

Mineralomimetic host–guest chemistry: the encapsulation of $[M^+C[2.2.2]cryptate]$ ($M = Na, K$) by saddle shaped Ni(II) macrocycles †

Michaele J. Hardie,^a Nino Malic^b and Colin L. Raston^{*a}

^a School of Chemistry, University of Leeds, Leeds, UK LS2 9JT.
E-mail: c.l.raston@chem.leeds.ac.uk

^b School of Chemistry, Monash University, Clayton 3800, Victoria, Australia

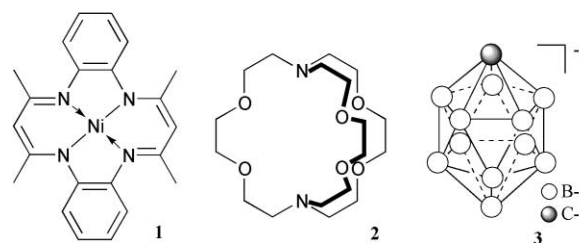
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The complex $[MC[2.2.2]cryptate][CB_{11}H_{12}][Ni(TMTAA)]_3$, $M = K, Na$ shows a range of supramolecular interactions to form a mineralomimetic structure corresponding to that of perovskite.

The degree of complexity shown by artificial supramolecular complexes is rapidly expanding and different modes of supramolecular behavior may be exhibited within a single system.¹ We report herein one such system where an array of supramolecular interactions including (i) the simple binding of alkali metals by a host molecule, (ii) host–guest complex formation through complementarity of curved surfaces and symmetry matching with subsequent host-in-host properties, (iii) the assembly of molecular components into polyhedra, and (iv) the binding of soft anions in hydrophobic spaces, combine to create a crystalline complex with an overall mineralomimetic structure, corresponding to that of perovskite. Mineralomimetic structures are usually assembled through highly directional interactions such as coordinate or hydrogen bonds,² but here it is simply the result of packing curved surfaces together coupled with the use of large, globular-like, weakly polarizing cations and anions.

The building blocks utilized here all have curved surfaces, and are: 5,7,12,14-tetramethyldibenzo[*b, l*]-1,4,8,11-tetraazacyclotetradecinenickel(II) or Ni(TMTAA) **1**, a rigid, saddle shaped macrocycle that forms complexes with neutral globular molecules such as fullerenes, *o*-carborane and P_4S_3 ,³ as well as acting as a second sphere host for $[(H_2O)_2\curvearrowright 18\text{-crown-6}]$ ⁴ and ionic species such as $[K^+C[2.2.2]cryptate]$ and the monoanion of cobalt(III)bis(dicarbollide).⁵ The versatility of Ni(TMTAA) as a receptor is due to its rigidity and the presence of two different concave surfaces, one benzo-lined, the other methyl-lined,⁶ allowing it to act as a heterotopic receptor, or to self-associate into a dimer which can effectively act as a homotopic divergent receptor. [2.2.2]Cryptand **2** is a classical host molecule capable of binding various metal ions to form cryptate host–guest complexes.⁷ The soft, weakly coordinating anion $[CB_{11}H_{12}]^-$ **3** was employed as a counter-ion.



The crystalline complexes $[MC[2.2.2]cryptate][CB_{11}H_{12}][Ni(TMTAA)]_3$, $M = K^+$ **4** and $M = Na^+$ **5** are formed in 59%

