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Synthesis, crystal structure of a new tridimensional family of materials: LnCHA$(H_2O)_2\cdot 2.5H_2O$ (Ln=Dy–Yb)

C. Daiguebonne[a], O. Guillou[a,*], Y. Gérault[a], K. Boubekeur[b]

[a]*Groupe de Recherches en Chimie et Métallurgie, INSA, 35043 Rennes, France*
[b]*CNRS FRE 2068, 44072 Nantes, France*

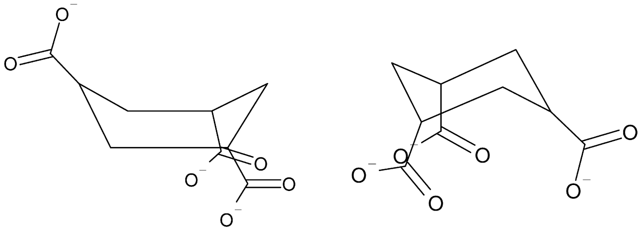
Abstract

The slow diffusion in water through a H-tube of trivalent lanthanide ions with CHA^{3-}, where CHA^{3-} stands for $[C_6H_6(COO)_3]^{3-}$, afforded single crystals suitable for crystalline resolution. The crystal structure has been solved for the Er(III) compound and is reported here. The chemical formula is $ErCHA(H_2O)_2\cdot 2.5H_2O$ and the space group of the crystalline structure is $C2/c$ with $a=13.3944(16)$ Å, $b=12.2501(9)$ Å, $c=15.9220(16)$ Å, $\beta=92.089(13)$ and $Z=8$. The structure presents a complex tridimensional network which can be described as the association of double-sheet network, via μ_2-oxo bridges between Ln^{3+} ions. The isostructurality of the other compounds has been assumed on the basis of X-ray powder diagrams and elementary cell determination. The thermal properties of these compounds have been studied and are reported here.

Keywords: Lanthanide; Coordination chemistry; Crystal structure; Porous solid

1. Introduction

In order to investigate the lanthanide contraction and the steric hindrances effects on rare earth complexation, we have, in the recent years, developed a crystalo-chemical study dealing with the lanthanide trimesate complexes where trimesate stands for benzene-1,3,5-tricarboxylate ($C_9H_3O_6^{3-}$); some interesting results have been obtained with rare earth ions ranging from Gd^{3+} to Lu^{3+} [1–5]. For instance, it appears that, despite a favorable oxidation numbers ratio 3+/2−, no tridimensional material was obtained. Even more, our study reveals that reactions between rare earth ions and planar dianionic ligands or transition metal ion monomeric complex generally leads to ladder-like monodimensional [6] or honeycomb-like bidimensional [7,8] molecular motifs. We have thus undertaken the study of the CHA^{3-} complexes with rare earth ions where CHA^{3-} symbolizes the cyclohexan-1,3,5-tricarboxylate ion (Scheme 1).



Scheme 1. Cyclohexan-1,3,5-tricarboxylate anion: boat-like (left) and chair-like (right) conformations.

This ligand is comparable with benzene-1,3,5-tricarboxylate. The main difference between the two is that in CHA^{3-}, the three carboxylato groups no longer lie in a plane. As expected, by reaction with trivalent lanthanide ions, the ligand tridimensional character leads to tridimensional organic–inorganic hybrid material. We wish to report here their synthesis, crystal structure and thermal study.

2. Experimental

2.1. Synthesis

Cyclohexan-1,3,5-tricarboxylic acid was purchased from Fluka and used without further purification. By reaction with NaOH, this acid provides the penta-hydrated sodium salt. The hydration degree of the salt was estimated on the

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*Corresponding author.

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basis of elemental analysis and thermogravimetric measurements. Anal. calc. (found) for $Na_3CHA{\cdot}5H_2O$: Na 18.8% (18.9%); C 29.4% (29.3%); H 3.8% (4.0%); O 47.9% (47.7%). Dilute aqueous solutions of Ln(III) chloride (0.25 mmol) (Ln=Ce and La) and the sodium salt of trimesic acid (0.25 mmol) were allowed to slowly diffuse through water in an H-shaped tube. After a few weeks, colorless plate-like single crystals were obtained. Anal. calc. (found) for $ErCHA(H_2O)_2{\cdot}2.5H_2O$: Er 36.2% (36.0%); C 23.4% (23.5%); H 3.9% (3.8%); O 36.4% (36.5%).

