Metallacrown-based compartments: selective encapsulation of three isonicotinate anions in non-centrosymmetric solids†

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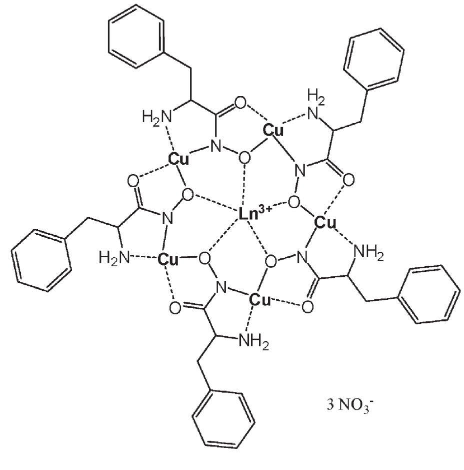
Upon crystallization in high yields, metallacrowns form compartments that are capable of asymmetrically encapsulating three isonicotinate guests.

Metallacrowns have been an active area of study for well over a decade.[1] Since the discovery of the structural and functional analogy between metallacrowns and crown ethers,[2] a plethora of structural diversities and potential applications emerged. Metallacrowns can function as selective cation-[3] and anion-binding agents,[4] chiral molecular recognition agents,[5] useful building blocks for chiral solids,[6] single-molecule magnets,[7] catalysts,[8] *etc.* Of particular interest is our previous observation that metallacrowns can form cavities that bind aromatic guest molecules such as the symmetrical 1,4-benzenedicarboxylate (terephthalate).[5] Metallacrowns can also encapsulate individual inorganic molecules such as molecular LiF, LiFHF and Na_2SiF_6.[9] Despite all of these studies, there are no examples of metallacrowns sequestering asymmetric molecules simultaneously using both Ln(III) and Cu(II) ions. Here we show that metallacrowns are able to form compartments in the solid state that selectively sequester three unsymmetrical 4-pyridinecarboxylate (isonicotinate) molecules.

When an aqueous solution of $Ln(NO_3)_3[Cu(\text{L-pheHA})]_5$ (0.1 mmol) (Scheme 1) (pheHA = phenylalanine hydroxamic acid) and isonicotinic acid (0.3 mmol) is left to evaporate slowly, dark-blue crystals of $(\text{isonicotinate})_3\subset\{Ln[Cu(\text{L-pheHA})]_5\}_2(\text{isonicotinate})(NO_3)_2(H_2O)_{19}$ (Ln = Gd, **1**; Dy, **2**; Y, **3**) are obtained in 85% yield.‡ Single crystal X-ray diffraction reveals that pairs of metallacrowns facing each other form compartments with a hydrophobic interior, housing three isonicotinate molecules (Fig. 1). On the exterior, an additional isonicotinate molecule binds to the lanthanide atom on one side, along with a nitrate that binds to a copper atom, while a water molecule binds to the other lanthanide atom on the opposite side of the compartment. The two metallacrown planes are roughly parallel, with an angle between the mean-planes defined by the sets of five copper atoms of 9°.



Scheme 1 Schematic structure of $Ln(NO_3)_3[Cu(\text{L-pheHA})]_5$.

Other chiral hydroxamic acid ligands (*e.g.*, L-tyrHA = L-tyrosine hydroxamic acid),[4a,10] also form face-differentiated 15-MC-5 structures. The five phenyl groups point to the same metallacrown face, yet they can assume different orientations relative to the metallacrown plane, due to the presence of flexible methylene linkers that connect them to the metallacrown skeleton. This conformational flexibility allows the phenyl groups of one metallacrown to interact with the phenyl groups of the facing metallacrown by aromatic interactions. In addition, the phenyl groups also interact with the aromatic isonicotinate guest molecules, thus forming an intricate array of π–π interactions.

The three isonicotinate molecules stretch across the two metallacrown planes within the compartment, with the pyridine nitrogen atom coordinating to the axial position of a copper atom from one metallacrown (Cu–N distances: 2.28–2.40 Å), and the carboxylate group bridging copper and gadolinium atoms on the

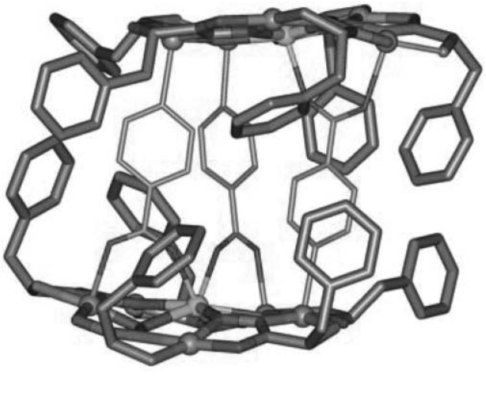


Fig. 1 Line-drawing of **1**. Hydrogen atoms, nitrates, coordinated and lattice water as well as the exogenous isonicotinate molecule are not shown. **2** and **1** are isomorphous and thus are isostructural.

