

Hexanuclear Lanthanide Clusters Encapsulating a $m_6\text{-CO}_3^{2-}$ Ion Displaying an Unusual Binding Mode

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Reaction of hydrated lanthanum halides (Ln = La, Pr and Nd) with LH_2 [1-(2-HydroxyPhenyl)-3-(2-thienyl)-1,3-Propanedione] in presence of excess triethylamine with methanol as a solvent resulted in the isolation and structural characterization of a series of novel hexanuclear lanthanide clusters templated by $m_6\text{-CO}_3^{2-}$ introduced via spontaneous fixation of atmospheric car-

bon dioxide depicting a new coordination mode of binding. This particular mode of bridging is a first report of its kind in lanthanide clusters. Magnetic analysis of the praseodymium and neodymium analogue shows strong antiferromagnetic interactions in case of praseodymium and weak antiferromagnetic interactions in case of neodymium.

Introduction

Assembling lanthanide based high nuclearity clusters where in lanthanides are bridged by an intervening 'O' or 'N' atom have received considerable attention in recent years owing to their potential applications in diverse fields like luminescence,^[1] catalysis^[2] and magnetism.^[3] In general, polynuclear lanthanide oxo/hydroxo clusters have been synthesized by treating hydrated lanthanide salts with complexing ligands like carboxylates,^[4] amino acids,^[5] alkoxides,^[6] β -diketones^[7] or Schiff bases^[8] in presence of excess base. This methodology has been extensively used to synthesize lanthanide oxo/hydroxo clusters displaying interesting magnetic properties. In recent years using anions like nitrates and carbonates as template / ligands for constructing novel metal organic frameworks (MOF) and polynuclear clusters have started gaining momentum.^[9] Carbonates have been inserted into molecular and supramolecular systems either by addition of carbonate source to the reaction mixture or by atmospheric fixation of carbon dioxide at room temperature. Recently Arikawa *et al.* have reported the utility of a ruthenium pincer complex for atmospheric fixation of carbon dioxide and have also successfully demonstrated the release of the absorbed carbonate by treating with a methylating reagents.^[10] Transition metal complexes with zinc, copper, cobalt, nickel, platinum and iridium have also been found to be useful in atmospheric fixation of CO_2 .^[11] Literature on lanthanide complexes regarding fixation of atmospheric CO_2 is sparsely re-

ported in comparison with transition metal based counterparts.^[12] Some interesting examples include lanthanide oxo-hydroxo clusters templated by carbonate anion insertion via spontaneous fixation of atmospheric CO_2 , like the dodecanuclear lanthanum cluster $[\text{La}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_4(\text{dbm})_{18}(\text{phgly})_2(\text{CO}_3)_2]$ (dbm = dibenzoyl methane, phgly = phenyl glycine) templated by two CO_3^{2-} anions.^[13] Another interesting report which needs mention is by Murray *et al.* where in hexanuclear lanthanide clusters $[\text{Ln}_6(\text{teaH})_2(\text{teaH}_2)_2(\text{CO}_3)(\text{NO}_3)_2(\text{chp})_7(\text{H}_2\text{O})]$ (tea = triethanolamine, chp = 6-chloro-2-hydroxypyridine) with trapped carbonate ion, the Tb, Dy derivatives exhibiting SMM behavior.^[14] Similarly, lanthanide clusters displaying SMM behaviour have been reported with varying nuclearities like octa, hexa and tetranuclear dysprosium clusters essentially templated by carbonate anions.^[15] Isolation of Er_{26} and Dy_{26} clusters incorporating nitrate anion^[16] and the spherical polycarbonate bound lanthanoid cluster along with a decanuclear cluster templated by carbonate ions indicate that anions other than hydroxides/oxides can as well be considered as promising candidates for assembling novel molecular architectures.^[17] These results clearly indicates a growing interest in synthesizing lanthanide clusters using CO_3^{2-} ions in a quest for achieving diverse molecular structures. In this background, the synthesis, structural elucidation and magnetic properties of hexanuclear lanthanide oxo cluster templated by $m_6\text{-CO}_3^{2-}$ displaying a new coordination mode of binding are presented.