White microcrystalline powders of $ErCHA(H_2O)_2{\cdot}2.5H_2O$ with Ln=Dy–Yb were obtained at room temperature by fast addition of an aqueous solution of $Na_3CHA{\cdot}5H_2O$ (1 mmol in 20 ml of water) to a dilute aqueous solution of lanthanide chloride (1 mmol in 20 ml of water). The obtained powders were characterized by elemental analysis and X-ray powder diagrams and revealed to be isostructural with the Er compound.

2.2. Thermal analysis

DTA and TGA curves were recorded, respectively using TDA Adamel Lhomargy 67 and TGA Linseis L81/064. Samples (100 mg) were heated under nitrogen flow in alumina (DTA) and quartz (TGA) crucibles to 450°C at a heating rate of 5°C min^{-1}.

2.3. X-ray powder experiments

X-ray powder patterns were collected using a Rigaku DMAX II diffractometer 30 kV, 10 mA for CuKα (λ= 1.5406 Å), with a scan speed of 0.1° min^{-1} and a step size of 0.002° in 2θ. The calculated patterns were produced using the CARINE 3.1 software program [9].

2.4. X-ray data collection and structure determination of $ErCHA(H_2O)_2{\cdot}2.5H_2O$

A transparent plate-like single crystal of $ErCHA(H_2O)_2{\cdot}2.5H_2O$ was sealed in a glass capillary and mounted on a STOE IPDS single ϕ axis diffractometer with a 2D area detector based on imaging plate technology. Using the rotation method ($0 \leq \phi \leq 260°$) with $\Delta\phi = 2.0°$ increments, 130 images were recorded at an exposure time of 3 min and a crystal-to-plate distance of 60 mm (EXPOSE [10]). The images were processed with the set of programs from STOE [10] (DISPLAY, PROFILE, INDEX, CELL, INTEGRATE) and the data were corrected by an empirical absorption correction [10] (ABSORB). The structure was solved by direct method and difference Fourier techniques and refined (on F^2 values) by full matrix least squares calculations using the software package SHELXS-86 [11] and SHELXL-93 [12]. All non-hydrogen atoms were anisotropically refined. Other pertinent data are listed in Table 1; see also Supplementary materials.

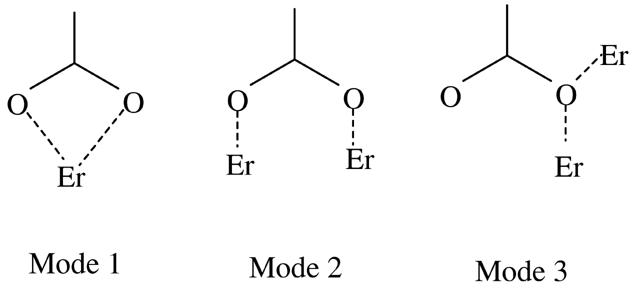
Table 1
Crystal and final structure refinement data of $ErCHA(H_2O){\cdot}2.5H_2O$

Molecular formula	$ErC_9O_{10.5}H_{18}$
Formula weight	461.49
Crystal dimensions (mm)	0.1×0.05×0.05
Temperature (K)	298
Crystal system	Monoclinic
Space group	*C2/c* (no.15)
a (Å)	13.3944(16)
b (Å)	12.2501(9)
c (Å)	15.9220(16)
β (°)	92.089(13)
V ($Å^3$)	2610.8(5)
Z	8
D_{calc} ($g\,ml^{-1}$)	2.348
$F(000)$	1792
μ (cm^{-1})	0.648
Radiation	Mo Kα
hkl Range	$-16 \leq h \leq 16$; $0 \leq k \leq 15$; $-18 \leq l \leq 18$
θ Range (°)	$2.25 \leq \theta \leq 25.88$
Data collected	2351
Observed data ($F_{obs} \geq 2\sigma(F_{obs2})$)	1514
Parameters refined	156
R^a (%)	5.30
$R_w{}^b$ (%)	11.71
Goodness of fit	0.933
Final shift/error	0.000
Residual density (e $Å^{-3}$)	0.304 (in the vicinity of Er)

[a] $R = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$.
[b] $R_w = \{\Sigma[w\,(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; $w = 1/[\sigma^2(F_o^2) + (0.0841P)^2 + 0.00P]$ where $P = [(F_o^2) + 2 \cdot F_c^2]/3$.