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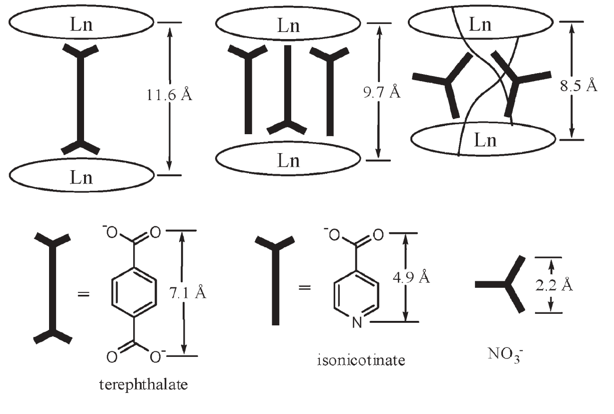
† The HTML version of this article has been enhanced with colour images.

other metallacrown (Cu–O distances: 2.27–2.40 Å, Gd–O distances 2.31–2.36 Å). The three isonicotinate molecules are in close proximity and form π–π contacts with one another and with the phenyl groups of the metallacrowns. The gadolinium atom of the metallacrown that has two pyridine groups and one carboxylate bound, is 7-coordinate (five O-atoms from the metallacrown, one O-atom from the carboxylate and another O-atom from the isonicotinate molecule bound on the outer side of the compartment); the gadolinium atom from the other metallacrown, which has one pyridine group and two carboxylates bound, is 8-coordinate (five O-atoms from the metallacrown, two O-atoms one from each carboxylate and another O-atom from the water molecule bound on the exterior).

We have shown that L-pheHA and L-tyrHA metallacrowns form compartments that may bind symmetric guests. As schematically illustrated in Scheme 2, the Ln–Ln distance of 9.7 Å within the compartment of **1** is considerably shorter than the 11.6 Å observed in the case of {Ln(terephthalate)[Cu(L-pheHA)]$_5$}$_2$$^{2+}$.[5] In the latter structure, the symmetrical terephthalate guest forms bidentate carboxylate chelates to the Gd(III) ions of each metallacrown, causing an expansion of the cylinder. In contrast, an even shorter Gd–Gd distance of 8.5 Å is observed inside the cavity formed by {Gd(NO$_3$)[Cu(L-tyrHA)]$_5$}$_2$$^{4+}$, which encapsulates two nitrate ions. The more condensed cavity of this metallacrown container is a direct result of the tyrosine hydroxamate ligand hydroxyl group from each metallacrown coordinating to a copper atom on the adjacent metallacrown.[4a] We observe that the smallest cavity occurs when the guest bridges Cu-atoms of the metallacrown, it expands with guests using both Cu(II) and Ln(III) as anchor points and is greatest when the guest spans both Ln(III) ions. Thus, we obtain metallacrown compartments that can accommodate guests having as much as 5 Å difference in length.

In order to assess the specificity of guest encapsulation into **1**, the possibility of incorporating similar guest molecules was explored with 4-pyridineboronic acid, 3-pyridinecarboxylic acid, 2-pyridinecarboxylic acid, 4-pyridineacetic acid, 3-pyridinepropionic acid and 4-(4-carboxyphenyl)pyridine. None of these guests formed similar structures under the same experimental conditions. Neither could a similar compartmented structure be obtained when the metallacrown-forming phenylalanine hydroxamate ligand was changed to glycine hydroxamate, an observation that points to the significance of the phenyl groups in forming the walls of the compartment.



Scheme 2 Schematic representation of guest binding to metallacrown containers. The thin lines connecting the two metallacrown rings represent bridging tyrosines.

