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## Highly selective CO<sub>2</sub> vs. N<sub>2</sub> adsorption in the cavity of a molecular coordination cage

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Two M<sub>8</sub>L<sub>12</sub> cubic coordination cages, as desolvated crystalline powders, preferentially adsorb CO<sub>2</sub> over N<sub>2</sub> with ideal selectivity CO<sub>2</sub>/N<sub>2</sub> constants of 49 and 30 at 298 K. A binding site for CO<sub>2</sub> is suggested by crystallographic location of CS<sub>2</sub> within the cage cavity at an electropositive hydrogen-bond donor site, potentially explaining the high CO<sub>2</sub>/N<sub>2</sub> 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;<sup>1-17</sup> covalent organic frameworks (COFs)/ microporous organic polymers (MOPs);<sup>18-24</sup> molecular cages;<sup>25-35</sup> and other molecular crystals.<sup>36-43</sup>

In the case of MOFs and MOPs, impressive gas uptake capacities have been reported, and extremely highly porous materials described.<sup>12,14,21</sup> 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.<sup>32</sup> 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<sup>1,7,13</sup> and extrinsically porous materials;<sup>17,37,42</sup> 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<sub>2</sub> adsorption selectivity in MOFs has been demonstrated by the addition of hydrogen-bonding sites<sup>3,11</sup> or the fluorination of pores.<sup>5,44,45</sup> 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<sub>8</sub>L<sub>12</sub>]X<sub>16</sub>, 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).<sup>46-52</sup> The ligand L may be unsubstituted (L<sup>o</sup>: R = H in the figure) in which case the cages are soluble in

polar organic solvents,<sup>47,48</sup> or may be substituted (L<sup>w</sup>: R = CH<sub>2</sub>OH in the figure) to make the cages water-soluble.<sup>49-52</sup> 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<sup>2</sup> – 10<sup>3</sup> M<sup>-1</sup>.<sup>47</sup> In water, the hydrophobic effect provides the dominant driving force for strong binding of hydrophobic guests with binding constants of up to 10<sup>8</sup> M<sup>-1</sup>.<sup>49-51</sup> Here we report an investigation into the gas sorption capability of these materials, demonstrating a high selectivity for CO<sub>2</sub> uptake over N<sub>2</sub> 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.<sup>47,53</sup>

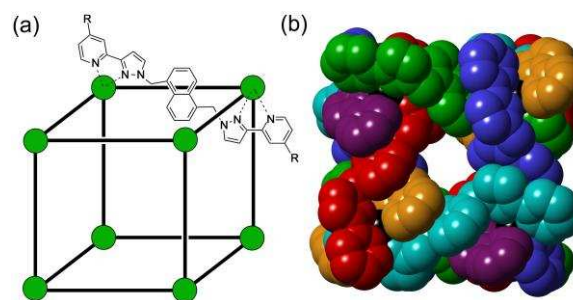
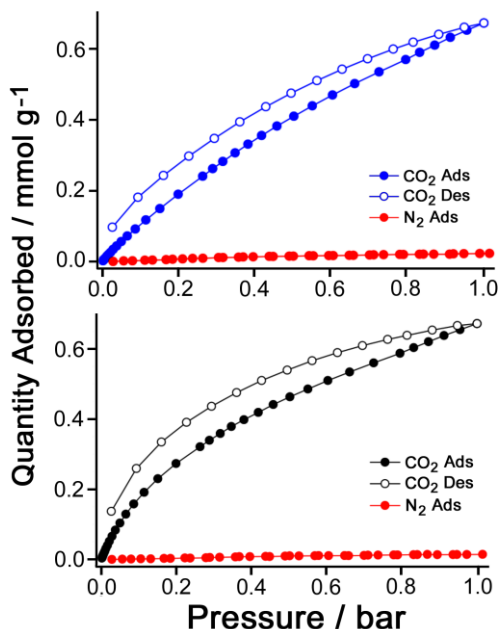


Fig. 1. General structure of host cages [M<sub>8</sub>L<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub>: types **A** (R = H, M = Cd) and **B** (R = CH<sub>2</sub>OH, M = Co). (a) A sketch emphasising the cubic array of M(II) ions and the disposition of a bridging ligand spanning an edge; (b) a space-filling representation of the complex cation with ligands coloured separately for clarity.

We used the cages [Cd<sub>8</sub>(L<sup>o</sup>)<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub> (**A**)<sup>48</sup> and [Co<sub>8</sub>(L<sup>w</sup>)<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub> (**B**),<sup>49</sup> 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<sup>†</sup> 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

retained even when solvent molecules are lost.<sup>†</sup> In **A** in contrast there are no such interactions between the exterior surfaces of adjacent cages and crystallinity is lost on desolvation. However, <sup>1</sup>H NMR and mass spectrometric analyses confirmed that the integrity of the molecular cages is retained even when the crystals are desolvated.