2.5. Description of the structure of $ErCHA(H_2O)_2\cdot 2.5H_2O$

The asymmetric unit, along with the atomic numbering scheme is depicted in Fig. 1a. Each Er atom is eight coordinated by six oxygen atoms from carbonato groups and two from coordination water molecules which form a slightly distorted square antiprism. The Er atom is surrounded by five CHA^{3-} ligands in a chair-like conformation. Four out of the five distribute in a slightly distorted plane and the fifth is in apical position (Fig. 1b). The two coordination water molecules distribute around the opposite apical direction. The three carboxylato groups adopt three different coordination modes, namely bidentate (mode 1), bridging (mode 2) and μ_2-oxo (mode 3) as shown in Fig. 1c and d. The three different coordination modes observed are depicted in Scheme 2.



Scheme 2.

The crystal structure can be described as thick molecular planes spreading in the $(\vec{a},\vec{c})$ plane linked to each other via Er–O–Er μ_2-oxo bridges. In such planes, each CHA^{3-} ligand is bounded to four Er atoms via bidentate and bridging CO_2^- groups (Fig. 2). The μ_2-oxo bridges imply rather short Er–Er distances. Indeed, the shortest inter-plane and intra-plane distances lie, respectively, around 4 and 5 Å. The crystal structure present rather large cavities spreading along the three crystallographic axis directions as shown in Figs. 2 and 3. The 2.5 crystallization water molecules per asymmetric unit are localized inside those cavities and are linked to the molecular skeleton via a complex hydrogen bond network. These water molecules progressively leave the molecular framework on heating from room temperature to 150°C. An elemental analysis reveals that the resulting powder chemical formula is ErCHA. This compound can reversibly bind water reforming $ErCHA(H_2O)_2\cdot 2.5H_2O$ when exposed to a wet atmosphere. The material has a reasonable degree of thermal