Saalfrank *et al.* have described a bis(double helicate) that forms a cryptatoclathrate as a solid.[11] Within the resulting compartments, two THF molecules are entrapped, but not coordinated to the host. Upon dissolution in chloroform, THF or benzene, this cryptatoclathrate dissociates. Based on these observations and the general similarity of interactions in the solid state between this cryptatoclathrate and **1**, we evaluated the solution behavior of **1** in polar, protic solvents which dissolve the metallacrown compartments. Electrospray ionization mass spectrometry of a MeOH or H_2O solution of **1** at room temperature shows two strong peaks in the cone voltage range of 25–75 V. At 25 V, the peak at *m/z* 744 can be assigned to {Gd(isonicotinate)[Cu(L-pheHA)]$_5$}$^{2+}$, while at 75 V the peak at *m/z* 1610 corresponds to {Gd(isonicotinate)$_2$-[Cu(L-pheHA)]$_5$}$^+$. A minor peak at *m/z* 1550, corresponding to {Gd(NO$_3$)(isonicotinate)[Cu(L-pheHA)]$_5$}$^+$, was also identified. No peak attributable to a {Gd[Cu(L-pheHA)]$_5$}$_2$(isonicotinate)$_x$-(NO$_3$)$_y$ species was detectable over the 0–75 V cone voltage range. Similar results were obtained with **2** and **3**. Also, no peaks corresponding to pyridine adducts were detectable when a metallacrown–pyridine solution was subjected to ESI-MS under the same conditions. These experiments suggest that in solution only the carboxylate group of the guest molecule binds significantly to the metallacrown, indicating dissociation of the metallacrown compartments in solution. Based on the Weber and Josel definition of solid state host–guest complexes,[12] we feel the best description of the metallacrown system is as a clathratocomplex since the interaction between the host and guest are retained by direct coordination bonds; however, the non-covalent association of the two metallacrowns observed in the solid state is disrupted in solution.

One potential application of these chiral compartments is in the preparation of non-linear optical (NLO) materials. Considerable attention has been focused on placing molecules with permanent dipoles into non-centrosymmetric environments in order to take advantage of second harmonic generation of these materials. Application of the metallacrowns to this purpose would appear straightforward as the molecules are inherently chiral, hence crystallizing in non-centrosymmetric space groups, and they afford cavities capable of binding guests. Essential to this function, the guest should contain a permanent dipole and be oriented to maximize the dipole vectors in the solid state. Thus, while one can prepare {Gd(terephthalate)[Cu(L-pheHA)]$_5$}$_2$$^{2+}$, the terephthalate molecule does not possess a permanent dipole and is symmetrically bridging the two gadolinium atoms of the two adjacent metallacrowns. In contrast, isonicotinate is an asymmetric ligand containing pyridyl and carboxylate donors, which we can exploit in order to arrange these asymmetric guests in the solid. In order for the guests to bind appropriately to Gd(III) and Cu(II), the (isonicotinate)$_3$⊂{Ln[Cu(L-pheHA)]$_5$}$_2$$^{3+}$ places two of the three isonicotinate molecules in a parallel orientation while the third one is antiparallel. As shown in Fig. 2, the resulting solid contains a dipole along the metallacrown cavity axis. In addition, a second net dipole is found nearly perpendicular to the metallacrown cavity axis and parallel to the hydrophilic metallacrown face. This intriguing combination of chirality and a permanent dipole promises an interesting supramolecular approach for designing and preparing non-linear optical materials.

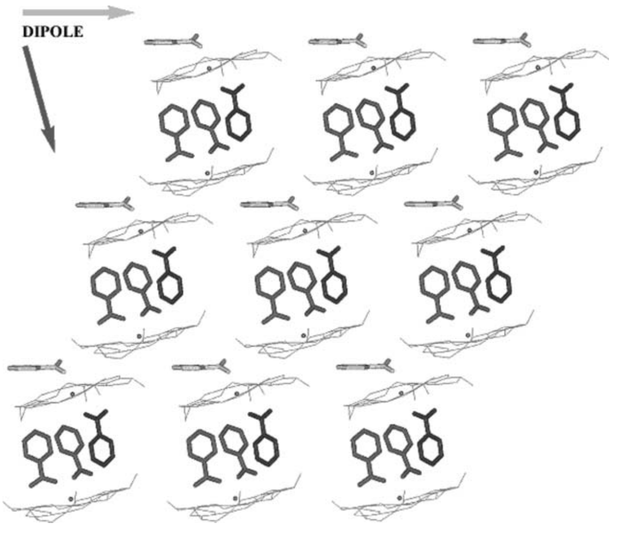


Fig. 2 Packing diagram illustrating the net dipole moment in crystals of **1**. Hydrogen atoms, phenyl groups, nitrates and water molecules are not shown.

