CH₂Cl₂][toluene] **2**: caesium cobalt(III) bis(dicarbollide) (8.4 mg, 18.4 μmol) was dissolved in CH₂Cl₂ (4 ml) with the aid of a few drops of acetone. To this was added **1** (15.6 mg, 21.2 μmol) followed by toluene (3 ml). The solution was allowed to slowly evaporate over three to four days. The dark green crystalline product which precipitated from solution was collected by filtration, washed with a little toluene and air dried. Yield 18 mg (71%), mp. 179–184 °C, C₄₈H₇₆B₁₈Cl₂CoCsNiO₉ requires: C 42.11, H 5.59, N 4.09. Found: C 42.07, H 5.49, N 4.07%. ¹H NMR (d_6-DMSO, 300 MHz, 25 °C) δ 2.03 (s, 12H, CH₃), 2.30 (s, 3H, CH₃-toluene), 3.18 (t br, 4H), 3.42 (t br, 4H), 3.49 (m, 4H), 3.54 (m, 4H), 3.68 (m br, 4H, CO₂CH₂CH_2), 3.99 (s br, 4H, BCH), 4.28 (m br, 4H, CO₂CH₂), 5.76 (s, 2H, CH₂Cl₂), 6.66–6.70 (m, 4H, ArH), 6.84–6.87 (m, 4H, ArH), 7.12–7.28 (m, 5H, ArH-toluene). ESI-MS (ES+, 85 v) m/z 734.24 [M⁺], 867.15 [M + Cs⁺], 1468.50 [2M⁺], 1601.41 [2M + Cs⁺].

‡ *Crystal data* for compound **2**: C₄₈H₇₆B₁₈Cl₂CoCsN₄NiO₉, M_r = 1369.16, orthorhombic, $P2_12_12_1$, a = 12.067(2), b = 17.667(4), c = 29.266(6) Å, V = 6239(2) Å³, D_c = 1.458 g cm⁻³, μ = 1.283 cm⁻¹ (semi-empirical), Z = 4, T = 123(2) K, 57742 reflections collected, 14823 unique reflections, R_{int} = 0.0979, θ_{max} = 28.30°, 9735 observed, $I > 2\sigma(I)$, 850 parameters, no restraints, R_1 = 0.0629, wR_2 = 0.1490, S = 1.030. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at geometrically estimated positions. Enraf-Nonius KappaCCD diffractometer, Mo-Kα radiation, crystals mounted in oil.

CCDC reference number 172615.

See http://www.rsc.org/suppdata/cc/b1/b108162d/ for crystallographic data in CIF or other electronic format.

1 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 4 and references therein.
2 P. Andrews, J. L. Atwood, L. J. Barbour, P. J. Nichols and C. L. Raston, *Chem. Eur. J.*, 1998, **4**, 1384; P. C. Andrews, P. D. Croucher, J. L. Atwood, L. J. Barbour, P. J. Nichols and N. O. Smith, *J. Chem. Soc., Dalton Trans.*, 1999, 2927; K. Baranyai, P. J. Nichols and C. L. Raston, *Angew. Chem., Int. Ed.*, 2000, **39**, 1842; P. D. Croucher, P. J. Nichols and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1999, 279.
3 M. J. Hardie, N. Malic, P. J. Nichols and C. L. Raston, *Tetrahedron Lett.*, 2001, **42**, 8075.
4 M. J. Hardie, Nino Malic and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
5 M. J. Hardie and C. L. Raston, *Chem. Commun.*, 2001, 905.
6 M. J. Hardie and C. L. Raston, *Angew. Chem., Int. Ed.*, 2000, **39**, 3835.
7 M. J. Hardie, N. Malic, C. L. Raston and B. A. Roberts, *Chem. Commun.*, 2001, 865.
8 Z. Xie, T. Jelínek, R. Bau and C. A. Reed, *J. Am. Chem. Soc.*, 1994, **116**, 1907.
9 N. S. Hosmane, T. Demissie, H. Zhang, J. A. Maguire, W. N. Lipscomb, F. Baumann and W. Kaim, *Organometallics*, 1998, **17**, 293.