**Fig. 2.** Volumetric gas sorption profiles for CO<sub>2</sub> and N<sub>2</sub> in cages **A** (top) and **B** (bottom) at 298 K. Filled circles represent adsorption and hollow circles represent desorption.

The cages were found to be non-porous having BET surface areas <20 m<sup>2</sup>/g. The volumetric gas sorption isotherms were measured for uptake of CO<sub>2</sub> and N<sub>2</sub> by both cages at 298 K (Fig. 2) and also at 273 K.<sup>†</sup> Both cages demonstrate highly selective uptake for CO<sub>2</sub> vs. N<sub>2</sub> at both temperatures. The gas uptake comparisons and selectivity constants are summarised in Table 1, and Henry's law calculation data is presented in the ESI.<sup>†</sup> The capacity for CO<sub>2</sub> uptake is very similar for both cages. Although the cages have identical internal cavities, as we mentioned above the supramolecular structure of the cages is different because of the presence (cage **B**) or absence (cage **A**) of inter-cage hydrogen-bonding interactions between peripheral functional groups. This suggests either that CO<sub>2</sub> uptake in the interstitial spaces between cages is very low, or that the void space between cages is similar in both materials (which in the case of the desolvated cage **B** is known to be small due to the hydrogen bonding, and therefore uptake here would be low anyway). We have noted in previous work that when crystalline cage samples are soaked in solutions of guests, quite large guest molecules can permeate the crystals and enter the cage cavities,<sup>50,52</sup> even when the windows are occluded in the crystal structure and when the guest dimensions are larger than the 4 Å windows<sup>47</sup> in the cage faces. Thus, for guest molecules as small as N<sub>2</sub> or CO<sub>2</sub>, differences in crystal packing are unlikely to prevent adsorption: the similarity in CO<sub>2</sub> uptake for both cage types therefore most plausibly relates to the similarity of the cavity inside cages **A** and **B**.<sup>49</sup>

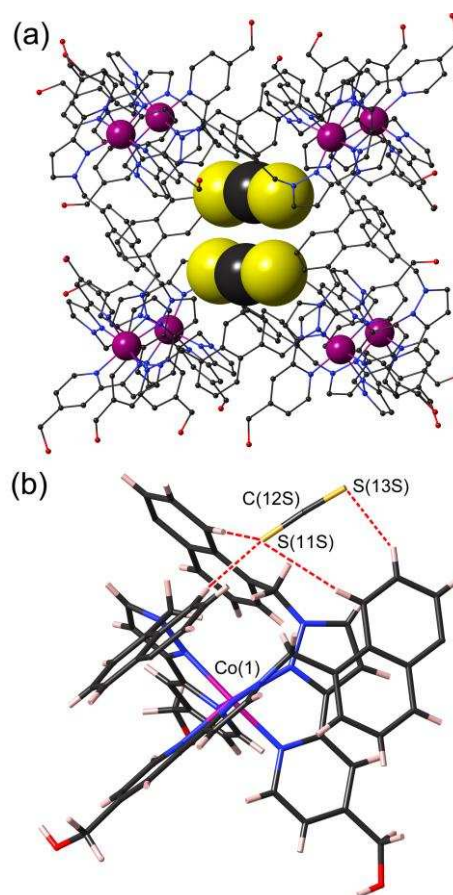
Attempts to locate CO<sub>2</sub> guests within the cages were made

using X-ray crystallography on single crystals under a CO<sub>2</sub> 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<sub>2</sub> – as a structural analogue of CO<sub>2</sub> – at 40 °C for 2 hours. This resulted in uptake of CS<sub>2</sub> into the cage cavity.

**Table 1.** Gas sorption quantities for CO<sub>2</sub> and N<sub>2</sub>, and CO<sub>2</sub>/N<sub>2</sub> selectivity constants, for both cages.

