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Binding CO\textsubscript{2} by a Cr\textsubscript{8} metallacrown


Abstract:

The \{Cr\textsubscript{8}\} metallacrown [CrF\textsubscript{2}(O\textsubscript{2}C\textsubscript{6}Bu\textsubscript{2})\textsubscript{2}], containing a F-lined internal cavity shows high selectivity for CO\textsubscript{2} over N\textsubscript{2}. DFT calculations and absorption studies support the multiple binding of F-groups to the C-centre of CO\textsubscript{2} \((\text{C} \cdots \text{F} = 3.190(9) \text{ to } 3.389(9) \text{ Å})\), 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,[1-5] but there is also significant work involving reaction with organic molecules to produce carbamates reversibly.[6] We were particularly intrigued by a report from Zawarotko and co-workers in which SiF\textsubscript{6}\textsuperscript{3-} anions were used as pillar ligands within SIFSIX-3-Zn, and the terminal fluorides, which project into the pores, were shown to bind CO\textsubscript{2}.[7]

This led us to examine the possible binding of CO\textsubscript{2} to the well-known metallacrown [CrF\textsubscript{2}(O\textsubscript{2}C\textsubscript{6}Bu\textsubscript{2})\textsubscript{2}] \textsubscript{1}, which contains a F-lined inner cavity. The octametallic metallacrown, [CrF\textsubscript{2}(O\textsubscript{2}C\textsubscript{6}Bu\textsubscript{2})\textsubscript{2}] \textsubscript{1}, first reported by Gerbeleu et al.,[8] has been shown to bind to small organic molecules by Larsen and co-workers,[9] and has also been extensively studied as a prototypical anti-ferromagnetically coupled ring.[10]

Compound 1 can be prepared in very high yield from the reaction of hydrated CrF\textsubscript{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\textsuperscript{III} sites with each Cr\textsuperscript{III}Cr\textsuperscript{III} edge bridged by a F\textsuperscript{-} and two pivalate ligands. The F\textsuperscript{-} ligands are alternately slightly above and below the plane formed by the eight Cr\textsuperscript{III} centres.

Crystals of 1 were exposed to an atmosphere of CO\textsubscript{2} at 290 K for 2 h to form the complex \textbf{1-0.79CO\textsubscript{2}}, as established by single crystal X-ray diffraction which shows (Figure 1) the binding of a CO\textsubscript{2} within the cavity of the (Cr\textsubscript{8}) metallacrown. The carbon atom of the CO\textsubscript{2} molecule is 1.31 Å above the mean plane of the eight Cr\textsuperscript{III} ions, with nearest contacts to five F\textsuperscript{-} ligands (F2, F4, F5, F6 and F8) which lie on the same side of the ring. These five C\cdots F contacts vary from 3.190(9) to 3.389(9) Å. The CO\textsubscript{2} molecule is linear, with the \(-\text{O=C-O} = 178.9(11)°\). Refinedment of the site occupancy shows a total of 0.787(7) molecules of CO\textsubscript{2} adsorbed per metallacrown, and this occupancy is in excellent agreement with the values for the CO\textsubscript{2} absorption capacity (see below). The presence of CO\textsubscript{2} in the structure is also shown by an FT-IR spectroscopy with bands observed at 2339 (asymmetric stretch) and 660 cm\textsuperscript{-1} (bending mode) (Figure S1).

Figure 1. View of single crystal X-ray structure of \textbf{1-0.79CO\textsubscript{2}}. C\cdots F contacts as dashed lines: C1\cdots F2 3.37(1), C1\cdots F4 3.190(9), C1\cdots F5 3.29(1), C1\cdots F6 3.35(1), C1\cdots F8 3.391(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 CO\textsubscript{2} gas at 195 K in a gas cell and this resulted in the formation of \textbf{1-1.3CO\textsubscript{2}}. The crystal structure was determined by \textit{in situ} diffraction and differs in two ways from that in the previous \textit{ex situ} study of \textbf{1-0.79CO\textsubscript{2}}: the internal cavity is now fully occupied by a CO\textsubscript{2} molecule and a second molecule of CO\textsubscript{2} is found between the [Cr\textsubscript{8}] rings with a partial occupancy of 30(5)%.

(Figure S3 and Supplementary information S4). Thermogravimetric analysis (TGA) of freshly prepared samples of \textbf{1-0.79CO\textsubscript{2}} shows gradual mass losses of 1.96% in the temperature range of 52-200 °C, consistent with the loss of one molecule of CO\textsubscript{2} per metallacrown. There is a further large mass

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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 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.

From combined TGA/DSC measurements and using variable temperature adsorption, it was possible to estimate 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 SIF₆³⁻ 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 (t) 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 (B3LYP/LDH3B/[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 Criii 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 (ms = +3/2) and spin down (ms = −3/2) Criii 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 diffraction (Figure 1, Table 1).

Table 1. Comparison of measured and DFT parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measured</th>
<th>DFT⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ uptake at 290 K</td>
<td>0.79a¹</td>
<td>n/a</td>
</tr>
<tr>
<td>CO₂ uptake under CO₂ at 190 K</td>
<td>1.30b²</td>
<td>n/a</td>
</tr>
<tr>
<td>Binding energy /kJ mol⁻¹</td>
<td>45(1)c³</td>
<td>56.2</td>
</tr>
<tr>
<td>C…F distances / Å</td>
<td>3.19 to 3.39d⁴</td>
<td>3.22 to 3.35</td>
</tr>
<tr>
<td>O=C-O angle /°</td>
<td>178.9(11)e⁵</td>
<td>179.8</td>
</tr>
</tbody>
</table>

a. Calculated for a structure with one CO₂ 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$^{19}$ 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 metalla crown show the calculated electrostatic potential (ESP) in 1-1CO$_2$ and 1 (Figure 3). Atomic partial charges were obtained through natural population analysis (NPA). 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).

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$_8$] metalla crown 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. Compound 1 is therefore the first metallobond 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. Compound 1 shows a breakthrough selectivity for a 50:50 CO$_2$/N$_2$ mixture of 6.2 similar to many MOFs. 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.

In the future we will explore this binding to see whether 1 can bind other small molecules, or whether related heterometallic rings 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**: Metalla crown • Single-crystal X-ray diffraction • Non-porous • gas adsorption

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Entry for the Table of Contents (Please choose one layout)

Green metallacrown for green applications: A Cr₃ ring is shown to bind CO₂ strongly and selectively through C•••F interactions.