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Highly selective CO$_2$ vs. N$_2$ adsorption in the cavity of a molecular coordination cage

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Two M$_8$L$_{12}$ cubic coordination cages, as desolvated crystalline powders, preferentially adsorb CO$_2$ over N$_2$ with ideal selectivity CO$_2$/N$_2$ constants of 49 and 30 at 298 K. A binding site for CO$_2$ is suggested by crystallographic location of Cs$_2$ within the cage cavity at an electropositive hydrogen-bond donor site, potentially explaining the high CO$_2$/N$_2$ selectivity compared to other materials with this level of porosity.

Porous solid-state materials are attractive for gas adsorption purposes, with several classes of porous material gaining increasing attention in recent years. These include metal-organic frameworks (MOFs)/coordination polymers,1-17 covalent organic frameworks (COFs)/ microporous organic polymers (MOPs),18-24 molecular cages;25-35 and other molecular crystals.36-43 In the case of MOFs and MOPs, impressive gas uptake capacities have been reported, and extremely highly porous materials described.12,14,21 However, higher uptake capacity in porous materials can come at the expense of selectivity between small gaseous molecular guests, as shown in previous work comparing porous organic cages of different pore sizes with each other, and with MOFs.32 Adsorbents which are selective for the desired adsorbate are desirable, but not necessarily at the expense of uptake capacity. For this purpose, the design of flexible adsorbents whose pores may open under the influence of an external stimulus has been demonstrated, both in MOFs;1,7,13 and extrinsically porous materials;17,37,42 this is still an emerging field.

Perhaps better developed is the functionalisation of the pore space of intrinsically porous materials, to enhance selectivity for binding of different gaseous guests. In particular, the improvement of CO$_2$ adsorption selectivity in MOFs has been demonstrated by the addition of hydrogen-bonding sites3,11 or the fluorination of pores.5,44,45 These internal surface modifications can however come at the expense of uptake capacity by occupying some of the interior space, so an adsorbent in which a binding site is built into the ‘walls’ of the cavity is desirable.

We have previously reported the structures and guest binding properties of the cubic coordination cages [M$_8$L$_{12}$]X$_{16}$, in which M are transition metal dications [usually Co(II)] located at the vertices of the cage, and L are bis(pyrazolyl-pyridine) bridging ligands which connect a pair of metal ions along every edge of the assembly (Fig. 1).46-52 The ligand L may be unsubstituted (L$^0$; R = H in the figure) in which case the cages are soluble in polar organic solvents;47,48 or may be substituted (L$^w$; R = CH$_3$OH in the figure) to make the cages water-soluble.49-52 These cages have been shown to bind a wide range of organic guests in the central cavity. In organic solvents guest binding is partly driven by hydrogen-bonding of electron-rich regions of guests to H-bond donor pockets located on the interior surface of the cage, in regions of high positive electrostatic potential; this affords binding constants in the range 10$^2$ – 10$^3$ M$^{-1}$.47,7 In water, the hydrophilic effect provides the dominant driving force for strong binding of hydrophobic guests with binding constants of up to 10$^5$ M$^{-1}$.49,51 Here we report an investigation into the gas sorption capability of these materials, demonstrating a high selectivity for CO$_2$ uptake over N$_2$ in the solid state, which we ascribe to the presence of the same H-bond donor sites on the cage interior surface that facilitate guest binding in solution.47,53

Fig. 1. General structure of host cages [M$_8$L$_{12}$]BF$_4$)$_{16}$: types A (R = H, M = Cd) and B (R = CH$_3$OH, M = Co). (a) A sketch emphasising the cubic array of M(II) ions and the disposition of a bridging ligand spanning an edge; (b) a space-filling representation of the complex cation with ligands coloured separately for clarity.

We used the cages [Cd$_8$(L$^0$)$_{12}$]BF$_4$)$_{16}$ (A)48 and [Co$_8$(L$^w$)$_{12}$]BF$_4$)$_{16}$ (B),45 both of which have been reported before. The compounds were prepared as methanol solvates, and then dried and thermally desolvated. Powder X-ray diffraction analysis of the dried materials showed that B retains the same phase that was observed in the single crystal structure of the methanol solvate, whereas A loses crystallinity and becomes amorphous. This is likely related to the fact that in B the presence of hydroxymethyl groups on the exterior surface of the cages results in a formation of an intermolecular O-H•••O hydrogen-bonding network of cage molecules which allows crystallinity to be
Attempts to locate CO$_2$ guests within the cages were made using X-ray crystallography on single crystals under a CO$_2$ atmosphere, but the crystals fractured rapidly into microcrystalline powder upon desolvation. Instead, using the method that has worked with other guests, single crystals of B (still solvated to prevent cracking) were soaked in liquid CS$_2$ – as a structural analogue of CO$_2$ – at 40 °C for 2 hours. This resulted in uptake of CS$_2$ into the cage cavity.

Table 1. Gas sorption quantities for CO$_2$ and N$_2$, and CO$_2$/N$_2$ selectivity constants, for both cages.