Cage	T / K	1 bar CO <sub>2</sub> uptake (mmol/g)	1 bar N <sub>2</sub> uptake (mmol/g)	CO <sub>2</sub> /N <sub>2</sub> selectivity constant	
				Simple (ideal)	Henry's law
<b>B</b>	273	1.003	0.0309	32	156
	298	0.672	0.0138	49	165
<b>A</b>	273	1.005	0.027	37	59
	298	0.673	0.022	30	32

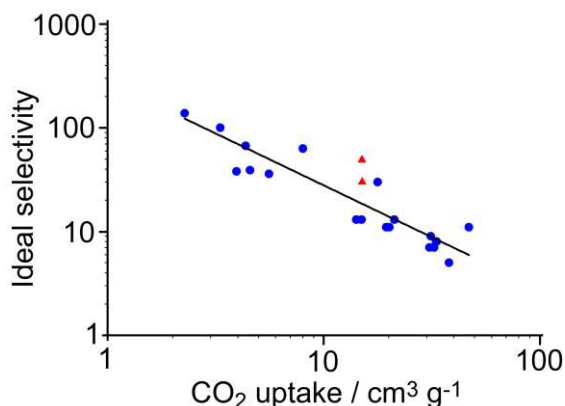
Crystallographic analysis<sup>†</sup> showed the structure to be [Co<sub>8</sub>(L<sup>w</sup>)<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub>•CS<sub>2</sub>•5H<sub>2</sub>O (Fig. 3) in which a molecule of CS<sub>2</sub> is located such that it interacts with one of the hydrogen-bond donor pockets on the interior surface which are located at the two fac tris-chelate sites at either end of the long diagonal of the approximately cubic assembly.<sup>47-49</sup>



**Fig. 3.** Crystal structure of the complex cation of [Co<sub>8</sub>(L<sup>w</sup>)<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub>•CS<sub>2</sub>•5H<sub>2</sub>O: (a) a view of the entire cage (in wireframe) with the CS<sub>2</sub> guest (50% site occupancy in each of two positions) shown space-filling; (b) a close-up of the hydrogen-bonding environment around the CS<sub>2</sub> guest, with the shortest CH...S contacts shown with red dashed lines.

The site occupancy of the CS<sub>2</sub> 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 CS<sub>2</sub> 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 CH<sub>2</sub> 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 CS<sub>2</sub> is opposite in sign to that of CO<sub>2</sub> so in terms of point charges it is denoted (δ<sup>+</sup>)-(δ<sup>-</sup>)-(δ<sup>+</sup>);<sup>55,56</sup> in this respect CS<sub>2</sub> is not electronically analogous to CO<sub>2</sub> although it is a reasonable geometric model. Nonetheless the ability of the S atoms of CS<sub>2</sub> to act as hydrogen-bond acceptors, based on the local electron density at the S atoms associated with lone pairs, is well established.<sup>57-60</sup> 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.<sup>47</sup> Given that phenol has been shown to be a sufficiently strong H-bond donor to form S...HX hydrogen bonds with CS<sub>2</sub>,<sup>57</sup> we propose that this structure of the B•CS<sub>2</sub> complex provides (i) a reasonable structural model for CO<sub>2</sub> binding in the cavity,<sup>54</sup> and (ii) a rationale for the strong preference of the cages for CO<sub>2</sub> vs. N<sub>2</sub> binding. We note also that CS<sub>2</sub> binds weakly in the cavity of B in aqueous solution; a standard <sup>1</sup>H NMR titration showed that CS<sub>2</sub> binds in fast exchange, with incremental shifts in the positions of some of the <sup>1</sup>H NMR signals of B during addition of CS<sub>2</sub> fitting a 1:1 binding isotherm with K = 2 M<sup>-1</sup>.<sup>†</sup>



**Fig. 4.** Logarithmic plot of ideal CO<sub>2</sub>/N<sub>2</sub> selectivity vs. CO<sub>2</sub> uptake capacity for a variety of porous materials. The linear trendline in black shows the general inverse relationship between gas uptake capacity and CO<sub>2</sub>/N<sub>2</sub> 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 CO<sub>2</sub> uptake, and CO<sub>2</sub>/N<sub>2</sub> 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 CO<sub>2</sub> 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.<sup>61,62</sup> On the basis of the structural model (based on CS<sub>2</sub>) this arises because of favourable polar interactions between the quadrupolar CO<sub>2</sub> guest and charge-assisted hydrogen-bond donor sites on the interior surface of the cage host;<sup>47,53,54</sup> these same structural features also result in particularly high selectivity for binding of polar CO<sub>2</sub> compared to non-polar N<sub>2</sub>.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: details of the crystal structure of [Co<sub>8</sub>(L<sup>3</sup>)<sub>12</sub>](BF<sub>4</sub>)<sub>16</sub>•CS<sub>2</sub>•5H<sub>2</sub>O; powder XRD analyses; gas sorption data at 273 K; NMR titration data for binding of CS<sub>2</sub> into B in aqueous solution; additional figures. See DOI: 10.1039/b000000x/

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