and 45% overall yield respectively, by the slow evaporation of a CH_2Cl_2 /toluene solution containing a 1 : 1 mixture of $[M^+C[2.2.2]cryptate][CB_{11}H_{12}]^-$ ($M = Na, K$) and Ni(TMTAA). The complexes were analysed by solution ¹H NMR and microanalysis. † The NMR spectrum shows a 3 : 1 ratio of Ni(TMTAA) to $[M^+C[2.2.2]cryptate]$, with the chemical shifts of the cryptate protons giving no indication of the formation of a higher level complex in solution. The solid state structures were determined from X-ray diffraction data. ‡ Complexes **4** and **5** are virtually isostructural with the most significant differences arising from the difference in size of the $[M^+C[2.2.2]cryptate]$ species. The extended structure has each $[M^+C[2.2.2]cryptate]$ shrouded by six Ni(TMTAA) macrocycles in a prism where each Ni(TMTAA) can be regarded as a face of a cube, and the Ni centres form the vertices of a near perfect octahedron, Fig. 1. Each octahedron has a facial arrangement with three adjacent Ni(TMTAA) molecules binding the cryptate through their benzo-lined concave surfaces, whilst the other three bind through the methyl-lined concave surfaces. The closest cryptate C–H \cdots Ni separation is 2.83 Å, while the closest approach between the Ni(TMTAA) macrocycles occurs between phenyl groups at a C–H \cdots C distance of 2.85 Å. The formation of the octahedral assembly can be attributed in part to the three-fold symmetry of the cryptate, which aligns along one possible three-fold axis of the octahedron. The potassium cryptate lies on a three-fold axis (N–K–N angle of 180°, K–N bond lengths 2.910(4) and 2.911(3) Å). The Ni \cdots Ni separations that define the octahedron range from 8.84 to 9.29 Å, with *cis* angles 87.6 to 91.6° and *trans* angles all 178.8°. Despite the induced contortion of the cryptand around the smaller sodium cation, forming a slightly smaller cryptate in complex **5** (N–Na–N angle of 180.0°, Na–N bond lengths 2.692(4) and 2.780(3) Å), the same cube-like structure is formed, with the Ni centres once again forming the vertices of an octahedron. The dimensions are very slightly smaller to compensate for the reduced size of the cryptate, with a largest Ni \cdots Ni separation of 9.19 Å. This shrinkage of the assembly is reflected in the unit cell volume for **5** being approximately 200 Å³ smaller than that for **4**.

The $\{[M^+C[2.2.2]cryptate]C[Ni(TMTAA)]_6\}$ assembly shown in Fig. 1 represents an usual example of a host–guest assembly being encapsulated within another host–guest assembly. Other recent examples include calixarenes surrounding metal–cryptate or metal–crown ether complexes,⁸ and a metal–crown ether complex within a Ga_4L_6 cage.⁹ The formation of octahedra also relates to polyhedral molecular assemblies with internal cavities that have received much attention in the recent literature.¹⁰ Unlike the structure described herein most examples are discrete assemblies, often able to exist in solution, and rely on relatively strong coordinate and/or hydrogen bonding interactions. There is no evidence for the $\{[M^+C[2.2.2]cryptate]C[Ni(TMTAA)]_6\}$ assembly existing in solution, which is unsurprising given the lack of such relatively strong directional interactions to hold the assembly together.

† Electronic supplementary information (ESI) available: synthetic details. See <http://www.rsc.org/suppdata/dt/b1/b111197n/>

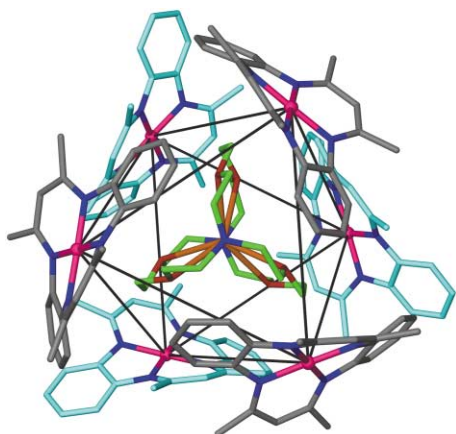


Fig. 1 $\{[K[C[2.2.2]cryptate]C[Ni(TMTAA)]_6]\}$ assembly from the crystal structure of **4**, an octahedron formed by the Ni centers is indicated, with three benzo-lined faces shown in gray, three methyl-lined faces in blue.

The octahedra in **4** and **5** are not discrete but form part of an extended 3D array. Each Ni(TMTAA) molecule belongs to two adjacent octahedra, with contacts to the $[M^+C[2.2.2]cryptate]$ core of one octahedron through its benzo-lined surface and to the cryptate of the other octahedron through its methyl-lined surface. In this way each octahedron is connected to six others in a vertex sharing lattice, Fig. 2. The carborane anions occupy

