This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
CO₂ as a Reaction Ingredient for the Construction of Metal Cages: A Carbonate-Panelled [Gd₆Cu₃] Tridiminished Icosahedron

Thomas N. Hooper, Ross Inglis, Maria A. Palacios, Gary B. Nichol, Mateusz B. Pitak, Simon J. Coles, Giulia Lorusso, Marco Evangelisti and Euan K. Brechin

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A CO₃²⁻-panelled [Gd₆Cu₃] cage conforming to a tridiminished icosahedron is synthesised by bubbling CO₂ through a solution of Gd(III) and Cu(II) ions.

The history of the carbonate ion as a bridging ligand for the formation of polymeric clusters containing transition metal and lanthanide metal ions is an intriguing one. A search of the CSD returns approximately 130 hits for metal cage complexes containing at least one carbonate ion. Of these ~70% contain transition metals, ~25% contain lanthanides, with the remainder containing at least one carbonate ion. Of these >70% contain the fixation of atmospheric CO₂ during aerobic reactions. There are approximately 25 cases in which Na₂CO₃ or NaHCO₃ have been deliberately added either initially or in an attempt to improve the yield of a serendipitously obtained product, and only five examples where CO₂ was deliberately employed as a reaction ingredient. Given the renowned precipitous nature of the former two – often producing insoluble and amorphous products – the lack of use of the latter is particular surprising. The CSD search also highlights the extraordinary flexibility of the CO₃²⁻ ion, revealing bridging modes ranging from bidentate to nonadentate (Figure S1). However in 85 of these examples (>65%) the ligand is tridentate, forming M₃ triangles. From a magnetochemists perspective this topology holds much fascination since the inherent magnetic frustration leads to fascinating and potentially useful physics. As yet, however there does not appear to have been a concerted effort to systematically investigate the use of CO₂ as an ingredient in reactions designed to construct polymetallic transition metal and lanthanide metal complexes. Herein we begin to address this oversight, by reporting the synthesis, structure and magnetic properties of the complex [Gd₆Cu₃(OH)(pdm)],(O₂C-Cu)₃(CO₃)₃(MeOH)ₙ ·7MeOH (1; MeOH; Figure 1).

The molecular structure of 1 viewed (A) parallel and (B) perpendicular to the three fold rotation axis. (C) The core of the complex highlighting the bridging modes of the CO₃²⁻ ions and the sole OH⁻ ion. (D) The metallic skeleton of the complex. Colour code: Gd = yellow; Cu = green; O = red; N = blue; C = black. H-atoms and some C atoms have been omitted for clarity.

The CO₃²⁻ ions are of two types (Figure 1C): three are μ₅-bridging, panelling the pentagonal [Gd₂Cu] faces of the prism, with each O-atom (O₄, O₉, O₁₀ and symmetry equivalents) bridging two metal centres. The remaining CO₃²⁻ ion is μ₆-bridging, sitting in the lower [Cu₂] triangular face (as drawn in Figure 1C) and further bridging to three Gd ions in the [Gd₃] triangle sitting above it. Each O-atom (O₃ and symmetry equivalent) is therefore bonded to one Gd ion and one Cu ion. The sole hydroxide ion (O₁₃) caps the upper [Gd₃] triangular face (O₁₃…Gd₂, ~2.4 Å), sitting ~0.8 Å above the [Gd₃] plane, with each edge of this [Gd₃] triangle bridged by a μ₅-pivallate. The six
remaining carboxylates are of two types: three span the Gd2…Gd1 edges of the [Gd3Cu] pentagons in a η1,η1,η1-fashion, while three simply chelate to Gd1. The three µ4-pdm2 ligands each bond to one Cu ion through the N- and both O-atoms, with the latter further bridging to Gd1 ions. The CuII ions are all 5-coordinate and in square-antiprismatic geometries, whilst the Gd1 ions are 9-coordinate and in square-antiprisms, whilst the Gd1 ions are 9-coordinate and in capped trigonal antiprismatic geometries.

In the crystal each molecule has three close contacts to three neighbouring cluster units in the ab plane. These are mediated via π-π stacking of the pdm2 rings, C-H(pdm2)…O(carboxylate) and C-H(pdm2)...O(carbonate) contacts, all in the ~3.3 – 3.5 Å range. Down the c-axis the clusters are stacked on top of one another, with the closest intermolecular contacts being between the Me-groups of the pivalates and the rings of the pdm2 ligands at a distance of approximately 3.7 Å. The result is an aesthetically pleasing honeycomb-like framework (Figure 2). There are no other [LnIII,μ3MII] complexes in the literature, with the only other reported trimidiminished icosahedron being the complex [Fe3O4(O3PPh)3(O2C5Bu)3].9

