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Confinement of the ions $[\mathrm{M}\subset[2.2.2]\mathrm{cryptand}]^+$ and [cobalt(III)-bis(dicarbollide)]$^-$ in the divergent curved surfaces of a Ni(II) macrocycle

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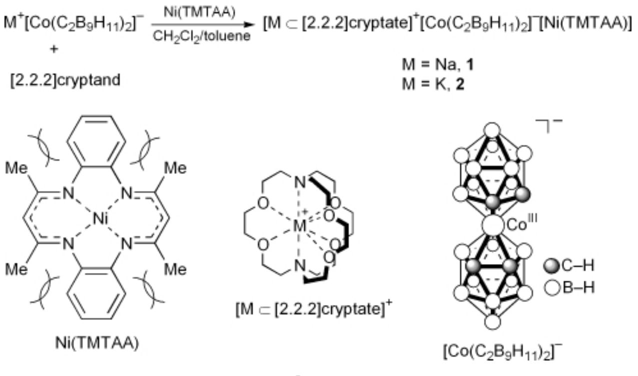
Treatment of $\mathrm{M[Co(C_2B_9H_{11})_2]}$, M = Na or K, with [2.2.2]cryptand and 5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraazacyclotetradecinenickel(II) results in a 1 : 1 : 1 complex, assembled with the cobalticarborane anion snugly residing in the phenyl lined face of the Ni(II) macrocycle through C–H···N and C–H···π interactions, with the ensuing $[\mathrm{M}\subset[2.2.2]\mathrm{cryptand}]^+$ supercation residing in the smaller methyl faced cavity of the macrocycle.

The nickel(II) macrocycle 5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraazacyclotetradecinenickel(II) [Ni(TMTAA)] is a versatile receptor for neutral molecules, forming supramolecular host–guest complexes, as perched structures, with a range of globular cage molecules including C_{60}, *o*-carborane (icosahedral 1,2-$C_2B_{10}H_{12}$) and the phosphorus chalcogenides P_4(S or Se)$_3$,[1,2] and also for disc-shaped $[(\mathrm{H_2O})_2\cap 18\text{-crown-}6]$[3] and torus shaped *cyclo*-octasulfur.[2] Ni(TMTAA) is a rigid, saddle-shaped macrocycle possessing two divergent concave surfaces which arise from the steric interactions of the methyl groups and the adjacent H-atoms on the aromatic rings. It can act as a heterotopic divergent receptor with C_{60}, or it can self-associate into dimers through the phenyl-lined face with the supermolecule acting as a homotopic divergent receptor for a range of molecules. A related macrocyle with two methyl groups on each of the aromatic rings (*trans* to the N-centres) forms 1 : 1 complexes with C_{60}[4] and C_{70}.[5]

We now report the formation of a multicomponent supramolecular array where the Ni(TMTAA) receptor acts as a divergent heterotopic receptor for globular-type ionic species, both the super-cationic and anionic species $[\mathrm{M}\subset[2.2.2]\mathrm{cryptate}]^+$, M = Na or K, and $[\mathrm{Co(C_2B_9H_{11})_2}]^-$, Scheme 1. For the anion this takes on a novel C–H hydrogen bonding array with Ni(TMTAA), with a pre-programmed complementarity of curvature of the two interacting components, which is also the case for the cation to macrocycle interplay. The cobalticarborane or cobalt(III) bis(dicarbollide) is a weakly coordinating anion,[6] able to act as a soft anion in building up supramolecular architecture.[7]

Slow evaporation of $\mathrm{CH_2Cl_2}$/toluene solutions containing a 1 : 1 : 1 mixture of sodium cobalticarborane, [2.2.2]cryptand and Ni(TMTAA) affords the complex $[\mathrm{Na}\subset[2.2.2]\mathrm{cryptate}]^+$-$[\mathrm{Co(C_2B_9H_{11})_2}]^-$[Ni(TMTAA)], **1**, in high yield, Scheme 1.‡ The potassium analogue **2** was similarly prepared by first converting the sodium salt of the cobalticarborane to the potassium salt by treating a 1 : 1 mixture of sodium cobalticarborane and [2.2.2]cryptand with excess $\mathrm{KPF_6}$. Both compounds were characterised by NMR and microanalysis and their structures in the solid state established from X-ray diffraction studies.§

