

Supramolecular Chemistry

A Multifunctional, Charge-Neutral, Chiral Octahedral $M_{12}L_{12}$ Cage

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Abstract: A chiral, octahedral $M_{12}L_{12}$ cage, which is charge neutral and contains an internal void of about 2000 Å³, is reported. The cage was synthesised as an enantiopure complex by virtue of amino-acid-based dicarboxylate ligands, which assemble around copper paddlewheels at the vertices of the octahedron. The cage persists in solution with retention of the fluorescence properties of the parent acid. The solid-state structure contains large pores both within and between the cages, and displays permanent porosity for the sorption of gases with retention of crystallinity. Initial tests show some enantioselectivity of the cage towards guests in solution.

Supramolecular coordination cages, or containers, are unrivalled in their ability for selective guest binding within a protected interior cavity.^[1] Cages can be designed to provide precise

fits for certain molecular guests within a 3D space to realise highly efficient host-guest systems.^[2] The literature contains many examples of cages that are able to not only accept guests within their cavities, but also catalyse reactions, enable non-preferred conformations, or stabilize molecules inside the cavity (i.e. reactive species).^[3]

Functionality of metal-organic cages arises from using reactive sites, either organic or metal-centred,^[4] or “spatial activity”, whereby the size/shape of the cage internal cavity gives rise to selectivity.^[5] In recent years, there has been an increased interest in chiral coordination cages which require ligands that are enantiopure or the chirality of which is imparted in the self-assembly process.^[6] Recent literature examples demonstrate a variety of synthetic routes to such cages, including tetrahedral iron-based species able to encapsulate tetrahedral ions, taking advantage of octahedral metal centres and tris-chelate coordination, and cages that contain chiral groups exterior to the polyhedron.^[7] Due to poor solid-state packing, X-ray diffraction is not often used to characterise such polyhedral species, although the fact that the majority of interesting host-guest behaviour is solution based means that analysis in the solid state is rarely explored.

LeuNDI, a leucine-substituted naphthalenediimide, and its analogues, alongside their application in engineering designed interpenetrated networks, has been reported by us.^[8] Particularly notable here is the ability of some coordination polymers to show separation of enantiomers within a small liquid chromatographic setup. More recently our attention has turned to discrete chiral species that undergo shifts in fluorescence emission upon the addition of solvent species and catenation.^[8f]

Herein, we report the formation and study of an octahedral chiral cage and its guest sorption in the solid state. During final preparation of this manuscript a paper was published by Ghosh and co-workers,^[9] in which the ligands that we have studied for the past few years are used to form analogous cages with ligands derived from alanine, phenylalanine, valine, and isoleucine. We further show that such materials are capable of enantioselective sorption and release of small analytes, in addition to solution-phase responses to aromatic species.

Reaction of H_2 LeuNDI with copper(II) chloride in basic conditions yields a pure, heavily solvated, crystalline product of $[Cu_{12}(LeuNDI)_{12}(OH_2)_{12}]$ (full synthetic and crystallographic details are provided in Supporting Information). The crystal structure, solved and refined in the space group $P2_1$, reveals the cage complex containing six Cu_2 paddlewheel motifs that

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occupy the vertices of an octahedron and 12 LeuNDI²⁻ ligands that act as the edges of this regular polyhedral cage (Figure 1). Although the cage is octahedral (considering only the geometric positioning of the nodes and connectors), the propeller-like paddlewheel nodes have a uniform direction of rotation due to the enantiopure ligand and hence the overall cage contains no mirror operations and is not described by the O_h point group, but rather by O . The cage appears to be stabilized by CH...O interactions involving the imide groups with both the α -carbon and NDI core (vide infra). The triangular faces of the

