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Binding CO_2 by a Cr_8 metallacrown

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Abstract:

The $\{Cr_8\}$ metallacrown $[CrF(O_2C^tBu)_2]_8$, containing a F-lined internal cavity shows high selectivity for CO_2 over N_2. DFT calculations and absorption studies support the multiple binding of F-groups to the C-centre of CO_2 [C•••F = 3.190(9) to 3.389(9) Å], as confirmed by single crystal X-ray diffraction.

The design of materials that bind and separate specific gases is a major activity at present. Much of this work has involved metal-organic framework (MOF) materials,[1-4] but there is also significant work involving reaction with organic molecules to produce carbamates reversibly.[5] We were particularly intrigued by a report from Zawarotko and co-workers in which SiF_6^{2-} anions were used as pillar ligands within SIFSIX-3-Zn, and the terminal fluorides, which project into the pores, were shown to bind CO_2.[6] This led us to examine the possible binding of CO_2 to the well-known metallacrown $[CrF(O_2C^tBu)_2]_8$ **1** which contains a F-lined inner cavity. The octametallic metallacrown, $[CrF(O_2C^tBu)_2]_8$ **1**, first reported by Gerbeleu *et al,*[7] has been shown to bind to small organic molecules by Larsen and co-workers,[8] and has also been extensively studied as a prototypical anti-ferromagnetically coupled ring.[9]

Compound **1** can be prepared in very high yield from the reaction of hydrated CrF_3 with pivalic acid. **1** normally crystallises with solvent molecules bound near the central cavity, but recrystallisation from 1-bromodecane for produces a desolvated version that is ideal for the studies we wished to pursue. The structure of **1** contains an octagon of Cr^{III} sites with each Cr•••Cr edge bridged by a F^- and two pivalate ligands. The F^- ligands are alternately slightly above and below the plane formed by the eight Cr^{III} centres.

Crystals of **1** were exposed to an atmosphere of CO_2 at 290 K for 2 h to form the complex **1-0.79CO₂**, as established by single crystal X-ray diffraction which shows (Figure 1) the binding of a CO_2 within the cavity of the $\{Cr_8\}$ metallacrown. The carbon atom of the CO_2 molecule is 1.31 Å above the mean plane of the eight $\{Cr_8\}$ ions, with nearest contacts to five F^- ligands (F2, F4, F5, F6 and F8) which lie on the same side of the ring. These five C•••F contacts vary from 3.190(9) to 3.389(9) Å. The CO_2 molecule is linear, with the <O=C=O = 178.9(11)°. Refinement of the site occupancy shows a total of 0.787(7) molecules of CO_2 adsorbed per metallacrown, and this occupancy is in excellent agreement with the values for the CO_2 absorption capacity (see below). The presence of CO_2 in the structure is also shown by an FT-IR spectroscopy with bands observed at 2339 (asymmetric stretch) and 660 cm^{-1} (bending mode) (Figure S1).

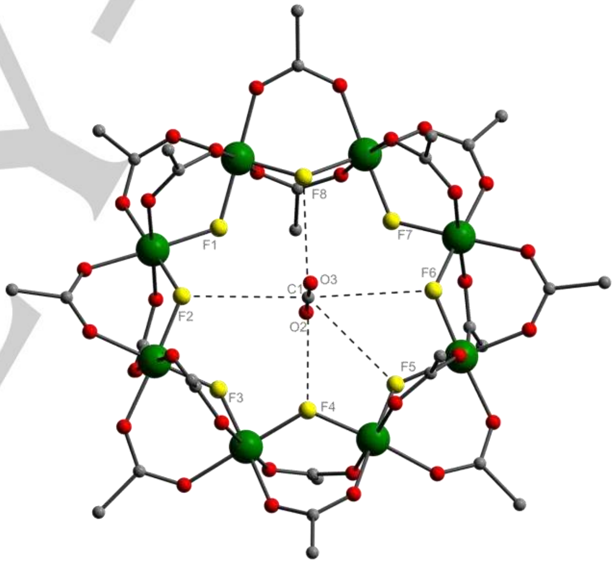

Figure 1. View of single crystal X-ray structure of **1-0.79CO₂**. C•••F contacts shown as dashed lines: C1•••F2 3.37(1), C1•••F4 3.190(9), C1•••F5 3.29(1), C1•••F6 3.35(1), C1•••F8 3.391) Å. Methyl groups of pivalates omitted for clarity. Cr, green; F, yellow; O, red; C, grey.

