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ARTICLE TYPE

CO₂ as a Reaction Ingredient for the Construction of Metal Cages: A Carbonate-Panelled [Gd₆Cu₃] Tridiminished Icosahedron

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A CO₃²⁻-panelled [Gd^{III}₆Cu^{II}₃] cage conforming to a tridiminished icosahedron is synthesised by bubbling CO₂ through a solution of Gd^{III} and Cu^{II} ions.

10 The history of the carbonate ion as a bridging ligand for the formation of polymetallic clusters containing transition metal and lanthanide metal ions is an intriguing one.¹ 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 being heterometallic *d/f* complexes.² In the vast majority of cases its appearance is entirely serendipitous in nature, resulting from the fixation of atmospheric CO₂ during aerobic reactions.³ 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,⁴ and only five examples where CO₂ was deliberately employed as a reaction ingredient.⁵ 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.⁶ 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)₃(O₂C^tBu)₉(CO₃)₄(MeOH)₃]·7MeOH (**1**·7MeOH; Figure 1).

40 Reaction of Cu(NO₃)₂·2.5H₂O, Gd(NO₃)₃·6H₂O, H₂pdm (pyridine-2,6- dimethanol)⁷ and NaO₂C^tBu in a basic methanolic solution afforded a dark blue solution. The sample was filtered and CO₂ gas was then bubbled through the filtrate for 1 minute. Slow evaporation of the resulting solution resulted in X-ray quality hexagonal blue crystals of **1**·7MeOH, after 3 days (see the ESI for full synthetic details). Complex **1** crystallises in the trigonal space group *P*-3c1. The metallic skeleton describes a distorted tridiminished icosahedron (Figure 1D), one of the

Johnson solids.⁸ The Gd...Gd distances within the upper [Gd₃] triangle (as drawn in Figure 1; Gd2 and symmetry equivalent) are ~4 Å in length, those between Gd1 and symmetry equivalent are ~6 Å, and those between Cu1 and symmetry equivalent are ~5 Å. The distances between the Gd2-Gd1, Gd1-Cu1 mean planes are ~4 Å and 1.4 Å, respectively.

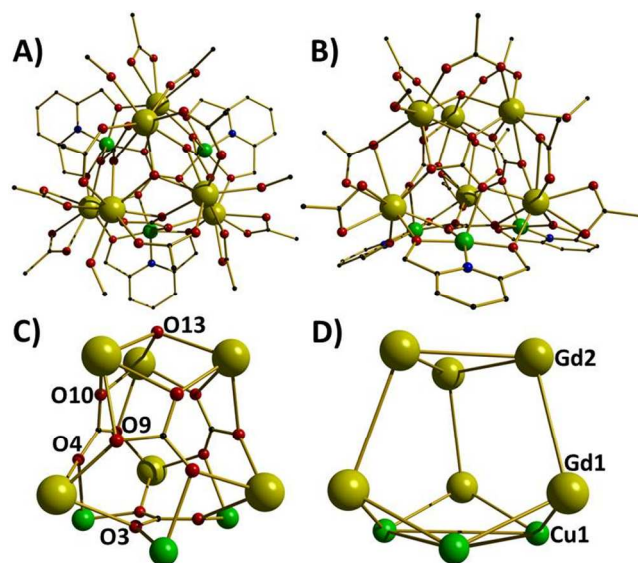


Fig. 1 The molecular structure of **1** viewed (A) parallel and (B) perpendicular to the three fold rotation axis. (C) The core of the complex highlighting the bridging modes of the CO₃²⁻ ions and the sole OH⁻ ion. (D) The metallic skeleton of the complex. Colour code: Gd = yellow; Cu = green; O = red; 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, paneling the pentagonal [Gd₄Cu] 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 [Cu₃] 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 ~0.84 Å above the [Gd₃] plane, with each edge of this [Gd₃] triangle bridged by a μ-pivalate. The six

remaining carboxylates are of two types: three span the Gd2...Gd1 edges of the [Gd₄Cu] pentagons in a η^1, η^2, μ -fashion, while three simply chelate to Gd1. The three μ_3 -pdm² ligands each bond to one Cu ion through the N- and both O-atoms, with the latter further bridging to Gd1 ions. The Cu^{II} ions are all 5-coordinate and in distorted square-pyramidal geometries, with [O₄N] donor sets. The Jahn-Teller axis of each lies along the apex of the square-based pyramid towards O4, one of the carbonate O-atoms (Cu1...O4, 2.341 Å). The Gd2 ions are 8-coordinate and in square-antiprismatic geometries, whilst the Gd1 ions are 9-coordinate and in capped trigonal antiprismatic geometries.

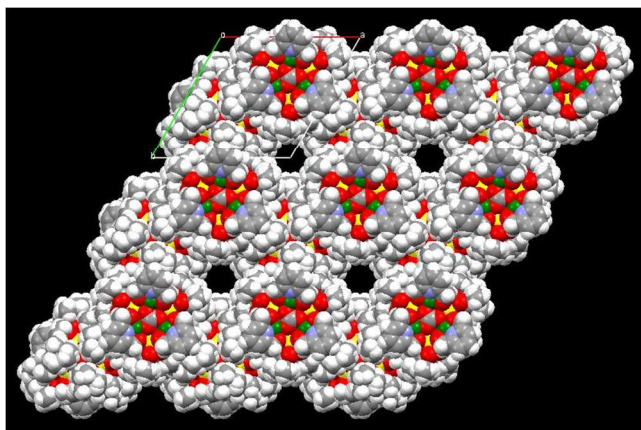


Fig. 2 The packing of **1** in the crystal viewed down the *c*-axis. Colour code: Gd = yellow; Cu = green; O = red; N = blue; C = grey.