Results and Discussion

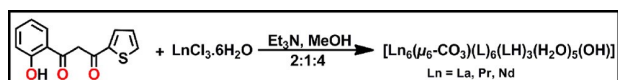
Synthetic procedure was adopted from literature studies. The hydrated lanthanum halides, ligand (LH_2) and triethylamine were reacted in methanol in 1:2:4 ratios, yielding the product as yellow precipitate. The product was characterized by standard analytical and spectroscopic techniques. The IR spectrum of 1–3 shows a characteristic band at around 1599 cm^{-1} corresponding to the —O stretch of the deprotonated β -diketone and a peak at 1258 cm^{-1} which can be attributed to the phenolic oxygen stretching vibration. IR spectra also displayed a signal at 1521 cm^{-1} suggesting the presence of carbonate ions

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in 1–3. Further ^{13}C -NMR spectrum of 1 show a signal at 177 ppm which is consistent with the signal observed for carbonate ions from literature reports suggesting the presence of carbonate ions in the synthesized cluster. Single crystal X-ray diffraction studies revealed the formation of hexanuclear lanthanide clusters $[\text{Ln}_6(\mu_6\text{-CO}_3)(\text{L})_6(\text{LH})_3(\text{H}_2\text{O})_5(\text{OH})]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) showing the presence of a carbonate anion obtained by fixation of atmospheric CO_2 . Single crystal X-ray analysis revealed that all the complexes are isostructural and crystallize in cubic space group $I-43d$. Cluster 1 is chosen as prototype for detailed structural description whose structure is shown in Figure 1a. The asymmetric unit contains one third of the cluster



Scheme 1. Synthesis of 1–3.

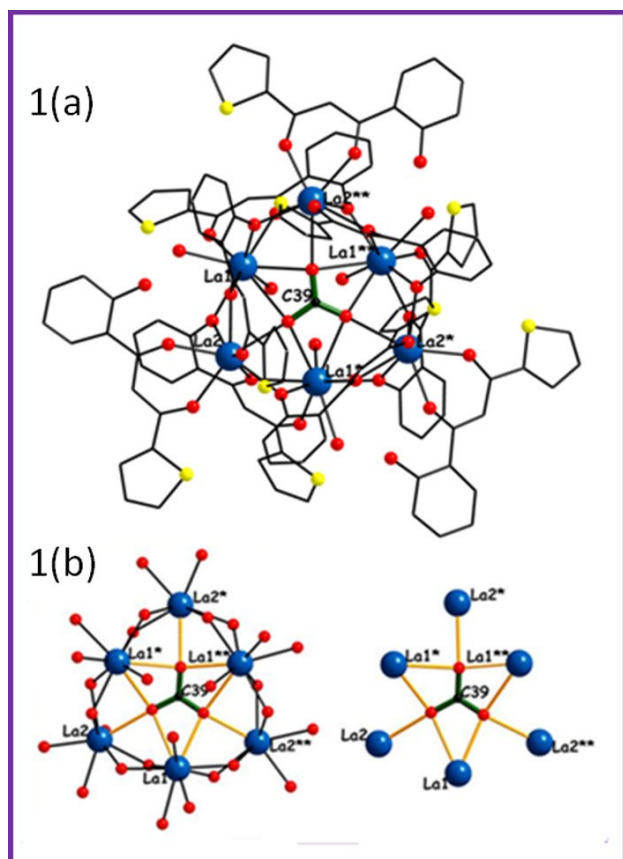


Figure 1. a: Molecular structure of compound 1. Hydrogen atoms are omitted for clarity; b: Core of the cluster showing coordination mode of CO_3^{2-} ($m_6\text{-}h^1\text{:}h^2\text{:}h^1\text{:}h^2\text{:}h^1\text{:}h^2$).