In a separate experiment, a single crystal of **1** was exposed to 1 bar of CO_2 gas at 195 K in a gas cell and this resulted in the formation of **1-1.3CO₂**. The crystal structure was determined by *in situ* diffraction and differs in two ways from that in the previous *ex situ* study of **1-0.79CO₂**: the internal cavity is now fully occupied by a CO_2 molecule and a second molecule of CO_2 is found between the $\{Cr_8\}$ rings with a partial occupancy of 30(5)%. (Figure S3 and Supplementary information S4).

Thermogravimetric analysis (TGA) of freshly prepared samples of **1-0.79CO₂** shows gradual mass losses of 1.96% in the temperature range of 52-200 °C, consistent with the loss of one molecule of CO_2 per metallacrown. There is a further large mass loss between 255-386 °C (Figure S2), which is also found for **1,** consistent with sample decomposition. An isothermal (45°C) TGA was also performed on **1-0.79CO₂** over a period of 4 h

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showing a gradual mass loss of 1.30%, consistent with the loss of 0.65 molecules of CO_2.

The porosity of compound **1** was investigated by running a N_2 adsorption isotherm at 77 K, which indicates that this material is essentially non-porous, with a saturation capacity of around 17 cm^3g^{-1} at a partial pressure (P/P_0) of 0.9, presumably due to the activation diffusion of N_2 molecules at 77 K (Figure S5).

Adsorption isotherms for N_2 and CO_2 in **1** collected at ambient temperatures (288 K) to a pressure of 5 bar both display typical type-I behavior. The adsorption of N_2 over this pressure range is very low, reaching 0.027 mmol g^{-1} at 1 bar, rising gradually to 0.076 mmol g^{-1} at 5 bar (Figure 2). The adsorption profile of CO_2 is markedly different to that of N_2, with a very sharp adsorption profile, reaching 0.33 mmol g^{-1} at 1 bar, and increasing gradually to 0.41 mmol g^{-1} at 5 bar and 288 K. CO_2 adsorption in this material at 1 bar is 12 times higher than the adsorption of N_2 under the same conditions, and is in excellent agreement with the value obtained for the structure of **1-0.79CO₂** (0.36 mmol g^{-1}, 290 K, 1 bar). Negligible CO_2 uptake is seen before 0.04 bar pressure, as the material is non-porous and hence this pressure is needed to provide enough energy to allow diffusion of CO_2 into the material.

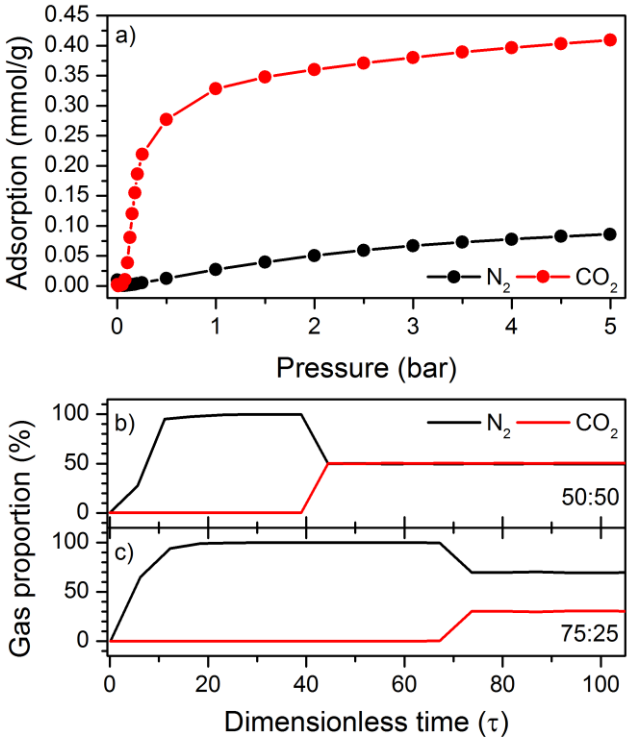

Figure 2. View of isotherms up to 5 bar for CO_2 and N_2 adsorption in **1** at 288 K (*top*) and the corresponding breakthrough plot for an equimolar and 75:25 N_2/CO_2 gas mixture in terms of dimensionless time (*bottom*). Dimensionless time represents the number of residency periods of the gas in sample chamber