Compounds **1** and **2** are isomorphous and isostructural, crystallising in the space group $P2_1/c$ with the asymmetric unit comprised of $[\mathrm{M}\subset[2.2.2]\mathrm{cryptate}]^+$, $[\mathrm{Co(C_2B_9H_{11})_2}]^-$ and one Ni(TMTAA) molecule. Salient features of the structure are borne out in Fig. 1. There is a striking snug fit of the cobalticarborane in the phenyl-lined face of the macrocycle. Moreover, the pairs of C–H groups (one from each carborane ligand) are adjacent to each other in a staggered conformation, as established elsewhere for this anion,[7] such that the C–H groups from each carborane ligand furthest from each other form non-classical C–H···π hydrogen bonds to their closest aromatic ring, and the other C–H groups form weak hydrogen bonds to a N-centre. Associated distances for C–H···π_{centroid} (C···π_{centroid}) are 2.60 (3.66) and 3.10 (4.14) Å for **1** and 2.72 (3.79) and 2.88 (3.94) Å for **2**. Distances for C–H···N (C···N) are 2.69 (3.63) and 2.46 (3.51) Å for **1** and 2.52 (3.56) and 2.73 (3.73) Å for **2**. The C–H···π_{centroid} distances are comparable with those reported for complexes of cyclotriveratrylene and *o*-carborane.[8–11] *Ab initio* calculations for a C–H···π interaction



Scheme 1

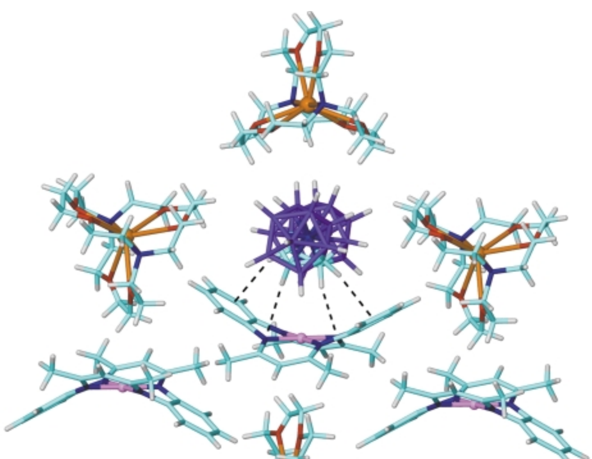


Fig. 1 Projection showing the interplay between the ions of $[\mathrm{K}\subset[2.2.2]\mathrm{cryptand}]^+$, $[\mathrm{Co(C_2B_9H_{11})_2}]^-$ and Ni(TMTAA). Broken lines correspond to C–H···π and C–H···N hydrogen bonding interactions.

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between the same carborane and benzene gave a C–H···π distance of 2.694 Å, and a weak energy of interaction of 2.72 kcal mol^{-1}.[8] The acidic C–H groups of carboranes also form hydrogen bonds to O-centres of 18-crown-6,[12] and to other hydrogen bond acceptors.[13] Recent studies have established that the cobalticarborane can form close inter-anion contacts associated with C–H···H–B interactions at 2.40 Å.[7]

The supercation [M⊂[2.2.2]cryptate]$^+$ also interacts with Ni(TMTAA), with one arm of the [M⊂[2.2.2]cryptate]$^+$ sitting in the methyl face of the macrocycle at the van der Waals limit, thereby maximising steric complementarity between the two curved surfaces. Thus, with the anion residing in the other face, Ni(TMTAA) acts as a divergent receptor for the ions as part of a linear array, Fig. 1. The other two arms of the supercation form a cavity in which the cobalticarborane anion sits, the closest B–H···O contacts being 3.40 Å. Related to this work is the binding of various metal ion complexes of [2.2.2]cryptand in bowl-shaped cavities of calix[4]resorcinarenes.[14]

The extended structure also has the aromatic protons of Ni(TMTAA) lying astride two arms of the cryptate, Fig. 1. This packing is more efficient for complex **2** compared with **1** which relates to the smaller size of the sodium cation (0.98 Å radius) with respect to the [2.2.2]cryptand cavity (approx. 1.4 Å radius).[15] Here the coordination environment is distorted, as evidenced by the N–Na–N angle at 168.57(7)° and acute O–Na–O angles at 57.78(6)–64.56(6)°. In contrast, the cavity is a better fit for the potassium cation (1.33 Å radius)[15] and the supercation approximates to D_{3h} symmetry (ignoring the ethylene linkages); the N–K–N angle is now 176.47(9)° and acute O–K–O angles more uniform at 57.36(10)–61.22(10)°. Metal to N- and O-centre distances in the supercations are unexceptional, Na–O 2.371(2)–2.919(2) Å, Na–N 2.668(2) and 3.014(2) Å, *cf.* K–O 2.730(3)–2.866(3) Å, K–N 2.993(4) and 3.014(4) Å.