One preliminary measurement of second-order NLO effects for the powder sample of **1** has been carried out.[13] The investigation probes properties associated with the determined symmetry group, in particular, the lack of an inversion center. Although the intensity of the green light (frequency-doubled output: λ = 532 nm) produced by **1** is much weaker than that of KDP powder (I_1/I_{KDP} = 1/100), it indicates that **1** has a non-centrosymmetric space group. We suspect that the dark-blue powder sample absorbs much of the second-harmonic generation (SHG) green light.

In conclusion, we have shown that the $Ln(NO_3)_3[Cu(\text{L-pheHA})]_5$ metallacrowns form compartments that are able to encapsulate three isonicotinate guest molecules. The length of the compartment can vary and it can accommodate guest molecules of different sizes. In the absence of guest molecules, the individual metallacrowns are loosely associated in the crystal lattice (Ln–Ln distance 12.0 Å).[5] Upon addition of appropriate guests, the metallacrown molecules are pulled closer to each other in pairs leading to shorter Ln–Ln distances and a more parallel orientation of the metallacrown planes within the resulting compartment. In order to generalize guest encapsulation, we are currently specifically functionalizing the pendant arms of these metallacrown compartments to achieve selective recognition of different anions. In addition, we are further assessing the NLO behavior of the present solids.

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Notes and references

‡ Compounds **1–3** were prepared by dissolving 0.1 mmol metallacrown in 70 ml H_2O–MeOH (1 : 1) mixture, followed by the addition of 0.3 mmol isonicotinic acid and one drop 30% aqueous ammonia solution. Crystals were obtained after 2 weeks in 85% yield upon slow evaporation of solvent. Elemental analyses: **1**: found: C, 37.28; H, 4.02; N, 9.93; calc. for $C_{114}H_{154}Cu_{10}Gd_2N_{26}O_{53}$: C, 37.13; H, 4.22; N, 9.88%. **2**: found: C, 37.50; H, 4.18; N, 9.88; calc. for $C_{114}H_{154}Cu_{10}Dy_2N_{26}O_{53}$: C, 37.03; H, 4.21; N, 9.85%. **3**: found: C, 38.70; H, 4.27; N, 10.22; calc. for $C_{114}H_{154}Cu_{10}Y_2N_{26}O_{53}$: C, 38.56; H, 4.38; N, 10.26%.

Crystallographic data: **1**: $C_{114}H_{154}Cu_{10}Gd_2N_{26}O_{53}$, M = 3686.53, T = 123 K, triclinic space group $P1$, a = 15.4229(8) Å, b = 15.6844(8) Å, c = 16.8056(9) Å, α = 88.247(3)°, β = 65.510(3)°, γ = 73.213(3)°, V = 3523.3(3) Å^3, Z = 1, μ = 2.499 mm^{-1}, 146480 reflections (R_{int} = 0.0314), 34804 independent reflections, for observed data R_1 = 0.0224, wR_2 = 0.0589, for all data R_1 = 0.0251, wR_2 = 0.0602. **2**: $C_{114}H_{154}Cu_{10}Dy_2N_{26}O_{53}$, M = 3697.03, T = 123 K, triclinic space group $P1$, a = 15.390(4) Å, b = 15.678(4) Å, c = 16.812(5) Å, α = 88.347(4)°, β = 65.423(4)°, γ = 73.167(4)°, V = 3511.3(16) Å^3, Z = 1, μ = 2.627 mm^{-1}, 112817 reflections (R_{int} = 0.0427), 34759 independent reflections, for observed data R_1 = 0.0293, wR_2 = 0.0662, for all data R_1 = 0.0369, wR_2 = 0.0695. CCDC 622377–622378. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614024f

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13 Powder SHG measurements were carried out on a sample of **1** by means of the Kurtz–Perry method (S. Q. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798). About 120 mg of pure crystal was ground into powder and pressed into a pellet which was then irradiated with a pulsed infrared beam (100 ns, 15 mJ, 10 Hz) produced by a Q-switched Nd:YAG laser of wavelength 1064 nm. A 532 nm filter was used to absorb the fundamental and pass the visible light onto a photomultiplier. A combination of a half-wave achromatic retarder and a polarizer was used to control the intensity of the incident power, which was measured with an identical photomultiplier connected to the same high voltage source. This procedure was then repeated using a standard nonlinear optical material, in this case microcrystalline KH_2PO_4 (KDP), and the ratio of the second-harmonic intensity outputs was calculated.