with a La dimer bridged by phenolic oxygen O_7 and by m_2 -oxygen of diketone O_2 , three b-diketone ligands are coordinated to the metal atoms out of which one is displaying both chelating and bridging, the other two are displaying chelating mode of bridging. Further La1 is coordinated to two water molecules

and to one of the carbonate oxygen atom O_8 . Symmetric operation on O_8 ($y-1, z, x+1$) generates the full unit. The hexanuclear cluster can be visualized to be built up of two triangular units La_1, La_2 and La_1^* bridged by one of the carbonate oxygen O_8 and the other two oxygens $\text{O}_8^*, \text{O}_8^{**}$ of the carbonate bridges another triangular unit $\text{La}_2^{**}, \text{La}_1^{**}$ and La_2^* . Further oxo groups of diketone connects these two trinuclear units leading to the formation of a novel hexanuclear cluster which is structurally different from hexanuclear clusters reported so far in literature.^[11h,14b] Carbonate anion is trapped in the center of the cluster core, interestingly here the carbonate anion adapts a new bridging mode $m_6\text{-}h^1\text{:}h^2\text{:}h^1\text{:}h^2\text{:}h^1\text{:}h^2$ as shown in Figure 1b, assignment of bridging carbonate was further confirmed by careful observation of X-ray diffraction data since carbonate source was not used in any stage of reaction. In the cluster core, two different sets of metal atoms are present; one set is nine coordinated with two coordinated water molecules and the other set is eight coordinated with a chelating diketone, and these two different sets are present alternatively in the solid state structure. Nine ligands are present in the peripheral part of the cluster, three ligand are acting as only chelating (monoanionic form) and the other six are acting as both chelating and bridging (dianionic form) by using their phenolic and diketone oxygens. For charge neutrality one of the oxygen atoms bound to metal ion is considered as hydroxide ion. La1 is nine coordinated with two water molecules O_9 and O_{10} , two phenolic oxygens O_7 and O_3 , three diketone oxygens $\text{O}_{11}, \text{O}_{12}, \text{O}_2^*$ two carbonate oxygen O_8 and O_8^* . La2 is eight coordinated with one chelating diketone oxygens O_4 and O_5 , two phenolic oxygen O_7, O_3 and three diketone oxygens O_1, O_2 and O_{12}^* and one carbonate oxygen O_8^* . The La–O phenolic bond distances are in the order of 2.416 to 2.418 Å, La–O bridging diketone oxygens are in the order of 2.505 to 2.629 Å. La–O chelating diketone Oxygens are in the order of 2.410 to 2.463 Å. La– $\text{O}_{(\text{water})}$ distances are in the order of 2.506 to 2.584 Å, metal-carbonate oxygen bonds are in the order of 2.687 to 2.817 Å which are consistent with the lanthanide carbonate compounds previously reported,^[18] in case of Nd the metal carbonate bonds are slightly longer than the earlier reports (2.927 Å). The bonding distances are at the extreme end of Ln–O bond lengths reported. The La–O–La angles fall in a wide range of 97.8 to 145.78. Intramolecular La...La distances are in the order of 3.848 to 3.859 Å. The Selected bond lengths (Å) and bond angles (°) for 1–3 are given in the supporting information (Table S2-4). Continuous shape measurement using *SHAPE* software^[19] indicates that the coordination sphere around La1 is Muffin geometry and La2 is in a triangular dodecahedron (Figure 2a). Complete results of geometric analysis are described in the supporting information (Table S5, S6). The carbonate ion present in 1–3 is due to the fixation of atmospheric CO_2 since no carbonate source was used in the synthetic pathway.

