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Binding CO₂ by a Cr₈ metallocrown

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Abstract:

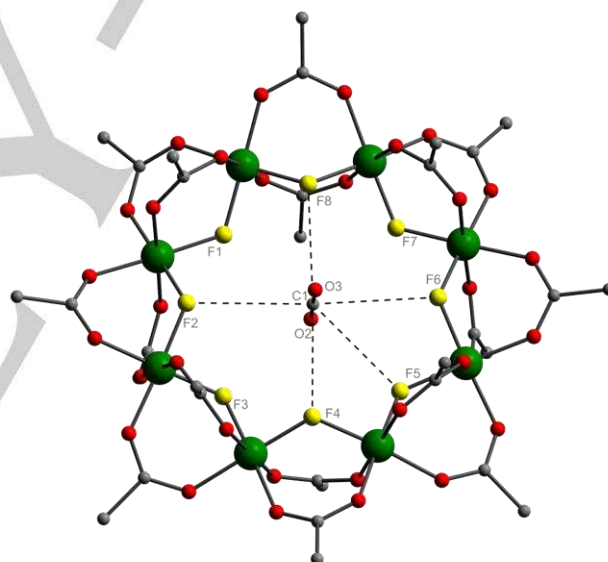
The {Cr₈} metallocrown [CrF(O₂C^tBu)₂]₈, containing a F-lined internal cavity shows high selectivity for CO₂ over N₂. DFT calculations and absorption studies support the multiple binding of F-groups to the C-centre of CO₂ [C•••F = 3.190(9) to 3.389(9) Å], as confirmed by single crystal X-ray diffraction.

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 SiF₆²⁻ anions were used as pillar ligands within SIFSIX-3-Zn, and the terminal fluorides, which project into the pores, were shown to bind CO₂.^[6] This led us to examine the possible binding of CO₂ to the well-known metallocrown [CrF(O₂C^tBu)₂]₈ **1** which contains a F-lined inner cavity. The octametallacrown, [CrF(O₂C^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 CrF₃ 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 CO₂ 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 CO₂ within the cavity of the {Cr₈} metallocrown. The carbon atom of the CO₂ molecule is 1.31 Å above the mean plane of the eight {Cr₈} 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 CO₂ 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 CO₂ adsorbed per metallocrown, and this occupancy is in excellent agreement with the values for the CO₂ absorption capacity (see below). The presence of CO₂ 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 3.39(1) 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 CO₂ 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 CO₂ molecule and a second molecule of CO₂ is found between the {Cr₈} 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 CO₂ per metallocrown. 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 CO₂.

The porosity of compound **1** was investigated by running a N₂ adsorption isotherm at 77 K, which indicates that this material is essentially non-porous, with a saturation capacity of around 17 cm³g⁻¹ at a partial pressure (P/P₀) of 0.9, presumably due to the activation diffusion of N₂ molecules at 77 K (Figure S5).

Adsorption isotherms for N₂ and CO₂ in **1** collected at ambient temperatures (288 K) to a pressure of 5 bar both display typical type-I behavior. The adsorption of N₂ 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 CO₂ is markedly different to that of N₂, 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. CO₂ adsorption in this material at 1 bar is 12 times higher than the adsorption of N₂ 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 CO₂ 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 CO₂ into the material.

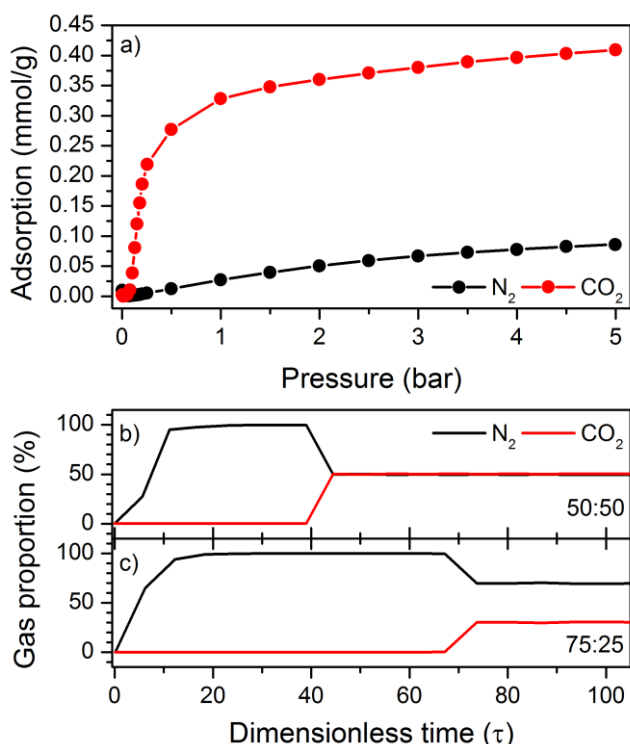


Figure 2. View of isotherms up to 5 bar for CO₂ and N₂ adsorption in **1** at 288 K (top) and the corresponding breakthrough plot for an equimolar and 75:25 N₂/CO₂ gas mixture in terms of dimensionless time (bottom). Dimensionless time represents the number of residency periods of the gas in sample chamber

The binding energy of CO₂ 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 CO₂ 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 CO₂ isotherms for SIFSIX-3-Zn (45 kJ mol⁻¹) in which CO₂ molecules interact with terminal fluorides of SiF₆²⁻ groups.^[6]

These results suggest a strong interaction of CO₂ with the central adsorption site of the metallacrown in comparison to N₂, which indicates that **1** might be able to selectively separate CO₂ from N₂. The CO₂/N₂ 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 N₂/CO₂ 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 N₂ 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 CO₂ breaks through.

