

Cite this: *Chem. Commun.*, 2012, **48**, 9915–9917

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## COMMUNICATION

Encapsulation of atmospheric CO<sub>2</sub> by a self-assembled decanuclear cadmium complex *via* unfamiliar perchlorato and carbonato bridges†Ana M. García-Deibe,<sup>a</sup> Cristina Portela-García,<sup>a</sup> Matilde Fondo,<sup>a</sup> Antonio J. Mota<sup>b</sup> and Jesús Sanmartín-Matalobos<sup>a\*</sup>

Received 18th July 2012, Accepted 17th August 2012

DOI: 10.1039/c2cc35171d

A decanuclear Cd complex has been found as a carbonate-containing capsule. The structure strongly resembles a ten-blade waterwheel with a central carbonate ligand surrounded by two superimposed Cd<sub>5</sub>O<sub>5</sub> crowns with a pentagonal antiprism-like disposition. The capsule is doubly capped by two pentadentate perchlorate anions.

The chemical reactivity of carbon dioxide at metal centres has drawn longstanding scientific interest both in terms of fundamental understanding and applicability.<sup>1</sup> A series of zinc, cadmium, copper, silver, cobalt, nickel and lanthanide complexes have been successfully used to afford carbonato complexes by reaction with atmospheric CO<sub>2</sub>.<sup>2–6</sup> Pariya *et al.*<sup>6a</sup> reported the first example of a dinuclear cadmium complex with a carbonato bridge by spontaneous reaction, under atmospheric conditions, of the starting mononuclear complex with CO<sub>2</sub>. Dinuclear cadmium hydroxo complexes have also been shown to react with atmospheric CO<sub>2</sub> to form carbonato-bridged species.<sup>6c–e</sup>

Studies on dinuclear zinc, nickel and cobalt complexes<sup>4a</sup> have shown that the formation of carbonato complexes in a basic reaction medium occurs through an attack of a hydroxo nucleophilic species to the electrophilic carbon atom of the CO<sub>2</sub> molecule. This hydroxo complex seems to derive from an aqua-bridged complex [M<sub>2</sub>L(μ-OH<sub>2</sub>)]<sup>+</sup>, where the aqua ligand is activated by the two Lewis-acidic metal centres, and this should favour its deprotonation to give a hydroxo-bridged complex of the type [M<sub>2</sub>L(μ-OH)]<sup>+</sup>.

In the course of our investigations to pursue systems with high nuclearity involving Cd<sup>II</sup> coordination, our synthetic attempts to introduce both the linear H<sub>2</sub>L [H<sub>2</sub>L = (*E*)-2-((1*H*-imidazol-2-yl)methyleneamino)phenol], Fig. 1 (middle)] and a non-planar molecule (perchlorate) as bridging ligands led to the isolation of

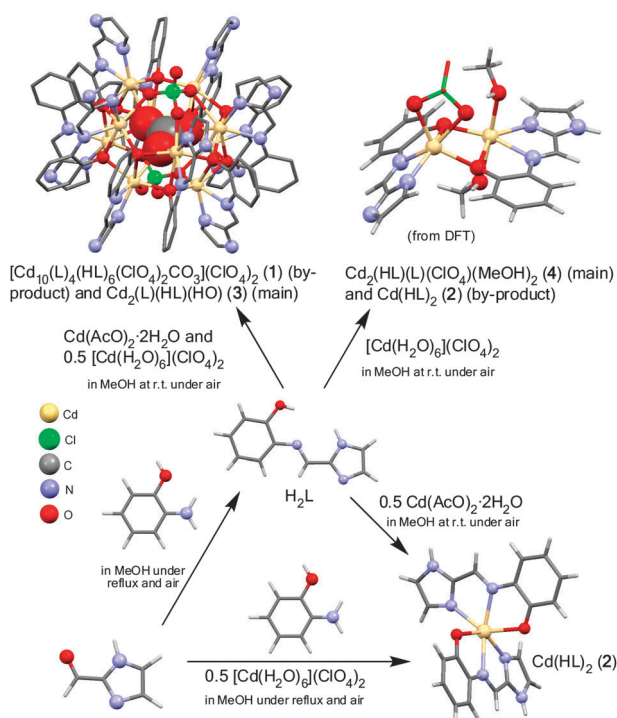


Fig. 1 Schematic representation of the reactions that give rise to the cadmium complexes presented in this work. See ESI† for details.