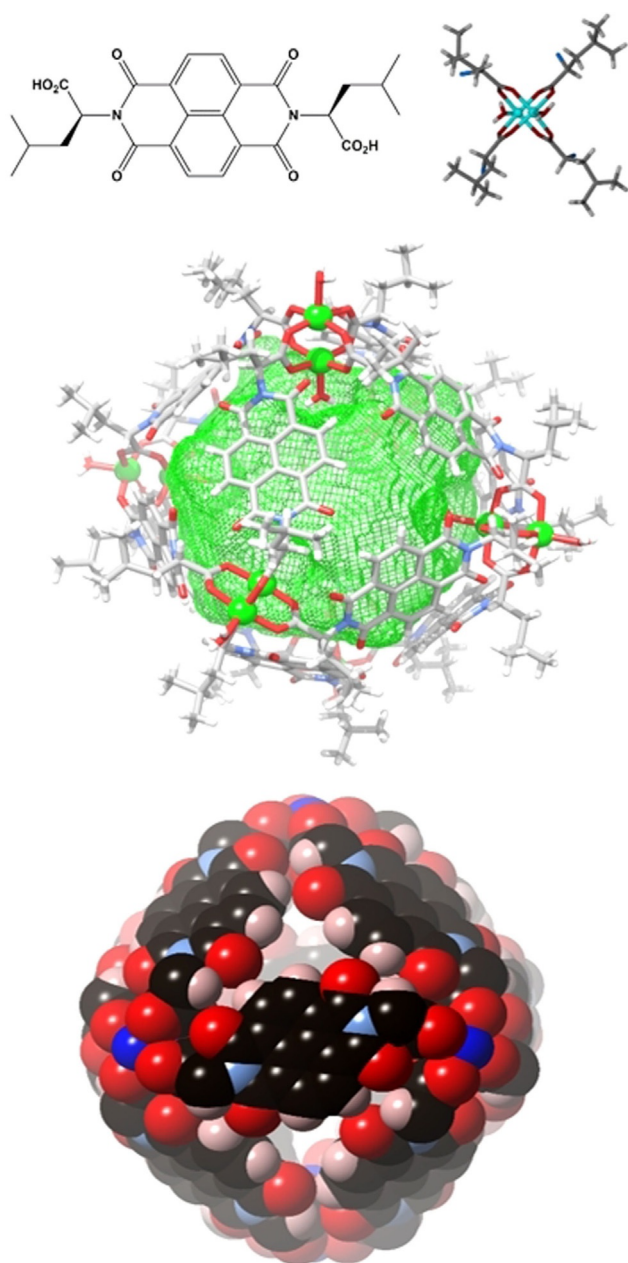


Figure 1. (Top left) The $H_2LeuNDI$ diacid. (Top right) The Cu_2 paddlewheel motif that occupies the vertices of the cage. (Centre) The octahedral, yet chiral, $[Cu_{12}(LeuNDI)_{12}]$ cage contains a roughly spherical cavity of ca. 2000 \AA^3 . (Bottom) The triangular faces of the cages contain small windows through which the interior can be accessed (amino acid side chains and coordinated solvent omitted for clarity).

octahedron, from the solid-state structure, were calculated using Zeo++ to contain gaps of largest dimension ca. 2.6 \AA , presumably locked into this conformation in the solid state (see Supporting Information).^[10] The octahedral cages contain a large internal void space, determined to be approximately 2000 \AA^3 , occupied by disordered solvent in the solid-state structure (calculated using PLATON).^[11] Pore space between the cages consists of a continuous 3D network, connected to the space within the cages (calculated by using a probe radius of 1.2 \AA) and isolated spaces that occupy the alternate corners of the cubic cell to the cages (overall ca. 47% of the cell volume, Figure 2).

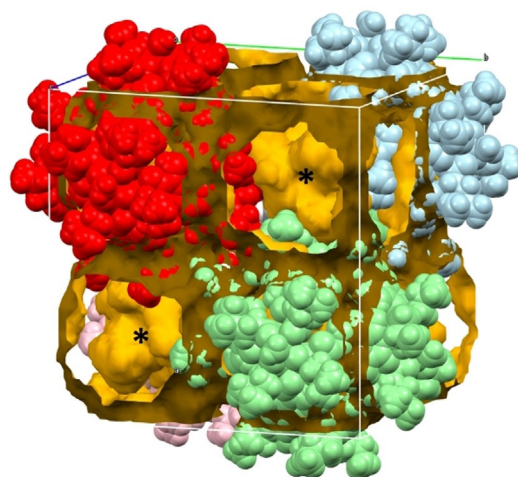


Figure 2. Packing of $[Cu_{12}(LeuNDI)_{12}]$ occurs such that the cages occupy alternating corners of the cubic cell alongside isolated voids (denoted by *). Additionally, there is a continuous void space that runs between and through the cages (probe radius 1.2 \AA). The four cages within the cell are coloured differently for clarity.