After identifying the presence of carbonate ions in 1–3 by IR, ^{13}C NMR (in 1) and structurally confirming its presence by single crystal X-ray diffraction studies, synthetic efforts were made to prepare carbonate inserted cluster directly. Despite several attempts, 1–3 could not be synthesized by any direct

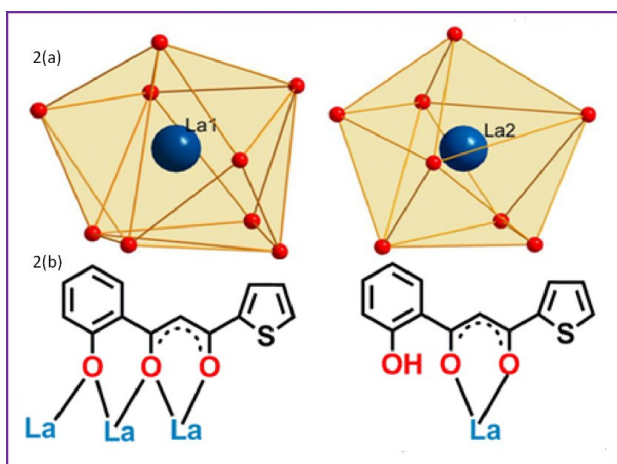


Figure 2. a: coordination geometry around La1 and La2; b: different coordination modes of LH2.

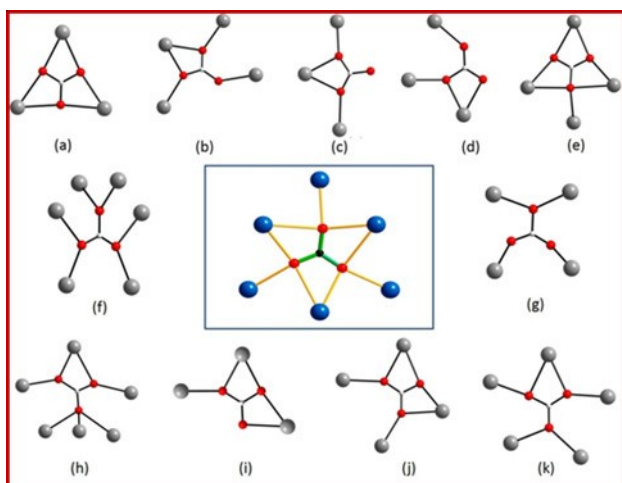


Figure 3. represents various coordination modes of carbonate anion (a),^[12a,c,d,e,f,g,i,14] (b),^[15a] (c),^[15b] (d),^[15c] (e),^[17] (f),^[12h] (g),^[12k] (h),^[13] (i),^[12b] (j),^[12] (k),^[12] The binding mode of carbonate observed in the present case is shown in the centre of the figure.

methods which involved the use of carbonate based reagents in the synthetic pathway. Further, the crystallization process was carried out in a closed system which also failed to produce crystals worthy of diffraction quality. Hence, the carbonate anion found in 1–3 is due to atmospheric fixation of CO₂ in the presence of basic medium as the triethylamine base is added in excess quantity in the reaction methodology. This is in concurrence to Murray's explanation for the formation of CO₃²⁻ ion from atmospheric CO₂ similar to the action of carbonic anhydrase.

Magnetic Studies

Susceptibility data were collected for 2 and 3 at 0.3 T applied field from 2 to 300 K. Below 30 K an additional data set was collected with an applied field of 0.02 T. As can be seen in Fig-

ure 4a, both data sets overlap. The cT product for 2 at 300 K has a value of 8.46 cm³ K mol⁻¹, just below the expected value