UV–Vis experiments were conducted for Ni(TMTAA) *versus* [Na⊂[2.2.2]cryptand]$^+$[Co($C_2B_9H_{11}$)$_2$]$^-$ in dichloromethane, nitromethane and chlorobenzene, albeit without any evidence of complex formation in solution. Electrospray mass spectra were collected of the complex **2** in dichloromethane/methanol solution. However, no peaks corresponding to any multicomponent species in the gaseous phase were observed.

In conclusion, we have established a new class of compounds based on a divergent receptor for supercations and anions which show steric and electronic complementarity, with the success of the work in part attributed to the rigidity of the Ni(II) macrocycle receptor.

We are grateful to the Australian Research Council for support of this work.

Notes and references

‡ *Synthesis* of [M⊂[2.2.2]cryptand][Co($C_2B_9H_{11}$)$_2$][Ni(TMTAA)] M = Na, **1**: Na[Co($C_2B_9H_{11}$)$_2$] (20 mg, 57.7 μmol) and [2.2.2]cryptand (22 mg, 57.7 μmol) were dissolved in CH_2Cl_2 (3 ml), then Ni(TMTAA) (23 mg, 57.7 μmol) was added followed by toluene (3 ml), after it had dissolved. Slow evaporation of the solvent over several days yielded a purple–brown crystalline solid. Yield 48 mg (74%), mp. 275 °C, $C_{44}H_{80}B_{18}CoN_6NaNiO_6$ requires: C 47.0, H 7.17, N 7.47%. Found: C 47.14, H 7.16, N 7.55%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 12H, CH_3), 2.64 (t, ^3J 5.1 Hz, 12H, NCH_2), 3.58 (t, ^3J 5.1 Hz, 12H, NCH_2CH_2), 3.62 (s, 12H, OCH_2), 3.98 (br s, 4H, BCH), 4.84 (s, 2H, CH), 6.53–6.57 (m, 4H, ArH), 6.65–6.70 (m, 4H, ArH).

For M = K, **2**: Na[Co($C_2B_9H_{11}$)$_2$] (15 mg, 43.3 μmol), [2.2.2]cryptand (16 mg, 42.5 μmol) and KPF_6 (300 mg) were dissolved in acetone. The acetone was quickly evaporated and the residue extracted with CH_2Cl_2 and filtered, whereupon the CH_2Cl_2 filtrate was evaporated. The dissolution–evaporation–extraction procedure was then repeated with a further 300 mg KPF_6. To the final, orange-coloured CH_2Cl_2 extract (*ca.* 4 ml) was added Ni(TMTAA) (32 mg, 79.8 μmol) followed by an equal volume of toluene, and the solution allowed to evaporate slowly overnight. The resulting crystalline precipitate was filtered off, washed with toluene and air dried. Mp 287 °C, $C_{44}H_{80}B_{18}CoKN_6NiO_6$ requires: C 46.34, H 7.07, N 7.37%. Found: C 46.35, H 7.06, N 7.27%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 12H, CH_3), 2.53 (t, 4.8 Hz, 12H, NCH_2), 3.53 (t, 4.8 Hz, 12H, NCH_2CH_2), 3.60 (s, 12H, OCH_2), 4.00 (br s, 4H, BCH), 4.84 (s, 2H, CH), 6.53–6.57 (m, 4H, ArH), 6.65–6.70 (m, 4H, ArH).

§ *Crystal data* for compounds **1** and **2** (in parentheses): [Na,K⊂[2.2.2]cryptand][Co($C_2B_9H_{11}$)$_2$], $C_{44}H_{80}B_{18}CoNa[K]N_6NiO_6$, M_r = 1124.35 (1140.46), monoclinic, $P2_1/c$, a = 19.5377(2) [19.7345(2)], b = 18.2124(2) [18.1965(2)], c = 16.3576(2) [16.5687(3)] Å, β = 108.487(1) [108.493(1)]°, V = 5520.13(11) [5642.57(13)] Å^3, D_c = 1.353 [1.342] g cm^{-3}, μ = 0.702 (0.753) cm^{-1} (no correction), Z = 4, T = 123(1) K, 66247 (77324) reflections collected, 11964 (11034) unique reflections, R_{int} = 0.097 (0.138), $2\theta_{max}$ = 55 (52)° [7729 (6314) observed, $I > 2\sigma(I)$, 698 (698) parameters, no restraints, R_1 = 0.0499 (0.0552), wR_2 = 0.0982 (0.1350)], S = 1.043 (1.029). Enraf-Nonius KappaCCD diffractometer, Mo-Kα radiation, crystals mounted in oil: The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at geometrically estimated positions.

CCDC 160797–160798. See http://www.rsc.org/suppdata/cc/b1/b102140k/ for crystallographic data in .cif or other electronic format.

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