

One-pot atmospheric carbon dioxide fixation and 'nitric acid' inclusion in the cylindrical micro-pores of the resulting lanthanide(III) oxalates

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One-pot activation, reduction and coupling of atmospheric carbon dioxide to polymeric $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ layers, the micro-cavities of which trap 'nitric acid' species, are described.

It is widely acknowledged that atmospheric carbon dioxide is a potentially important source of industrial carbonaceous compounds and its exploitation could minimize global warming concerns.¹ However, carbon dioxide is inert, its activation is difficult and successful attempts have so far been largely those involving electrocatalytic, photoelectroreduction and photochemical reduction conditions or highly reactive and moisture- and air-sensitive organo-lanthanide compounds.^{1,2}

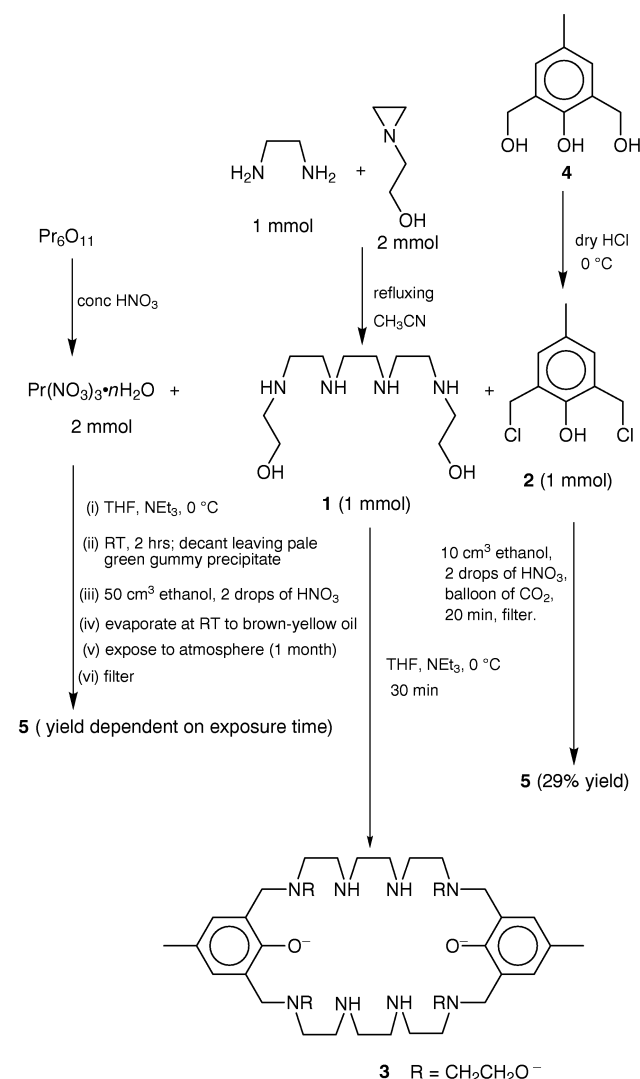
Herein we report a simple one-pot activation, reduction and coupling of atmospheric carbon dioxide to oxalates mediated by a mixture of the alkylamine alcohol **1**, the dichloro derivative **2** and acidic light lanthanide(III) nitrates, $[\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}]$; $\text{Ln} = \text{La}, \text{Pr}$.

Because of our interest in macrocyclic chelates capable of dinucleating lanthanide(III) ions³ we synthesized **1**. Cyclization of **1** with dihalo derivatives such as **2** in the presence of lanthanide(III) ions (as templates) was expected to produce neutral dinuclear compounds $[\text{Ln}_2(\text{3})]$ (Scheme 1), which are desirable as components of biomedical diagnostics.⁴ Surprisingly, when a mixture of **1**, **2** and the light lanthanide(III) nitrates obtained from such a cyclization experiment is acidified with nitric acid and then allowed to evaporate to an oil at room temperature (*ca.* 297 K), crystalline platelets that turned out to be of $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$, $\text{Ln} = \text{La}, \text{Pr}$ (**5**), were gradually deposited. These crystals continued to grow in size for as long as they were left open to the atmosphere with sufficient lanthanide(III) ions. However, crystals of $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ were not obtained when heavier lanthanides (namely, $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$ and Dy) or a nitrogen atmosphere were used; omission of nitric acid or the organic compounds **1** and **2** also failed to produce **5**. Deposition of **5** occurred quickly (within 20 min with a yield of about 29% based on Pr) when a straight mixture of **1**, **2**, $\text{Pr}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and two drops of concentrated nitric acid in 10 cm³ of methanol was exposed to a balloon full of carbon dioxide at *ca.* 297 K.