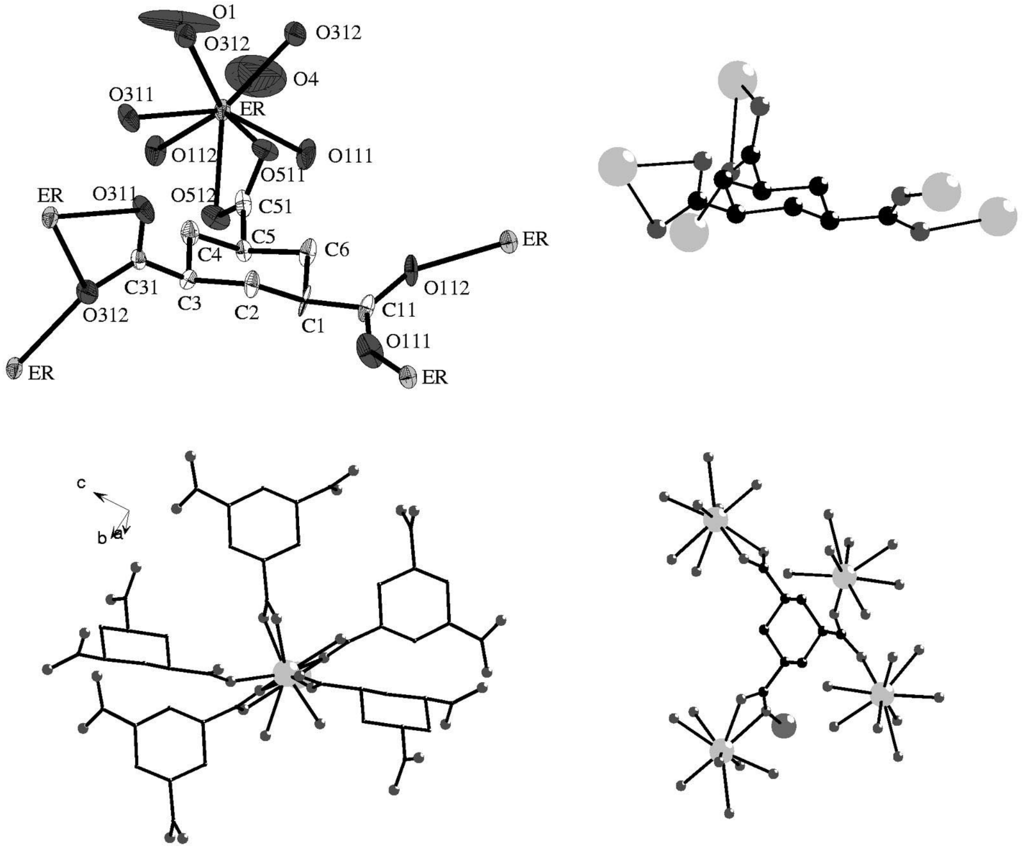


Fig. 1. (a) Top-right: extended asymmetric unit of $ErCHA(H_2O)_2\cdot 2.5H_2O$. (b) Bottom-right: Er^{3+} ion surrounding. (c and d) Left: Er^{3+} ions linked to a CHA^{3-} anion.

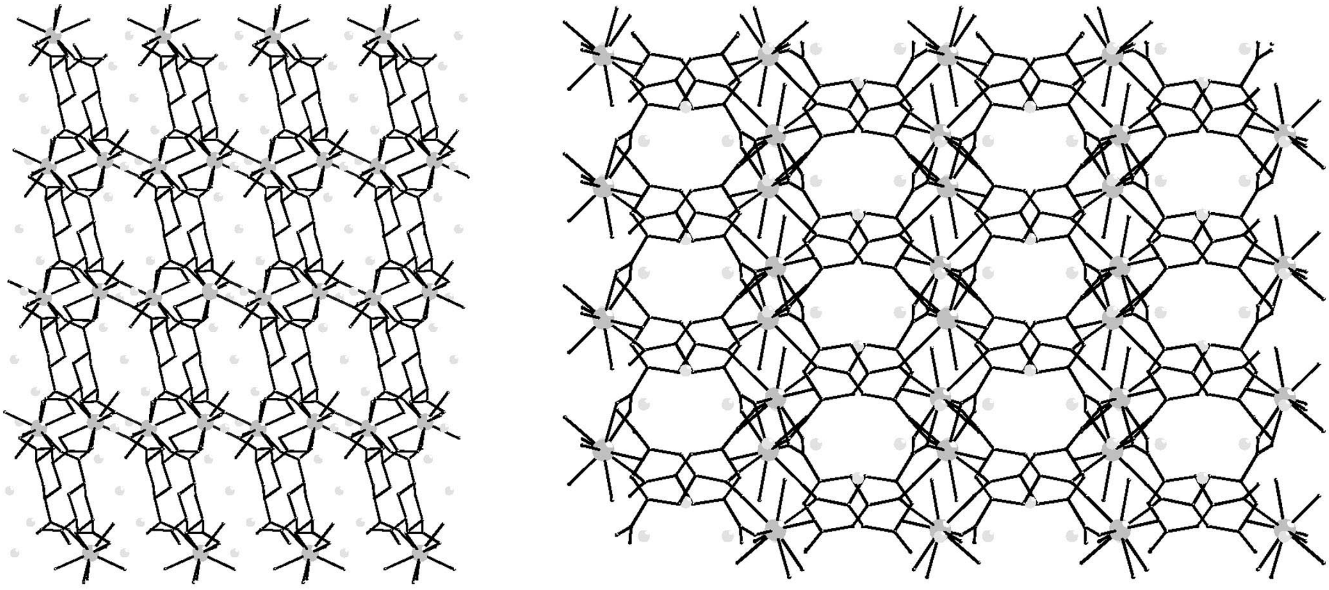


Fig. 2. View along the $\vec{b}$ (right) and $\vec{a}$ (left) axis of the crystal structure.

stability (up to 250°C), and the lability of the water molecules could allow their replacement by other molecules.

3. Conclusion and outlook

The crystal structure reported here could be of great interest as far as *4f* containing organic–inorganic hybrid materials are concerned. Analogous materials containing lighter rare earth ions also exist. Unfortunately, our attempts at obtaining single crystals of compounds belonging to this second family have, until now, failed. It could also be of some interest to investigate the replacement of the water molecules by other neutral molecules. Lastly, we are trying to structurally study the anhydrous materials obtained by dehydration.

4. Supplementary material

Complete lists of bond length and angles (Tables S1 and S2) and listing of calculated and observed structure factors (Table S3) may be obtained on request from the authors.