The binding energy of CO_2 in the metallacrown can be estimated from the simultaneous thermal analysis by thermogravimetry and differential scanning calorimetry (Figure S8). A sample of **1** was activated at 150 °C then cooled to 25 °C under a flow of CO_2 and the heat flow was measured directly. A spike in the heat flow upon guest adsorption represents a heat of adsorption in the region of 45(1) kJ mol^{-1}. This value is similar to the heat of adsorption reported using variable temperature CO_2 isotherms for SIFSIX-3-Zn (45 kJ mol^{-1}) in which CO_2 molecules interact with terminal fluorides of SIF_6^{2-} groups.[6]

These results suggest a strong interaction of CO_2 with the central adsorption site of the metallacrown in comparison to N_2, which indicates that **1** might be able to selectively separate CO_2 from N_2. The CO_2/N_2 selectivity of this material was calculated by comparison of the single gas isotherms to be 12 and 5 at 1 and 5 bar, respectively. Henry's Law selectivity calculations reveal a selectivity factor of *ca* 37 (Figure S7). The selectivity of this material was further investigated by breakthrough experiments, where 50:50 and 75:25 mixtures of N_2/CO_2 were flowed over a packed bed of **1** at 298 K, and the outflow measured by mass spectrometry. The column of **1** was found to have a significantly different retention time for these two gases, with pure N_2 eluting from the column at dimensionless times (τ) of 39 and 67 for 50:50 and 75:25 mixtures, respectively, (Figure 2 b &c) before CO_2 breaks through.

To understand the binding of CO_2 to **1** we performed calculations using density functional theory (DFT) including an empirical dispersion term (BP86[11,12]-D3BJ[13,14]/Def2-SVP[15]). The calculations assumed unit occupancy of CO_2 in the central cavity of the metallacrown, *i.e.* **1-1CO₂**. The electronic structure of the Cr_8 wheel presents significant challenges as it incorporates eight open-shell Cr^{III} ions. At the DFT level it is necessary to use a spin-unrestricted approach leading to a highly broken symmetry solution. The obvious choice of spin-pairing corresponds to an alternating set of spin up (m_s = +3/2) and spin down (m_s = –3/2) Cr^{III} ions to give an S = 0 ground state, but combinatorically there are 70 possible choices of spin pairing that can yield an overall S = 0. To treat all structures using a consistent computational model, full geometry optimizations of the complex (**1-1CO₂**), the wheel (**1**) and CO_2 were carried out (for details see SI). C•••F distances in the optimized structure ranged from 3.224 – 3.352 Å, in good agreement with that obtained by single crystal X-ray crystal diffraction (Figure 1, Table 1).

Table 1. Comparison of measured and DFT parameters

	Measured	DFT[a]
CO_2 uptake under 1 bar CO_2 at 290 K	0.79(1)[b]	n/a
CO_2 uptake under 1 bar CO_2 at 195 K	1.30(5)[b]	n/a
Binding energy /kJ mol^{-1}	45(1)[c]	56.2
C⋯F distances / Å	3.19(1) to 3.39(1)[b]	3.22 to 3.35
O-C-O angle/ °	178.9(11)[b]	179.8

a. Calculated for a structure with one CO_2 per metallacrown
b. From X-ray single crystal diffraction
c. From combined TGA/DSC measurements

A value of 179.8° was obtained for <O=C=O compared with 178.9(11)° in the crystal structure. The main difference in the

structures is that the CO_2 molecule is more symmetrically distributed within the wheel in the calculated structure, with the C centre of CO_2 sitting only 0.189 Å above the centroid of the eight Cr^{III} ions. Including counterpoise corrections we obtain a binding energy between **1** and CO_2 of 56.2 kJ mol^{-1} in reasonable agreement with the binding energy measured by DSC.

Edge-on views of metallacrown show the calculated electrostatic potential (ESP) in **1-1CO$_2$** and **1** (Figure 3). Atomic partial charges were obtained through natural population analysis (NPA).[16] The F atoms of the wheel are found to carry partial charges of –0.33. The carboxylate O atoms have charges in the range –0.54 to –0.58, and +0.79 for the Cr atoms. The CO_2 unit carries charges of +1.01 on C and –0.50/–0.51 on the two O atoms; these partial charges are almost identical to those found in the optimized isolated CO_2 (C +0.98, O –0.49).