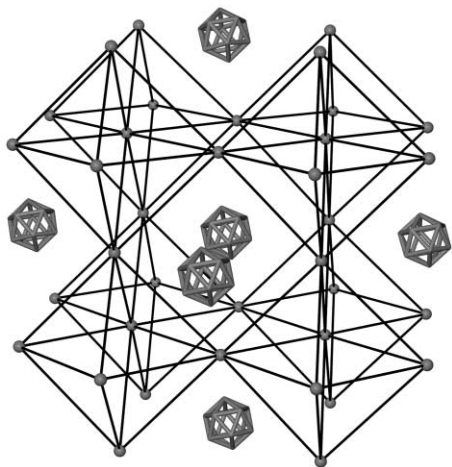


Fig. 2 Extended structure of $[K[2.2.2]cryptate][CB_{11}H_{12}][Ni(TMTAA)]_3$. Only the Ni positions from Fig. 1 are shown, and form a vertex sharing 3D lattice of octahedra, with $[CB_{11}H_{12}]^-$ anions occupying the interstitial site.

the interstitial spaces within this lattice (Fig. 2), each sitting in a non-polar environment comprised of aromatic-H and methyl-H groups from twelve surrounding Ni(TMTAA) molecules.

The overall structure is mineralomimetic with the relative positions of the molecules or discrete supermolecules corresponding to the atomic positions of the mineral perovskite, $CaTiO_3$. This is illustrated in cartoon form in Fig. 3, where an idealized perovskite unit-cell is shown along with the corresponding molecular positions within complexes **4** and **5**. In perovskite the oxide anions are arranged in an octahedron around a central Ti cation, with Ca cations at the cube corners.¹¹ In complexes **4** and **5**, the perovskite oxide positions are occupied by the Ni centers of Ni(TMTAA) macrocycles, the central Ti position by $[M^+C[2.2.2]cryptate]$ and Ca positions by $[CB_{11}H_{12}]^-$ anions. In the extended structures of **4** and **5** the $[CB_{11}H_{12}]^-$ anions do form a near cubic arrangement with respect to each other, with ideally right angles between the carborane centroids ranging from 88.4 to 91.3° for **4** and 88.9 to 91.1° for **5**.

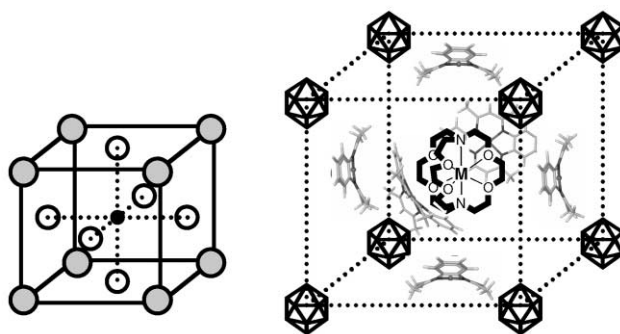


Fig. 3 Schematic diagram illustrating the relationship between the perovskite structure on the left (black circle is Ti^{4+} , open O^{2-} and shaded Ca^{2+}) and the arrangement of components within **4** and **5** on the right. This does not represent the crystallographic unit cell for **4** or **5**.

The octahedral arrangement of Ni(TMTAA) around slightly different supermolecules suggests that larger globular-type molecules and ions may be shrouded by Ni(TMTAA) or other curved molecules into larger and/or more complicated polyhedral structures. Moreover, using the principles of supramolecular chemistry with large molecular building blocks in mineralomimetics is likely to lead to the rational design of new materials.

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Notes and references

‡ Crystal data for **4** (**5** in parentheses). $C_{85}H_{114}B_{11}KN_{14}Ni_3O_6$ ($C_{85}H_{114}B_{11}N_{14}NaNi_3O_6$): $M_r = 1762.04$ {1745.93}, $T = 123(1)$ K, Mo- K_α radiation, trigonal (hexagonal), $R3c$, $a = 18.0689(2)$ {18.0480(1)}, $c = 46.1059(3)$ {45.4396(7)} Å, $V = 13036.2(4)$ {12818.1(2)} Å³, $Z = 6$ {6}, 35176 {28096} data collected, 6885 {6810} unique ($R_{int} = 0.047$ {0.035}), 366 {366} parameters, 1 restraint, $R_1 = 0.0339$ {0.0266} [5589 {6347} data $I > 2\sigma(I)$], $wR_2 = 0.0783$ {0.0694} [all data], $S = 1.044$ {1.050}. CCDC reference numbers 157600 and 157601. See <http://www.rsc.org/suppdata/dt/b1/b111197n/> for crystallographic data in CIF or other electronic format.

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