<table>
<thead>
<tr>
<th>Cage</th>
<th>T / K</th>
<th>1 bar CO$_2$ uptake (mmol/g)</th>
<th>1 bar N$_2$ uptake (mmol/g)</th>
<th>CO$_2$/N$_2$ selectivity constant</th>
<th>Simple (ideal)</th>
<th>Henry’s law</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>273</td>
<td>0.0138</td>
<td>0.0309</td>
<td>32</td>
<td>49</td>
<td>165</td>
</tr>
<tr>
<td>A</td>
<td>273</td>
<td>0.0138</td>
<td>0.027</td>
<td>37</td>
<td>49</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>0.0138</td>
<td>0.022</td>
<td>30</td>
<td>49</td>
<td>165</td>
</tr>
</tbody>
</table>

Crystallographic analysis showed the structure to be [Co$_3$(L$_w$)$_2$]([BF$_4$]$_6$)$_{10}$•CS$_2$•5H$_2$O (Fig. 3) in which a molecule of CS$_2$ is located such that it interacts with one of the hydrogen-bond donor pockets on the interior surface which are located at the two fac tris-chelate sites at either end of the long diagonal of the approximately cubic assembly.

![Fig. 2. Volumetric gas sorption profiles for CO$_2$ and N$_2$ in cages A (top) and B (bottom) at 298 K. Filled circles represent adsorption and hollow circles represent desorption.](image)

![Fig. 3. Crystal structure of the complex cation of [Co$_3$(L$_w$)$_2$]([BF$_4$]$_6$)•CS$_2$•5H$_2$O: (a) a view of the entire cage (in wireframe) with the CS$_2$ guest (50% site occupancy in each of two positions) shown space-filling; (b) a close-up of the hydrogen-bonding environment around the CS$_2$ guest, with the shortest CH•••S contacts shown with red dashed lines.](image)
The site occupancy of the CS₂ in each of the two pockets is 0.5, i.e. in the crystal structure there is one guest molecule per cage but it is disordered equally over the two possible sites. The CS₂ guest is oriented such that the S atom ([S(11S)]) that is directed into the corner pocket is involved in several CH•••S contacts (C•••S distances in the range 3.5 – 3.7 Å) with H atoms from CH₂ groups and naphthyl groups that converge around the guest binding site; the (non-bonded) Co(1)•••S(11S) separation is 5.65 Å. The other S atom of the guest S(13S) is also involved in a short CH•••S contact (3.51 Å) with an inwardly-directed naphthyl CH proton. This set of interactions is emphasised in Fig. 3(b).

The quadrupole moment of CS₂ is opposite in sign to that of CO₂ so in terms of point charges it is denoted (δ⁺–δ⁻)–(δ⁻).55,56 in this respect CS₂ is not electronically analogous to CO₂ although it is a reasonable geometric model. Nonetheless the ability of the S atoms of CS₂ to act as hydrogen-bond acceptors, based on the local electron density at the S atoms associated with lone pairs, is well established.57-60 We showed a while ago that the convergent array of CH donors located close to the Co(II) ions at the fac tris-chelate cage corners, in a region of high positive electrostatic potential, provides an H-bond donor site to guests that is comparable in strength to phenol.57 Given that phenol has been shown to be a sufficiently strong H-bond donor to form ·H•••NX hydrogen bonds with CS₂,58 we propose that this structure of the B-CS₂ complex provides (i) a reasonable structural model for CO₂ binding in the cavity,54 and (ii) a rationale for the strong preference of the cages for CO₂ vs. N₂ binding. We note also that CS₂ binds weakly in the cavity of B in aqueous solution; a standard ¹H NMR titration showed that CS₂ binds in fast exchange, with incremental shifts in the positions of some of the ¹H NMR signals of B during addition of CS₂ fitting a 1:1 binding isotherm with K = 2 M⁻¹.†

![Fig. 4.](image)

**Fig. 4.** Logarithmic plot of ideal CO₂/N₂ selectivity vs. CO₂ uptake capacity for a variety of porous materials. The linear trendline in black shows the general inverse relationship between gas uptake capacity and CO₂/N₂ selectivity. Data for the coordination cages in this work are shown as red triangles. Data for porous materials from other groups are shown for comparison as blue circles (Cooper group, ref. 32; Zhang group, refs. 34, 35; various selected MOFs, see references within ref. 32).

The balance between absolute CO₂ uptake, and CO₂/N₂ uptake selectivity, is amongst the best known in any kind of porous material. Fig. 4 shows data for a range of other porous materials; on this graph the results for cages A and B are clearly better than the average performance for selectivity vs. uptake for many other materials, with the results for cage B at 298 K lying furthest above the trend-line of any of the representative set of examples included in the figure.

In conclusion we have demonstrated good CO₂ uptake by a molecular cage complex in which the gaseous guest binds in the central cavity even when the bulk materials are not conventionally porous. Such examples of gas sorption into the cavities of molecular cages – in contrast to porous network materials – are very rare.61,62 On the basis of the structural model (based on CS₂) this arises because of favourable polar interactions between the quadrupolar CO₂ guest and charge-assisted hydrogen-bond donor sites on the interior surface of the cage host;63,53,54 these same structural features also result in particularly high selectivity for binding of polar CO₂ compared to non-polar N₂.

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### Notes and references

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† Electronic Supplementary Information (ESI) available: details of the crystal structure of [Co(salen)₂]BF₄·CS₂·5H₂O; powder XRD analyses; gas sorption data at 273 K; NMR titration data for binding of CS₂ into B in aqueous solution; additional figures. See DOI: 10.1039/b000000x/

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