The persistence of $[Cu_{12}(LeuNDI)_{12}]$ in solution was confirmed by using 1H NMR spectroscopy, circular dichroism (CD) spectroscopy and mass spectrometry (Supporting Information). Although somewhat paramagnetically broadened and shifted, the 1H NMR spectrum of the cage clearly shows two signals corresponding to the hydrogen atoms of the NDI cores. In the free ligand, these hydrogen atoms are equivalent. Once the octahedral cage is formed, these hydrogen atoms exist in two distinct environments due to the presence of inter-ligand CH...O hydrogen bonds across the faces of the triangular windows. Mass spectrometry of the cage proved challenging, with the Cu_{12} species being neutral with a formula weight of $6888.6 \text{ g mol}^{-1}$. Electrospray ionisation mass spectrometry of $[Cu_{12}(LeuNDI)_{12}]$ dissolved in acetonitrile with 1% (v/v) acetic acid added immediately prior to measurement was used to confirm the existence of the cage by observation of multiple, variously solvated, doubly and triply protonated $[Cu_{12}(LeuNDI)_{12}]$ ions (see Supporting Information). Although the imide functional group is relatively non-basic in solution, the gas-phase basicity (GB) of imide functional groups are exceedingly high (e.g. the GB of *N*-acetylacetamide is 1422 kJ mol^{-1}).^[12] Circular dichroism confirms the presence of a

chiral assembly in solution with a distinctly enhanced signal contrasted to that of the parent diacid.

Interestingly, an analogous synthetic preparation using H₂GlyNDI, the achiral cousin of H₂LeuNDI and related ligands, did not yield a discrete cage, rather it formed a two-dimensional coordination polymer as the sole isolable crystalline product under similar reaction conditions (see Supporting Information). It is noted that the solvent differs between the two syntheses (DMF vs. DMA), which is also a possible cause for structural difference with no crystalline products isolated from the opposite experiments, although in related systems we have been able to access discrete glycine complexes regardless of solvent.^[13] This coordination polymer still contains a copper paddlewheel motif, although it is centrosymmetric (unlike those in the cage complex). An achiral analogue of the Cu₁₂ cage was expected, similar to our previous results with Cu₄L₄ cages,^[13] however it appears that the presence of the amino acid side chain may play a very strong sterically directing role in the formation of the cage (and in their stability as per the findings of Ghosh).^[9] It is possible that less sterically encumbering side chains may allow for arrangements around the paddlewheel other than the propeller motif required to form the discrete Cu₁₂ cages.

As noted above, the solid-state structure of [Cu₁₂(LeuNDI)₁₂] contains significant solvent-occupied voids. After solvent exchange with methanol and subsequent desolvation under vacuum, the material was exposed to a variety of gases to probe its capacity for absorption. Powder X-ray diffraction (PXRD) after solvent exchange, evacuation and repeated sorption experiments confirms that the crystallinity of the sample remains largely unchanged (see Supporting Information). It remains relatively rare for discrete metal-organic cages to display permanent porosity, with retention of crystallinity, with recent notable examples including those of Yaghi,^[14] Furukawa,^[15] Bloch,^[16] Zhou,^[17] and the nanoballs of Batten.^[18]

N₂ uptake measurements give a Brunauer–Emmett–Teller (BET) surface area of 693 m² g⁻¹. Low pressure uptake of CO₂ indicates incomplete sorption at the limits of the instrumentation (see Supporting Information), leading to high pressure experiments being performed to gauge whether there was a pressure barrier to access the pore space within the cages. High pressure data were collected at multiple temperatures for CO₂, H₂, CH₄, and N₂O. Uptake plots for methane and hydrogen follow similarly shaped curves (see Supporting Information) and the overall uptake volumes in cm³ g⁻¹ are 82 (273 K) and 172 (77 K), respectively (c.f. the recent CH₄/cage record of 194 cm³ g⁻¹ at 65 bar for a Cr-based cage).^[16] CO₂ uptake plateaus at about 170 cm³ g⁻¹ (at ca. 1700 kPa, 273 K, Figure 3). To investigate the nature of the sorption sites of the materials, the enthalpy of CO₂ sorption over the gas loading range was calculated. At initial CO₂ loading the isosteric enthalpy of sorption for the gas is -29 kJ mol⁻¹. CO₂ sorption enthalpies in this range are typical of CO₂ binding to non-polarising surfaces.^[19] This result implies that the axial paddlewheel sites remain unavailable for the gas. The sorption enthalpies over the entire CO₂ loading range remain largely unchanged. N₂O, which is isoelectronic and of comparable size to CO₂ and is of impor-