the cage structure [Cd<sub>10</sub>(L)<sub>4</sub>(HL)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>(CO<sub>3</sub>)]<sup>2+</sup> (1), shown in Fig. 1 (top left), which resembles a ten-blade waterwheel based on a decorated Cd<sub>10</sub>O<sub>10</sub> double crown (Fig. S1 in the ESI† file).

The study was initiated with the reaction between imidazole-2-carboxaldehyde (1 equiv.), 2-aminophenol (1 equiv.) and [Cd(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (0.5 equiv.). Under these conditions, only Cd(HL)<sub>2</sub> (2, Fig. S3 in ESI†) is formed in bulk form (Fig. 1, right bottom). 2 was also obtained from Cd(AcO)<sub>2</sub>·2H<sub>2</sub>O (0.5 equiv.) and isolated H<sub>2</sub>L (1 equiv.) as starting reagents (Fig. S4 in ESI†). However, when both Cd(AcO)<sub>2</sub>·2H<sub>2</sub>O and [Cd(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (1 and 0.5 equiv., respectively) were used, the main reaction product was Cd<sub>2</sub>(L)(HL)(HO) (3, see ESI†). Moreover, the decanuclear cadmium cluster 1 was also obtained in small amount (~2%), by extended exposure of the mother liquor (MeOH) to an air atmosphere, while being slowly evaporated (top-left in Fig. 1). This suggests that,

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† Electronic supplementary information (ESI) available: Syntheses and characterization of the ligand and its complexes, X-ray diffraction data of 1, 2, and H<sub>2</sub>L, additional views of 1, and computational details of 4. CCDC 892600–892602 (1, 2, and H<sub>2</sub>L). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc35171d

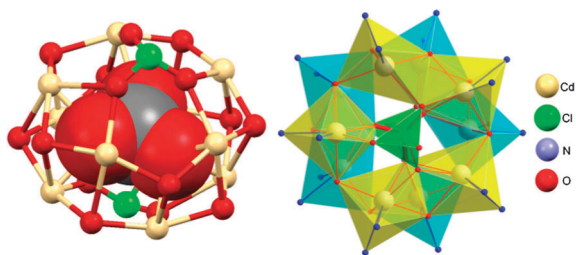
similarly to that reported for other dinuclear metal complexes,<sup>4a</sup> the carbonato complex **1** could be formed by an attack of the hydroxo species **3** to the carbon atom of the CO<sub>2</sub> from the atmosphere. Both, water present in starting metal salts and Lewis acidity of Cd<sup>2+</sup> could have assisted in the formation of **3**.

With the aim of checking if the hydroxo dinuclear complex **3** could give rise to the carbonate encapsulation by reaction with CO<sub>2</sub>, we have passed a stream of this gas through a methanol solution of **3**, after adding cadmium perchlorate. Powder X-ray diffraction studies on the bulk solid isolated upon filtration matched well with the diffraction pattern obtained from the single-crystals of **1**, which indicates the participation of **3** in the formation of **1**. Complex **1** gave satisfactory elemental analysis, and its IR spectrum shows not only bands associated with the phenol-based ligand and the perchlorate group, but also the presence of two strong bands at 1463 and 1440 cm<sup>-1</sup>, consistent with C–O stretching frequencies observed for carbonato bridges.<sup>4d,h,5b,6b</sup>

With the aim of establishing the significance of the presence of the acetate species as a source of hydroxide in the enhancement of the reactivity of the cadmium complexes towards atmospheric CO<sub>2</sub>, we also performed another reaction in the absence of Cd(AcO)<sub>2</sub>·2H<sub>2</sub>O, *i.e.* we only used [Cd(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (1 equiv.) and H<sub>2</sub>L (1 equiv.) as starting reagents. As a result, a compound with Cd<sub>2</sub>(L)(HL)(ClO<sub>4</sub>)(MeOH)<sub>2</sub> stoichiometry (**4**) (main), and Cd(HL)<sub>2</sub> (**2**) (by-product) were obtained (top-right in Fig. 1), showing that the presence of acetate is critical to form the carbonato complex **1**.