The experimental magnetic susceptibility (χ) for complex 1, shown in the top panel of Figure 3, has the expected room-temperature value for six GdIII and three CuII ions with an isotropic g = 2.0 (48.37 cm−1 mol−1). On lowering T, χT remains nearly constant down to ~50 K, below which it increases, indicative of the presence of dominant ferromagnetic interactions. The spin nuclearity of complex 1 makes modelling of the susceptibility data somewhat problematic. However, given that the GdIII ions are expected to promote very weak superexchange interactions, we have assumed interactions involving pairs of GdIII ions to be negligible. Thus, in a first approximation, we can ignore the upper [Gd3] triangle (Figure 1) and assume the magnetic skeleton to be limited to the [Gd3Cu2] triangle shown in the top inset of Figure 3, within which each CuII ion is located between two GdIII ions. The corresponding Hamiltonian that describes the magnetic interactions in 1 is:

\[ \mathcal{H}_{\text{ex}} = -6J_{\text{Cu-Cu}} S_{\text{Cu}} S_{\text{Cu}} - 12J_{\text{Gd-Cu}} S_{\text{Gd}} S_{\text{Cu}} \tag{1} \]

By considering the YIII-CuI,2 (2) analogue of complex 1 (see the ESI for full details), we simplify yet further and can consider just the CuII-GdIII interactions shown in the scheme depicted in the bottom inset of Figure 3. The simulation of the susceptibility for 2 yields \( J_{\text{Cu-Cu}} = +0.40 \text{ K} \). The positive sign denotes ferromagnetic coupling. Fixing the value of \( J_{\text{Cu-Cu}} \) in equation (1), then affords \( J_{\text{Gd-Cu}} = +0.90 \text{ K} \) from the simulation of \( \chi T \) for 1. The GdIII-CuII interaction is also ferromagnetic.9 From the so-obtained values of the super-exchange interactions we calculate the isothermal magnetisation (M) curves which reproduce the experimental data of 1 satisfactorily (Figure S2).

**Fig. 2** The packing of 1 in the crystal viewed down the c-axis. Colour code: Gd = yellow; Cu = green; O = red; N = blue; C = grey.

**Fig. 3** Temperature dependence of the molar susceptibility \( \chi T \) for 1 (circles) and 2 (squares) in presence of the external field \( B = 0.1 \text{ T} \). Solid lines are calculations, see main text. Insets from top to bottom: schemes of the exchange coupling used to fit 1 and 2, respectively.

Next, we evaluate the magnetothermal properties of 1. We apply the equation \( S = \int C/T \text{d}T \) to the measured heat capacity (C) in order to obtain the entropy (S) of the system (Figure S3). Then, we calculate the MCE, viz., the magnetic entropy change, \( \Delta S_m \), and the adiabatic temperature change, \( \Delta T_{ad} \), which are depicted in the top and bottom panels of Figure 4, respectively. A maximum of \( \Delta S_m = 34.5 \text{ J kg}^{-1} \text{ K}^{-1} \) (equivalent to 55.5 mJ K−1 cm−3) can be observed for \( T = 2.1 \text{ K} \) and an applied field change \( \Delta B = 7 \text{ T} \). Magnetisation data (Figure S2) can also be employed to estimate the MCE, if one makes use of the Maxwell equation \( \Delta S_m = \int \left[ \partial M/\partial T \right] \text{d}B \). The so-obtained entropy change (Figure 4) is in agreement with that estimated from heat capacity. Concomitantly with \( \Delta S_m \), \( \Delta T_{ad} \) rises to 9.3 K for the same \( T \) and \( \Delta B \). Such a large MCE puts complex 1 amongst the finest magnetic refrigerants containing GdIII and CuII ions yet reported.11
be an excellent candidate for the construction of molecules.

Environmental Sciences, University of Southampton, Southampton SO17 Mains Road, Edinburgh, Scotland, EH9 3JJ. Fax: +44 113 1165016453; Zaragoza, Spain. Email: evange@unizar.es

The fortuitous appearance of CO$_2$ as a reaction ingredient and CO$_2$ as a structure-directing templating ion in the construction of polymeric cages containing paramagnetic metal ions. The preponderance of carbonate to be fixed into Ln-based materials is particularly striking and suggests that bubbling CO$_2$ through solutions of Ln$^{III}$ salts may be particularly successful. Given its small relative molecular mass and its ability to flexibly coordinate a number of metal ions the CO$_2$ ion also appears to be an excellent candidate for the construction of molecular cryocoolers.

Conclusion

The fortuitous appearance of CO$_2$ in many transition metal and lanthanide molecular complexes has inspired us to begin a systematic exploration of the use of CO$_2$ as a reaction ingredient and CO$_2$ as a structure-directing templating ion in the construction of polymeric cages containing paramagnetic metal ions. The preponderance of carbonate to be fixed into Ln-based materials is particularly striking and suggests that bubbling CO$_2$ through solutions of Ln$^{III}$ salts may be particularly successful. Given its small relative molecular mass and its ability to flexibly coordinate a number of metal ions the CO$_2$ ion also appears to be an excellent candidate for the construction of molecular cryocoolers.

Notes and references

EKB thanks the EPSRC for funding. G.L. and M.E. acknowledge financial support by the Spanish MINECO through grant MAT2012-38318-C03-01. G.L. is also grateful to EC for a Marie Curie-IEF (PIEF-GA-2011-299356).

Fig. 4 Top: magnetic entropy changes for the labelled magnetic field changes, as obtained from heat capacity (empty markers) and magnetisation (full markers) data. Bottom: adiabatic temperature changes corresponding to the indicated magnetic field changes and obtained from heat capacity measurements.