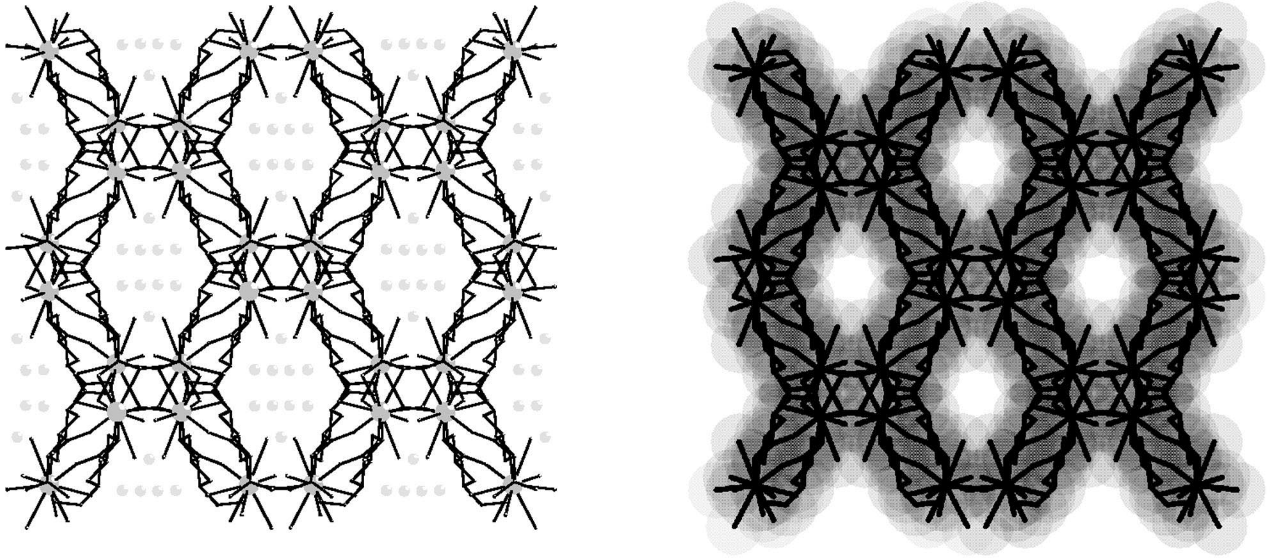


Fig. 3. Projection along the $\vec{c}$ axis of the crystal structure exemplifying the crystallization water molecules localization together with the cavities spreading along the $\vec{c}$ axis.

Full details of the X-Ray structure determination of $ErCHA(H_2O)_2 \cdot 2.5H_2O$ has been deposited with the Cambridge crystallographic data center and can be obtained, on request, from the authors and from the reference to this publication.

Acknowledgements

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References

[1] C. Daiguebonne, Y. Gérault, O. Guillou, K. Boubekeur, Inorgan. Chim. Acta 284 (1999) 139–145.
[2] C. Daiguebonne, Y. Gérault, O. Guillou, A. Lecerf, K. Boubekeur, P. Batail, M. Kahn, O. Kahn, J. Alloys Comp. 275–277 (1998) 50–53.
[3] D. Zhi-Bang, J. Zhong-Sheng, W. Ge-Cheng, N. Jia-Zan, J. Huaxue, J. Struct. Chem. 9 (1) (1990) 64.
[4] D. Zhi-Bang, J. Zhong-Sheng, W. Ge-Cheng, N. Jia-Zan, J. Less-Common Met. 171 (1991) L1–L3.
[5] C. Daiguebonne, O. Guillou, K. Boubekeur, Inorgan. Chim. Acta, 2000, in press.
[6] R.L. Oushoorn, K. Boubekeur, P. Batail, O. Guillou, O. Kahn, Bull. Soc.. Chim. Fr. 133 (1996) 77.
[7] C. Daiguebonne, R.L. Oushoorn, O. Guillou, K. Boubekeur, O. Kahn, Inorg. Chem. (2000) in press.
[8] W.W. Butcher, F.H. Westheimer, J. Am. Chem. Soc. 77 (1955) 521.
[9] C. Boudias, Y. Breton, Ca. R. Ine 3.1.
[10] STOE IPDS Software Manual V2.75, Stoe and Cie, Darmstadt, 1996.
[11] G.M. Sheldrick, SHELX 86, Acta Crystalogr. A46 (1990) 467–473.
[12] SHELX 93, Program For the Refinement of Crystal Structures, University of Göttingen, 1993.