To understand the binding of CO₂ 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 CO₂ in the central cavity of the metallacrown, *i.e.* **1-1CO₂**. The electronic structure of the Cr₈ 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 combinatorially 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 CO₂ 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

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

diffraction (Figure 1, Table 1).

- Calculated for a structure with one CO₂ per metallacrown
- From X-ray single crystal diffraction
- 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 CO₂ molecule is more symmetrically distributed within the wheel in the calculated structure, with the C centre of CO₂ 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 CO₂ 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 **1-1CO₂** 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 CO₂ 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 CO₂ (C +0.98, O -0.49).

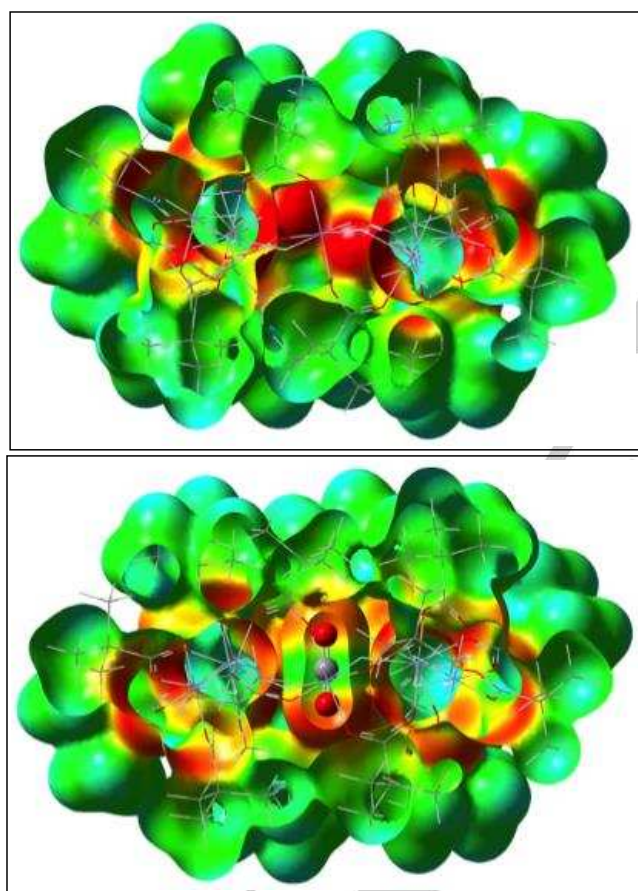


Figure 3. Side view of electrostatic potential (BP86-D3/Def2-SVP) mapped on to the total density at an isosurface value of 0.004 au. Top panel **1**, bottom panel **1-1CO₂**. Blue/green/red refer to positive/neutral/negative values, the range is +0.06 - -0.06. The CO₂ is shown as ball and stick with other atoms shown as wireframe for clarity.

The distribution of the ESP of the CO₂ 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 CO₂ guest molecule and the {Cr₈} 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 CO₂ molecule, as concluded by Nugent *et al.*^[6] Compound **1** is therefore the first metallocrown to bind CO₂. The closest example is a 16-MC-4 compound reported by Gätjens *et al.*, which reacts with CO₂ to produce a bound bicarbonate.^[17] Compound **1** shows a breakthrough selectivity for a 50:50 CO₂/N₂ mixture of 6.2 similar to many MOFs.^[18-19] For example, a perfluorinated triazine-based framework takes around 10 minutes for CO₂ to pass through a packed bed sample when an N₂:CO₂ (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

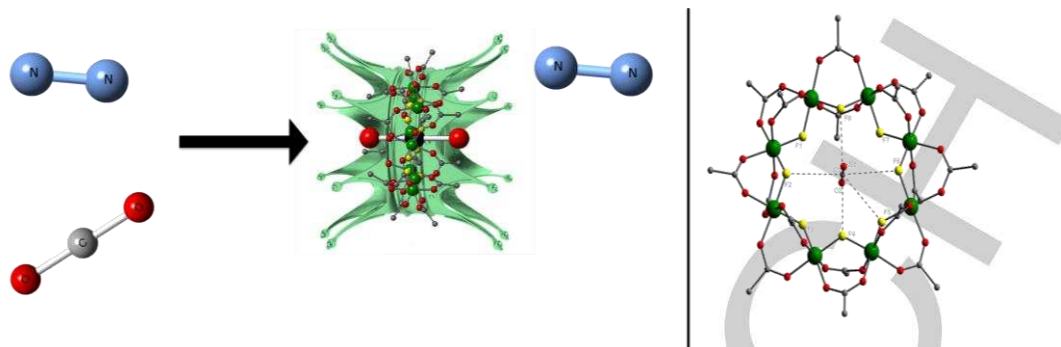
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Keywords: Metallacrown • Single-crystal X-ray diffraction • Non-porous • gas adsorption

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