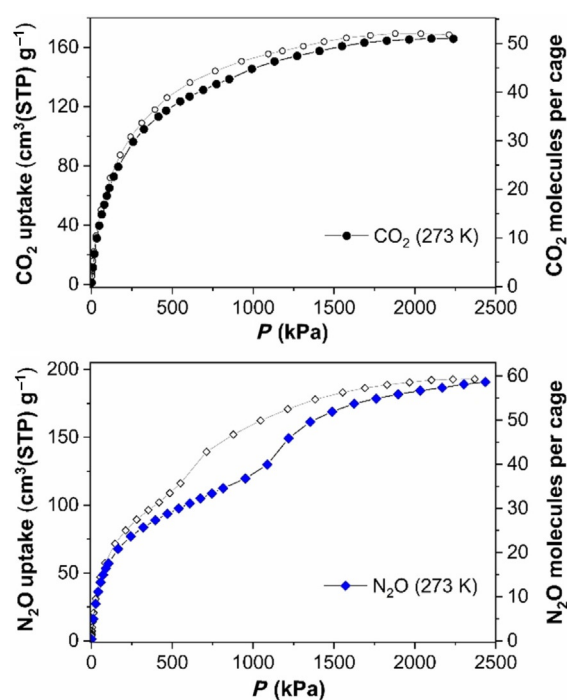


Figure 3. High-pressure gas sorption isotherms of a crystalline sample of [Cu₁₂(LeuNDI)₁₂(OH₂)₁₂] for (top) CO₂ and (bottom) N₂O.

tance as a mild anaesthetic, displays a markedly different sorption profile, with hysteresis, and a higher maximum uptake (190 cm³ g⁻¹ at 220 kPa, 273 K). The reason for the difference in behaviour between CO₂ and N₂O is not immediately obvious. It is possible that there is an artefact associated with sluggish N₂O sorption in certain regions leading to a flattening of the inflection. However, similar step-wise profiles are observed in the desorption process, suggesting that some kind of gating mechanism may be present for N₂O but not for CO₂ due to the relative sizes of their dynamic radii. Similar gating process have been observed recently for a crystalline metal-organic cage.^[15a]

We have previously demonstrated that the LeuNDI ligand can exhibit broad, redshifted and often enhanced fluorescence emission due to formation of exciplexes with other aromatic species.^[8f,20] Exciplex formation can also occur involving NDI-based ligands incorporated into larger structures and aromatic molecules in solution, or even in gas phase,^[21] and provides readily detectable confirmation of their formation. The emission intensity of [Cu₁₂(LeuNDI)₁₂] in MeCN and CHCl₃ was very weak. However, in *o*-/*m*-/*p*-xylene and toluene there was a weak but measurable solvent-dependent emission in the range 450–510 nm, similar to that of the parent diacid H₂LeuNDI in these solvents (see Supporting Information). Larger aromatic molecules, naphthalene and triphenylene, were introduced to solutions containing [Cu₁₂(LeuNDI)₁₂], whereby their fluorescence intensity was reduced. Titrations of [Cu₁₂(LeuNDI)₁₂] against these polyaromatic species reveals quenching of their emission with increasing concentration of the cage (Figure 4 and Supporting Information). Stern–Volmer plots yield quenching constants of 0.182 M⁻¹ for naphthalene (at 337 nm) and 0.265/0.084 M⁻¹ for triphenylene (at 373 and 421 nm, respec-

