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Efficient fixation of atmospheric CO₂ as carbonate by lanthanide-based complex via synergistic effect of zinc iont

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Reactions of [Zn(L)(H₂O)] precursor and EuCl₃ with the aid of CO₃² ⁻ ions derived from atmospheric CO₂ affording an unusual heteropolynuclear cluster [Zn₄L₄Eu₄(CO₃)₆]·EtOH. In the core of the cluster, four hetero-binuclear [ZnLEu] units linked by six CO32anions forms a well defined [Zn₄Eu₄] skeleton with good planarity, which plays an important role in stabilizing the cluster.

As is well-known, carbon dioxide has become a major contributor to climate change as the fossil-fuel-dependent development results in the sharp increase of CO₂ concentration in the atmosphere over recent times. Therefore, reducing the CO₂ concentration in the atmosphere is currently a top priority.¹ Among different methods developed for capturing aerial carbon dioxide from the viewpoint of better utilization of carbon resources and the increasing concern on our environment,² porous materials consisting of metal-organic frameworks (MOFs) have shown great potential in CO₂ adsorption due to their high specific surface areas (SSAs) (up to 5000 m² g^{-1}) and pore size (up to 5 cm³ g⁻¹).³ However, most MOFs utilized for this application are very expensive and moisture sensitive.⁴ An alternative method for efficient atmospheric CO₂ fixation is the absorption of CO₂ with an *in situ* generated carbonato-bridged complexes.⁵ In this regard, more recently, polynuclear lanthanide complex seems more promising in view of the strong ability of lanthanide(m) hydroxides to interact with carbon dioxide in air and the diversified coordination mode of center ions.6 This kind of carbonato-bridged polynuclear lanthanide complexes, although still rare, have proven to exhibit not merely appealing structures and unique magnetic properties, but also potential applications in fixing atmospheric CO₂ under ambient conditions.⁷

Despite the advantages of these kinds of clusters, the synthesis of multinuclear lanthanide(III) complexes that efficiently capture aerial carbon dioxide still remains a great challenge.8 This is particularly due to the ligand controlled hydrolysis processes of lanthanide(m)-based compounds are hard to control, which are especially favorable for the formation of lanthanide carbonates.⁹ To the best of our knowledge, only two carbonatobridged lanthanide(III) clusters with the CO₃²⁻-Ln³⁺ ratio higher than 1:1 was obtained from fixation of atmospheric CO₂.^{7d,10} Considering the fact that zinc-containing enzymes carbonic anhydrase plays a critical function in respiration, transporting CO₂ between metabolizing tissues and the lungs, which has inspired numerous studies about zinc(II) hydroxide complexes as potential candidates for CO2 capture in the past two decades.¹¹ Thus, we sought to develop Zn(II)-Ln(III) heteronuclear complexes and to investigate whether it is possible for zinc ions to play a synergistic effect in improving the ability of lanthanide(m) clusters to capture carbon dioxide in air.

It is well known that the hexadentate Schiff-bases with alkoxy groups at the 3-position can improve metal-bridging capability and are useful for obtaining the 3d-4f heterometallic complexes.¹² And a variety of binuclear [MLn] complexes have been successfully obtained employing compartmental ligands and demonstrated practical applications arising from different metal ions.13 We herein decide to use hexadentate Schiff-base as ligand to investigate the synergistic effect of zinc ion in improving the ability of lanthanide-based complex for fixing CO₂. In this communication, the reaction of europium trichloride and $[ZnL(H_2O)]$ precursor $(H_2L = N,N'-bis-$ (3-methoxy-salicylidene)-1,2-propanediamine) with the aid of CO₃²⁻ ions derived from atmospheric CO₂ under proper conditions results in a new heteropolynuclear cluster [Zn₄L₄Eu₄- $(CO_3)_6$] EtOH, which contains a metal- CO_3^{2-} core with high CO_3^{2-} -metal (Zn²⁺ and Eu³⁺) ratio of 3:4. To the best of our knowledge, this is the first carbonato-bridged 3d-4f heteropolynuclear cluster generated by fixation of atmospheric CO₂.

The mononuclear precursor, $[Zn(L)(H_2O)]$, was prepared in excellent yield (92%) by a similar method according to the literature.14 Air and moisture stable cluster was then synthesized

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[†]Electronic supplementary information (ESI) available: Synthetic part, Fig. S1, Tables S1 and S2. CCDC 910926 for [Zn₄Eu₄L₄(CO₃)₆] EtOH. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50230a



Fig. 1 Molecular structure of $[Zn_4Eu_4L_4(CO_3)_6]$ ·EtOH. Solvent molecules and hydrogen atoms are omitted for clarity.

by the reaction of EuCl₃·6H₂O with [Zn(L)(H₂O)] in the molar ratio of 1 : 1 in ethanol with the presence of triethylamine (for detailed synthesis see ESI[†]). Prismatic yellow crystals of [Zn₄Eu₄L₄(CO₃)₆]·EtOH suitable for X-ray diffraction were obtained in 32% yield by slow evaporation of the solution under aerobic conditions over two weeks. The sample was confirmed by elemental analysis and IR spectroscopy (ESI[†]). The strong absorption bands at around 1536 and 1505 cm⁻¹ can be assigned to the stretching vibrations ν (C–O) of the two kinds of CO₃²⁻ ions. The out-of-plane bending vibration of π (C–O) appears at 849 cm⁻¹ as a relatively weak absorption band. More carefully identification of different C–O vibration modes seems impractical owing to the disturbance of Schiff-base absorptions.