Single-crystal X-ray diffraction analysis reveals that in **1**, perchlorato, carbonato and phenoxo bridges, *i.e.* metal–ligand interactions, are responsible for the self-assembly event through reaction with atmospheric CO<sub>2</sub>. This decanuclear cadmium complex shows several remarkable features such as a high nuclearity that results in the formation of a 28 vertex capsule (Cd<sub>10</sub>Cl<sub>2</sub>O<sub>16</sub>) (Fig. 2, left), in which the metal ions are either penta-, hexa-, or heptacoordinated (Fig. 2, right). Taking only the cadmium centres into consideration, the cage strongly resembles the geometrical structure of a Cd<sub>10</sub>O<sub>10</sub> pentagonal antiprism, giving the appearance of a wheel or a double crown (Fig. S1, ESI†).

Furthermore, this cage is formed from two previously unreported pentacoordinate perchlorato ligands (μ<sub>5</sub>), and ten pentacoordinate phenol-based ligands displaying the very rare μ<sub>3</sub> bridging mode.<sup>7</sup> The binding sites of the phenol-based ligands form ten of the edges of the capsule in a similar manner to that reported in scaffold architectures involving 1D ligands.<sup>8</sup>



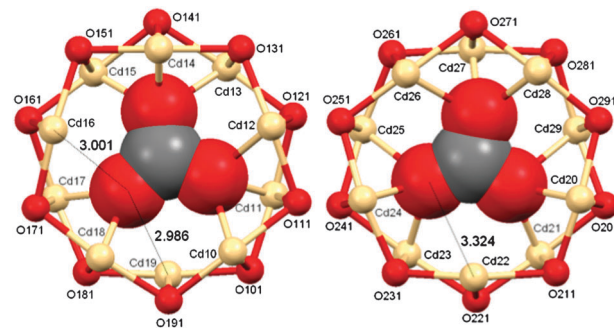
**Fig. 2** Two views of the Cd<sub>10</sub>Cl<sub>2</sub>O<sub>16</sub> capsule. Left: the cage containing a carbonato ligand as an encapsulated guest. Right: the pseudo-pentagonal antiprism of the decanuclear cluster showing the coordination polyhedra of cadmium ions with both capping perchlorato ligands.

Two of the faces of the final structure are formed by the two perchlorato ligands that, since they bridge more than two metal atoms, can be considered as 2D ligands.<sup>9</sup> Fig. S6 (top), in the ESI† file, shows the coordination modes (μ<sub>2</sub>, μ<sub>3</sub>, μ<sub>4</sub> and μ<sub>12</sub>) described to date when a perchlorate anion acts as a bridging ligand in polynuclear compounds.<sup>10</sup>

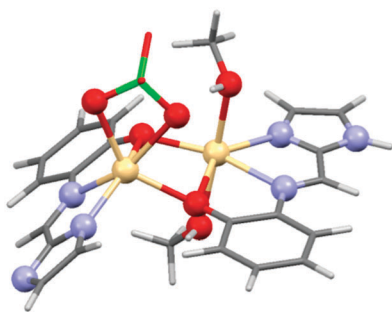
Finally, the cage contains a single carbonato ligand presenting two new coordination modes (μ<sub>8</sub> and μ<sub>9</sub>) in the two cations of **1** found in the asymmetric unit of the crystal (Fig. 3). The coordination modes described to date for carbonate anions acting as bridging ligands in polynuclear compounds<sup>11</sup> (μ<sub>2</sub>, μ<sub>3</sub>, μ<sub>4</sub> and μ<sub>6</sub>) are summarised, in the ESI† file, in Fig. S6 (bottom). The structure of the capsule shows evidence that carbonate becomes permanently trapped within it and cannot be released without breaking one or more chemical bonds.