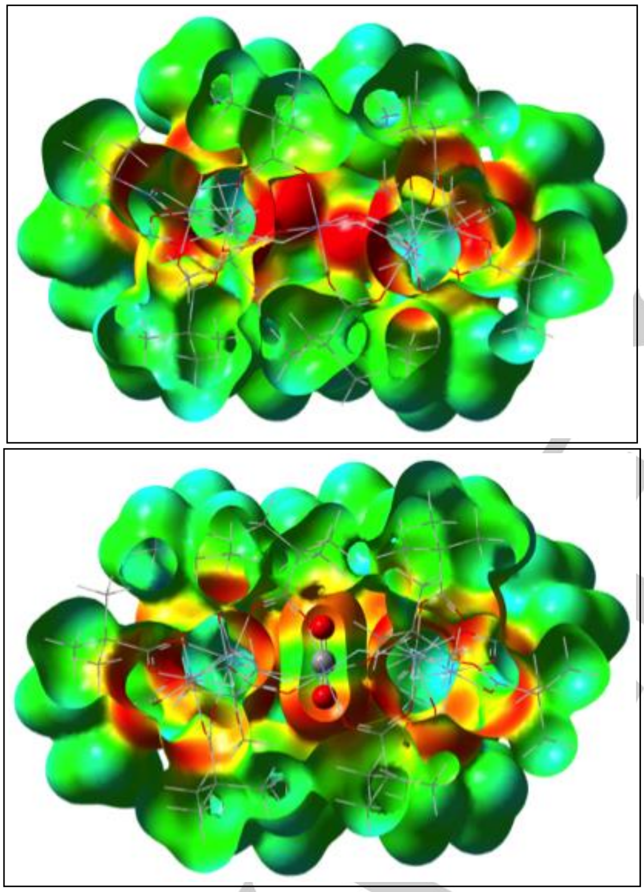

Figure 3. Side view of electrostatic potential (BP86-D3/Def2-SVP) mapped on to the total density at an isosurface value of 0.004 au. Top panel **1**, bottom panel **1-1CO$_2$.** Blue/green/red refer to positive/neutral/negative values, the range is +0.06 - –0.06. The CO_2 is shown as ball and stick with other atoms shown as wireframe for clarity.

The distribution of the ESP of the CO_2 unit in the cavity of the wheel clearly shows the potential for strong electrostatic interactions, in keeping with our interpretation of this non-covalently bound complex. Therefore, the origin of the interaction between the CO_2 guest molecule and the $\{Cr_8\}$ metallacrown is due to the electrostatic attraction between the partial negative charge of the F^- centres and the partial positive charge of the C centre of the CO_2 molecule, as concluded by Nugent *et al*.[6] Compound **1** is therefore the first metallocrown to bind CO_2. The closest example is a 16-MC-4 compound reported by Gätjens et al, which reacts with CO_2 to produce a bound bicarbonate.[17] Compound **1** shows a breakthrough selectivity for a 50:50 CO_2/N_2 mixture of 6.2 similar to many MOFs.[18-19] For example, a perfluorinated triazine-based framework takes around 10 minutes for CO_2 to pass through a packed bed sample when an N_2:CO_2 (90:10) mixture is added.[20] In the future we will explore this binding to see whether **1** can bind other small molecules, or whether related heterometallic rings[21] also bind small molecules, and perhaps be used to activate them.

Experimental Section

See the Supporting Information for full details of synthesis, measurements and theoretical modelling

Acknowledgements

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Keywords: Metallacrown • Single-crystal X-ray diffraction • Non-porous • gas adsorption

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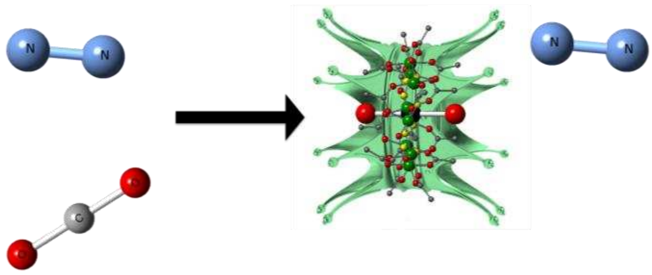

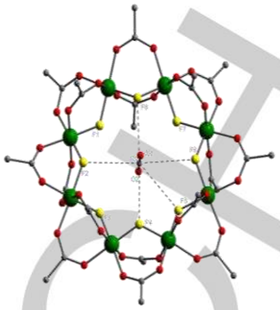

Layout 1:

COMMUNICATION

Green metallacrown for green applications: A Cr_8 ring is shown to bind CO_2 strongly and selectively through C•••F interactions.

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Page No. – Page No.

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