The molecular structure of the complex, determined by single-crystal X-ray diffraction, is depicted in Fig. 1. The crystal parameters are shown in Table S1,[†] and selected bond lengths and angles are given in Table S2 ESI.[†] Structural analysis shows that the complex is crystallized in the triclinic space group $P\overline{1}$. The asymmetric unit comprises only half of the molecules, with the other half being generated by a centre of inversion. And the molecule contains four nine-coordinated Eu(m) and four five-coordinated Zn(n) cations, four ligands (H₂L) and six CO₃^{2–} anions.

As shown in Fig. 1, the outer O_2O_2 moieties of the [ZnL] components coordinate to Eu^{3+} ions, resulting in the formation of hetero-binuclear [ZnLEu] units with the Zn…Eu separation of 3.4158(7)–3.4328(8) Å. The dinuclear units interact with six carbonate ions through both chelating and bridging modes resulting in a heteropolynuclear cluster [Zn_4Eu_4L_4(CO_3)_6]·EtOH.

Each Zn^{2+} ion has a usual five-coordinate environment and adopts a distorted square pyramidal geometry, composed of the inner N_2O_2 core from the Schiff-base ligand (L^{2-}) as the basal plane and one coordinated O atom from the coordinated CO_3^{2-} occupying the apical position. The zinc atoms lie slightly above the N_2O_2 planes with atom-to-plane distances of 0.5959 Å and 0.5772 Å for Zn1 and Zn2 respectively (Fig. 2). Moreover, in the asymmetric unit, two N_2O_2 basal planes are almost perpendicular to one another with a dihedral angle of 87.863°. The average bond lengths for Zn–O (phenolic) (2.028 Å) and Zn–N (2.040 Å) are comparable to those found in the literature.¹⁵ Notably, the Zn–O bond lengths depend on the nature of the oxygen atoms, in which the bond lengths



Fig. 2 The cluster core bridged by carbonate ion and the pseudo-octahedron formed by $[Eu_4(CO_3)_2]$.

(1.952(4)-1.970(3) Å) from O atoms of carbonate groups are significantly shorter than those from the phenoxo oxygen atoms. The strong interactions between Zn^{2+} ions and carbonate anions imply that zinc ions may play a pivotal role in the efficient adsorption process of CO₂.

The four Eu(III) ions are situated in very similar coordination environments. Each Eu³⁺ ion is located in the outer O₂O₂ site of the [ZnL] component, and is surrounded by nine oxygen atoms with a distorted tri-capped trigonal prismatic geometry. Four oxygen atoms are arising from the phenolic groups and the methoxy side arms of the Schiff-base ligand, and the remaining five oxygen atoms are provided by four carbonate anions with both chelating and bridging modes. The Eu-O bond lengths, involving the bridging/chelating deprotonated phenol oxygen atoms in the range of 2.402(3) Å to 2.437(3) Å, are significantly shorter than those associated with the chelating methoxy oxygen atoms (2.768(4)-2.794(3) Å, average 2.781 Å), which are similar to those reported in the literature.¹⁶ The Eu–O bond lengths from oxygen atoms of CO₃²⁻ anions are with an average of 2.433 Å, which are in good agreement with those previously reported in the literature.⁶

One of the most notable structural features of the cluster is that four hetero-binuclear [ZnLEu] units linked by four carbonate groups forms two well defined parallelogram skeletons (Zn_4, Eu_4) with good planarity. In addition, they are all located in the same plane. The Eu…Eu distances range from 4.1475(5) Å to 4.1528(4) Å and the angles vary from 88.950(9)° to 91.050(9)°, while the Zn…Zn distances are from 8.1905(7) Å to 8.3003(7) Å and the angles are from 89.929(9)° to 90.071(9)°, respectively (Fig. S1[†]). The four carbonate anions serve as tridentate bridges, which link the $Zn(\pi)$ ion to the adjacent $Eu(\pi)$ ions in a $\mu_3 - \eta^1 : \eta^2 = \eta^2$ fashion. The other two CO_3^{2-1} ions lying above and below the main plane are located on the inversion centre. Each of them bridges four Eu ions in a $\mu_4-\eta^1:\eta^1:\eta^2$ fashion, resulting in a pseudo-octahedron core formed by $[Eu_4(CO_3)_2]$ as shown in Fig. 2. This coordination mode is rarely observed in carbonato-bridged polynuclear lanthanide complexes, which may play an important role in stabilizing the cluster. In other words, the overall structure of the complex can be well described as a pseudo-octahedron $[Eu_4(CO_3)_2]$ core surrounded and stabilized by four [ZnN₂O₃] square pyramids.