The products, $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ ($\text{Ln} = \text{Pr}, \text{La}$), were identified by elemental analyses, permanganate titrations and infrared spectra; the latter featured both carboxylate (*ca.* 1600 cm⁻¹) and nitrate (*ca.* 1300–1400 cm⁻¹) absorptions. But the interesting inclusion of 'nitric acid' in the cylindrical micro-pores of the polymeric layers formed by lanthanide(III) and oxalate ions was revealed by the X-ray analysis⁵ (Fig. 1) of **5**.

In the praseodymium complex, **5**, each metal atom is coordinated by three chelating oxalate anions and three water molecules to produce a coordination sphere approximating a

trigonal prism with the rectangular faces capped. The triangular faces are defined by O5, O7, O9 and O2, O3, O8 with O1, O4, O6 as the face-capping atoms. The dihedral angle between the triangular faces is 6(1)° while the average angle between the plane defined by the capping atoms and these faces is 9.7(5)°. Each oxalate ion bridges two metal atoms, leading to a



Scheme 1

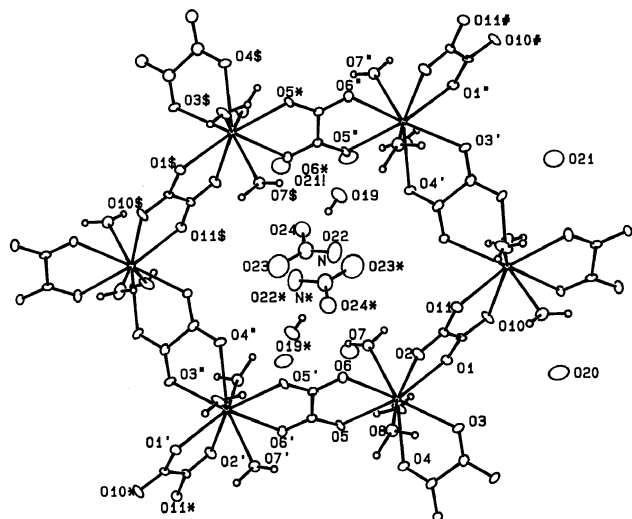


Fig. 1 Part of the polymeric $[\text{Pr}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$ sheet of $\{[\text{Pr}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$, **5**, showing the network of cylindrical micro-cavities formed by oxalate and Pr^{3+} ions and the trapped disordered 'nitric acid'. Location of the proton on HNO_3 is unknown

structure consisting of $[\text{Pr}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$ sheets approximately perpendicular to the b axis, a portion of which is shown in Fig. 1. The sheets are held together by hydrogen bonds such that the overall structure is very similar to that found previously for $\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot n\text{H}_2\text{O}$.⁶ In the latter structure, the lattice waters are located in the large voids within and between the $[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$ sheets; the same situation is obtained here with the additional feature that the crystal 'nitric acid' species reside within the cylindrical cavities of the $[\text{Pr}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$ sheet. It should be mentioned that our inability to locate all of the hydrogen atoms renders it impossible to determine where that arising from the 'nitric acid' of solvation resides, particularly since this molecule is disordered. Whenever the proton on crystal HNO_3 is localized, two of the N—O distances tend to fall in the range of 1.18–1.23 Å, while that involving the protonated oxygen, N—OH, is much longer (1.30–1.34 Å).⁷ With co-crystallized NO_3^- and HNO_3 , the nitrate anion is distinguished by the pattern of two N—O distances in the range of 1.21–1.23 Å and a third rather longer N—O distance (1.26–1.28 Å,⁷ albeit shorter than N—OH in HNO_3). On the other hand, the N—OH distance⁸ of H-bonded crystal HNO_3 is similar to the longest of the nitrate anion N—O bond lengths.⁷ Consequently, whereas the N—O distances in **5** [1.20 (N—O24), 1.22 (N—O23) and 1.28 (N—O22) Å] are consistent with those of NO_3^- , it is not possible to be sure that they are not of a hydrogen-bonded crystal HNO_3 , hence the term 'nitric acid' is used in this report.