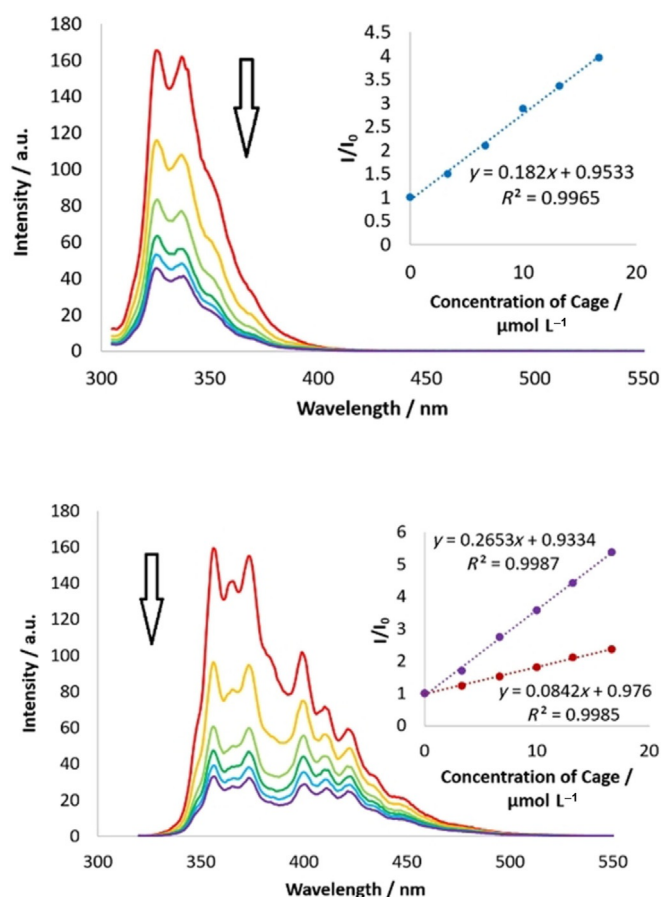
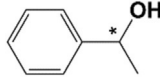
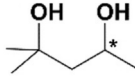
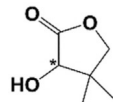


Figure 4. Titrations of (top) naphthalene and (bottom) triphenylene against $[\text{Cu}_{12}(\text{LeuNDI})_{12}]$ showing the quenching of fluorescence emission of the polyaromatic molecules upon addition of the cage demonstrated by Stern–Volmer plots (insets) against maxima at 337 nm (naphthalene), 373 and 421 nm (triphenylene, purple and red, respectively).

tively). This response of the NDI cores within $[\text{Cu}_{12}(\text{LeuNDI})_{12}]$ to aromatic molecules indicates potential for using its fluorescence as a reporting mechanism.

The octahedral cage, as stated above, is chiral due to the presence of amino acid residues on the ligand enforcing a single direction of rotation of the ligands around the copper paddlewheel motifs. Detection of chiral molecules, and particularly separation of enantiomers from racemic mixtures, remains an important area of separations sciences,^[22] and therefore the crystalline material of $[\text{Cu}_{12}(\text{LeuNDI})_{12}(\text{OH}_2)_{12}]$ underwent some preliminary testing for its capacity to sorb and release some small chiral analytes from solution through a sorption/desorption process. Samples of the crystalline material were soaked in racemic mixtures of 1-phenylethanol, 2-methyl-2,4-pentanediol (hexyleneglycol) and pantolactone in methanol or heptane (see Supporting Information for full details). After soaking for 24 hours the crystalline material was recovered by filtration, rinsed to remove any analytes on the surface, and placed in fresh methanol to allow the sorbed guests to desorb. A sample of supernatant was analysed by GC to determine the *ee* value (Table 1). Modest enantioselective uptake was observed, although it is noted that the analytes were present at relatively

Table 1. Results of sorption testing through solution sorption–desorption, given as *ee* (%), from small racemic analytes in either methanol or hexane solutions.

1-Phenylethanol	2-Methyl-2,4-pentanediol	Pantolactone
		
MeOH: 2.5 % (<i>S</i>) C ₇ H ₁₆ : 8.2 % (<i>S</i>)	MeOH: 13 % (<i>R</i>) C ₇ H ₁₆ : 8.7 % (<i>S</i>)	MeOH: 7 % (<i>R</i>) C ₇ H ₁₆ : insoluble

high concentrations (ca. 1 M) and this may artificially lower the observed %*ee* if the host framework is overloaded. These results are very promising and suggestive that this class of material has good potential as a solid support for separation techniques. Separation of 2-methyl-2,4-pentanediol produced an unexpected result, with the preferentially sorbed isomer dependent on the solvent used. A possible explanation for this is that coordination at the apical sites of the paddlewheels is involved for this guest, and therefore methanol competes for these sites whereas heptane will not; further studies are required to fully determine the mechanism of the host–guest interaction.

In conclusion, we have shown that the chiral “octahedral” cage complex $[\text{Cu}_{12}(\text{LeuNDI})_{12}]$ has great versatility, being able to demonstrate markedly different gas sorption profiles for closely related gaseous guests (CO₂ vs. N₂O), quenching response to aromatic species in solution and enantioselective sorption and release of small analytes from solution. The charge-neutrality, stability and chirality of this metal–organic cage set it apart from most others and suggest potential for further solution-based applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chirality • gas storage • metal–organic cage • self-assembly • supramolecular chemistry

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