The above results illustrated that the presence of ZnL as a seed may be critical for the formation of carbonato-bridged 3d–4f heteropolynuclear cluster generated by fixation of

atmospheric CO₂. As an attempt to lend credence to the mechanism, we design a simple experiment to validate whether [Zn- $(L)(H_2O)$] plays a synergistic effect in fixing CO₂. The CO₂ is bubbled through ethanol solution of the precursor [Zn(L)-(H₂O)] containing NEt₃ as a base at room temperature for about three hours, the resultant precipitate is obtained by evaporating the solvent under reduced pressure. A comparison of the IR spectra of the precipitate with that of $[Zn(L)(H_2O)]$ provides evidence for the formation of [LZn-OCO₂H]⁻ species. The signals corresponding to ν (C–O) at 1697 and 1295 cm⁻¹ are in good agreement with those of [ZnOCO₂H]⁻ in other systems.¹⁷ The peaks at 696 and 835 cm⁻¹ can be assigned to the rocking vibration of $\rho_r(OCO)$ and out-of-plane bending vibration of π (C–O) respectively.¹⁸ Moreover, the broad vibration at 3456 cm⁻¹ in the resultant precipitate compared with that of $[Zn(L)(H_2O)]$ at 3418 cm⁻¹ is considered as evidence that there exists an -OH group of the [LZn-OCO₂H]⁻. Considering that the conversion of CO_2 to CO_3^{2-} may be similar to the mechanism of carbonic anhydrase demonstrated in a series of zinc(II) complexes.¹⁹ It is reasonable to assume that the initial deprotonation of zinc-bound water molecule [Zn(L)(OH)]⁻ plays a fundamental role in the formation of zinc bicarbonate derivative [LZn-OCO₂H]⁻, which involves the nucleophilic attack of hydroxo species to the electrophilic C atom of CO₂. The suggested reaction scheme is illustrated in Fig. 3.

The above experiment results illustrate that the ZnL species bound to the Eu ions may act as nucleophiles in the hydration of CO₂ and play a synergistic effect in fixing CO₂, which should be critical to the formation of the cluster. Therefore, the overall reaction pathways for the formation of the final cluster can be recommended as the following steps: (i) instant formation of $[Zn(L)(H_2O)Eu(H_2O)_4]^{3+}$ hydrate (A) upon addition of EuCl₃ into the ethanol solution of $[Zn(L)(H_2O)]$ with the presence of triethylamine,¹² (ii) deprotonation of the zinc-bound water molecule with Et₃N to give the active zinc hydroxide derivative $[Zn(L)(OH)Eu(H_2O)_4]^{2+}$, followed by nucleophilic attack of the zinc bound hydroxide at the carbon dioxide substrate to give a hetero-binuclear bicarbonate intermediate $[Zn(L)(OCO_2H)Eu(H_2O)_4]^{2+}$ (B), (iii) reaction with transformation of species B into species C through further CO₂ uptake



Fig. 3 The suggested reaction scheme for the formation of zinc bicarbonate derivative $[LZn-OCO_2H]^-$. The labelling of atoms is illustrated on the individual structures.



Fig. 4 The suggested reaction pathway for the formation of $[Zn_4L_4Eu_4(CO_3)_6]$ cluster. The labeling of atoms is illustrated on the individual structures.

reaction, (iv) assembly and rearrangement of the intermediate C resulting in the formation of the final product (D). The suggested reaction pathway is depicted in Fig. 4. However, due to the diversified coordination modes of europium ion, the presence of other intermediates in the reaction process can not be completely excluded. Further work is needed to fully understand the reaction mechanism.

In conclusion, we have described the preparation and structural characterization of a new carbonato-bridged 3d-4f heteropolynuclear cluster, and the result shows that this complex could efficiently capture atmospheric CO₂ under ambient conditions. To the best of our knowledge, such a lanthanidebased polynuclear complex with the high CO32--Eu3+ ratio of 3:2 (CO₃²⁻-metal of 3:4) is very scarce in the literature.^{10b} This characteristic may provide important evidence for the synergistic effect of the Zn²⁺ ions in improving the ability of Eu³⁺ ions to capture carbon dioxide in air. Remarkably, this synthetic approach may represent a promising new route towards the design of new lanthanide clusters for enhancement of CO₂ capture as well as novel functional materials with intrinsic properties arising from different meal ions. Studies focused on magnetic properties of the Gd(III) and Dy(III) analogues and a spectroscopic study of Nd(III) clusters are in progress.

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