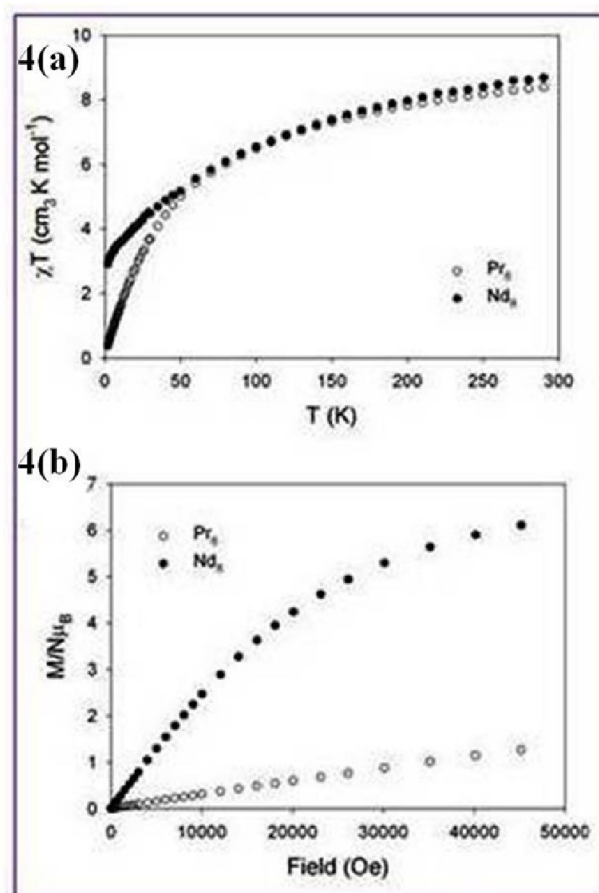


Figure 4. a: Magnetic susceptibility as a function of temperature for compound 2(Pr) and 3(Nd), shown as cT product; b: Magnetization vs. field plot at 2.0 K for 2 and 3.

for six Pr(III) ion (³H₄, 1.5 cm³ K mol⁻¹ for one isolated Pr(III) ion, S = 1, L = 5, J = 4 and gJ = 4/5). As temperature decreases, the cT product also decreases. The cT product for 3 at 300 K has a value of 8.73 cm³ K mol⁻¹, just below the expected value for six Nd(III) ions (1.64 cm³ K mol⁻¹ for one Nd(III) S = 3/2, L = 6 J = 9/2 ; ⁴I_{9/2}, and gJ = 8/11). As temperature decreases the cT product decreases, in a less pronounced manner than for 2.

The decrease observed is mostly caused by the depopulation of the M_J states of the Ln(III) ion. At low temperature the cT product for 2 is almost zero suggesting strong anti-ferromagnetic coupling in 2, while 3 is paramagnetic. This reflected in the magnetization vs. field plot at 2.0 K shown in Figure 4b. For 2 the magnetization does not reach saturation at 5 T and rises linearly with the applied field, indicating the population of the Zeeman split M_J levels and possibly an anti-ferromagnetically coupled ground state, since the value observed is very low compared to the expected for six Pr(III) ions be understood as the para-

magnetic behavior of six Nd(III) ions that are practically isolated.

Conclusions

Hexanuclear lanthanide based oxo clusters (Ln=La, Pr and Nd) templated by a carbonate anion introduced via spontaneous fixation of atmospheric CO₂ have been synthesized and structurally characterized. The carbonate anion displays a bridging mode $m_6-h^1:h^2:h^1:h^2:h^1:h^2$ which is encountered for the first time in lanthanide chemistry. Magnetic studies on 2 and 3 reveal strong antiferromagnetic interaction in case of compound 2 and weak antiferromagnetic interactions in case of compound 3. Spontaneous fixation of atmospheric CO₂ leading to the formation of carbonates anions offers newer paths towards designing novel carbonate bridged lanthanide clusters.

Supporting Information

General methods, general procedure, characterization of all compounds and molecular structures of compounds 2 and 3. Crystal data and structure refinement parameters table, bond lengths, bond angles and shape analysis tables for all compounds are available.

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Keywords: Carbonate insertion · *b*-diketone · Lanthanide clusters · Magnetism · New bridging mode

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