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 $\sim 3.3 - 3.5$ 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 [Ln^{III}₆M^{II}₃] complexes in the literature, with the only other reported trimidiminished icosahedron being the complex [Fe₉O₄(O₃PPh)₃(O₂C^tBu)₁₃].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 Gd^{III} and three Cu^{II} ions with an isotropic $g = 2.0$ ($48.37 \text{ cm}^3 \text{ K mol}^{-1}$). 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 Gd^{III} ions are expected to promote very weak superexchange interactions, we have assumed interactions involving pairs of Gd^{III} 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 [Gd₃Cu₃] triangle shown in the top inset of Figure 3, within which each Cu^{II} ion is located between two Gd^{III} ions. The corresponding Hamiltonian that describes the magnetic interactions in **1** is:

$\mathcal{H}_{ex} = -6J_{Cu-Cu}S_{Cu}S_{Cu} - 12J_{Gd-Cu}S_{Gd}S_{Cu}$ (1). By considering the Y^{III}₆Cu^{II}₃ (**2**) analogue of complex **1** (see the ESI for full details), we simplify yet further and can consider just the Cu^{II}-Cu^{II} interactions shown in the scheme depicted in the bottom inset of Figure 3. The simulation of the susceptibility for **2** yields $J_{Cu-Cu} = +0.87$ K. The positive sign denotes ferromagnetic coupling. Fixing the value of J_{Cu-Cu} in equation (1), then affords $J_{Gd-Cu} = +0.40$ K from the simulation of χT for **1**. The Gd^{III}-Cu^{II} interaction is also ferromagnetic.¹⁰ 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).

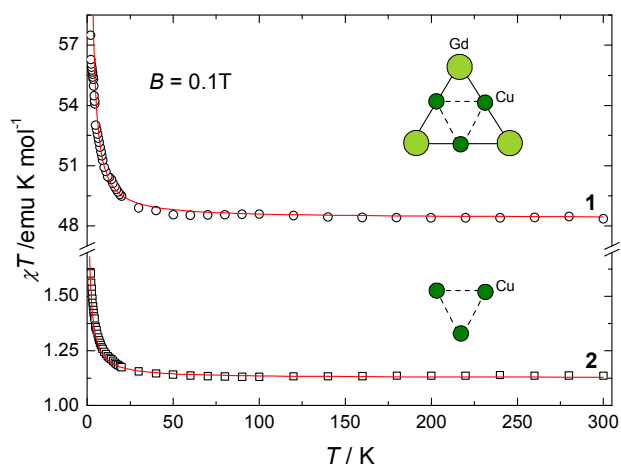


Fig. 3 Temperature dependence of the molar susceptibility χT for **1** (circles) and **2** (squares) in presence of the external field $B = 0.1$ T. Solid lines are calculations, see main text. Insets from top to bottom: schemes of the exchange coupling used to fit **1** and **2**, respectively.

Next, we evaluate the magnetothermal properties of **1**. We apply the equation $S = \int C/T dT$ 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, ΔS_m , and the adiabatic temperature change, ΔT_{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 $55.5 \text{ mJ K}^{-1} \text{ cm}^{-3}$) can be observed for $T = 2.1$ K and an applied field change $\Delta B = 7$ T. Magnetisation data (Fig. S2) can also be employed to estimate the MCE, if one makes use of the Maxwell equation $\Delta S_m = \int [\partial M / \partial T] dB$. The so-obtained entropy change (Figure 4) is in agreement with that estimated from heat capacity. Concomitantly with $-\Delta S_m$, ΔT_{ad} rises to 9.3 K for the same T and ΔB . Such a large MCE puts complex **1** amongst the finest magnetic refrigerants containing Gd^{III} and Cu^{II} ions yet reported.¹¹

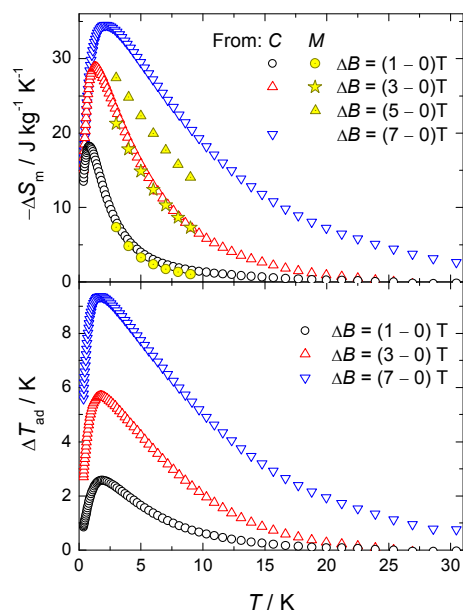


Fig. 4 Top: magnetic entropy changes for the labelled magnetic field changes, as obtained from heat capacity (empty markers) and magnetisation (full markers) data. Bottom: adiabatic temperature changes corresponding to the indicated magnetic field changes and obtained from heat capacity measurements.

Conclusion

The fortuitous appearance of CO_3^{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_3^{2-} as a structure-directing templating ion in the construction of polymetallic 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_3^{2-} ion also appears to be an excellent candidate for the construction of molecular cryocoolers.

Notes and references

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