The structure of Cd<sub>2</sub>(L)(HL)(ClO<sub>4</sub>)(MeOH)<sub>2</sub> (**4**), which did not crystallise in our hands, was elucidated on the basis of IR, NMR and mass spectroscopies. The mass spectrum of this complex shows a peak at 696.8 *m/z* with an isotopic profile which matches well with that calculated for the cationic species [Cd<sub>2</sub>(L)(HL)(ClO<sub>4</sub>) + H]<sup>+</sup> (Fig. S7, ESI†). The IR spectrum of **4** contains triply split band maxima at about 1145, 1120 and 1087 cm<sup>-1</sup> and two peaks at about 636 and 625 cm<sup>-1</sup> that were attributed to a perchlorato ligand with local C<sub>2v</sub> symmetry, supporting its coordination in a chelating bidentate fashion.<sup>12</sup> A strong complex absorption with numerous submaxima originating from non-fundamental ν(NH) modes and ν(CH) vibrations is present between 3150 and 2500 cm<sup>-1</sup> in the IR spectrum of H<sub>2</sub>L, although the NH stretching would be expected<sup>13</sup> at around 3090 cm<sup>-1</sup>. Upon complexation, the relative intensities of the NH absorptions decrease and, as a result, the more prominent band (which is around 3060 cm<sup>-1</sup>) could be used as a sign of the presence of the NH group in **4** (Fig. S8, ESI†). Compared with the <sup>1</sup>H-NMR spectrum of H<sub>2</sub>L, that of **4** shows a typical pattern of a coordinated Schiff-base ligand with imine and aromatic protons showing only small shifts.<sup>14</sup> The signals at about 3.16 (3H) and 4.12 (1H) ppm reveal the presence of coordinated methanol (Fig. S9, ESI†).

Computational studies<sup>15</sup> were undertaken in order to gain insight into the structure and type of perchlorato coordination mode involved in **4**. Theoretical calculations (DFT/B3LYP, see ESI† for further details) performed in gas phase predict



**Fig. 3** Cd<sub>10</sub>O<sub>10</sub> double crowns with their carbonate guests, showing two new coordination modes μ<sub>8</sub> (left) and μ<sub>9</sub> (right), found in the asymmetric unit of **1**. Non-coordination Cd–O distances (Å) are indicated (see ESI†).



**Fig. 4** DFT/B3LYP calculated structure for complex **4**, from the collected spectroscopic data.

that the perchlorate bridged isomer ( $\mu_2:\eta^2$ ) is less stable than the mono-coordinated one by 6.0 kcal mol<sup>-1</sup> ( $\Delta H = +4.3$ ,  $\Delta G = +4.2$ ), although several species (Fig. S5, ESI†) could participate in a complex equilibrium before delivering the final product. The structure of the chelating bidentate isomer of the dinuclear cadmium complex is shown in Fig. 4. Interestingly, the L<sup>-</sup> form is much more stable than the methoxo form by 13.6 kcal mol<sup>-1</sup> ( $\Delta H = +12.8$ ,  $\Delta G = +10.7$ ), allowing us to correctly balance the negative charge, indeed.

In conclusion, we reported the synthesis of a novel closed structure by metal-directed self-assembly, using both one-dimensional and two-dimensional ligands. The capsule shows evidence that a CO<sub>3</sub><sup>2-</sup> ion, which is derived from atmospheric CO<sub>2</sub> through chemical conversion in the presence of a weak Brønsted base, becomes permanently trapped within it. In the core of the cage, the carbonate ligand adopts new bridging modes ( $\mu_8$  or  $\mu_9$ ) to link the Cd<sup>2+</sup> ions. In the shell of the cage, each one of the perchlorato ligands adopts an unprecedented  $\mu_5$  bridging mode. Moreover, the phenolato ligands close the cage *via* a very rare  $\mu_3$  bridging mode.

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