The formation of $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ ($\text{Ln} = \text{Pr}, \text{La}$) is important for two reasons. First, CO_2 fixation to oxalate anions is achieved under relatively milder conditions than in previous attempts^{1,2} and, unlike catalytic transition metal complexes of ammonia and macrocyclic polyamines that require strong bases to convert CO_2 to carbonates,⁹ the processes mediating the formation of the oxalato compounds $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ ($\text{Ln} = \text{Pr}, \text{La}$) (Scheme 1) require acidic media. Secondly, the micro-porous nature (cavity diameter and depth of ca. 2–10 and 2–3 Å, respectively) of crystalline oxalato complexes of lanthanide(III) and many other metal ions,¹⁰ as well as the elegant variations in their micro-cavity shape and size, have been known for a long time. But besides water⁶ and, very recently, the PhMe_3N^+ cation,¹¹ these cavities have not been known to trap other molecules. The versatility of the oxalate anion as a synthon for one- and

two-dimensional structural motifs has been widely exploited in rational design of materials with unusual electronic and magnetic molecular behaviour.¹² However, the potential of extensive porous layers, like those of **5**, as reaction micro-vessels in which supramolecular interactions are exploited to control the nature of the products and their formation processes, is largely unexplored. Clearly, cationic, neutral and perhaps anionic species can be trapped in these micro-cavities; the challenge is to find suitable conditions for doing so and develop synthetic procedures to exploit them.

Finally, a cationic Schiff base macrocyclic europium(III) complex¹³ and, possibly, a neutral gadolinium(III) compound of the 1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane macrocycle¹⁴ are known to facilitate the activation and hydration of carbon dioxide to carbonates. The formation of oxalates from carbon dioxide, however, requires both activating and reducing agents.¹ We speculate that activation of CO_2 by lanthanide(III) complexes, followed by reductive action by, for example, aldehydes and/or NO_2 species (generated by auto-decomposition of concentrated nitric acid and/or its oxidative action on alcoholic functionalities), may produce activated $\text{CO}_2/\text{CO}_2^{\cdot-}$ species. These species usually undergo fast coupling¹⁵ to C_2 compounds and can thus be expected to lead to the formation of $\{[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{HNO}_3\}_n$ ($\text{Ln} = \text{Pr}, \text{La}$). Other contributory factors may be the high stability of the resulting polymeric $[\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$ layer structure and the better solubility of CO_2 in alkylammonium salts.¹⁶ Firm mechanistic views should, however, await a better understanding of the nature of the active lanthanide(III) compounds and the corresponding reductants, which is being sought.

Acknowledgements

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- 5 Crystal data: formula: $\text{Pr}_2\text{O}_{22.5}\text{N}_{0.5}\text{C}_6\text{H}_{18.5}$; $M = 739.51$; monoclinic ($P2_1/c$); $a = 10.337(1)$ Å, $b = 9.5924(7)$ Å, $c = 20.467(2)$ Å, $\beta = 92.23^\circ$; $U = 2035.8(6)$ Å³; $Z = 4$; $T = 293$ K; $\mu = 46.3$ cm⁻¹; unique reflections = 3993, observed data = 2674 [$I \geq 3\sigma(I)$]; $R = 0.031$, $R_w = 0.067$. All crystallographic data are provided as supplementary material: CCDC reference number 440/050.
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