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A new bidimensional material: $Ln_2(CO_3)_3.8\ H_2O$ (Ln=La, Ce) Synthesis and crystal structure

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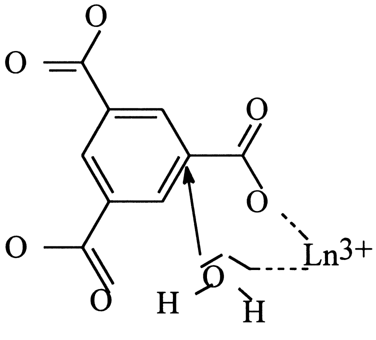
Abstract

The slow diffusion through gel in a U-tube of trivalent lanthanide ions with TMA^{3-}, where TMA^{3-} stands for $[C_6H_3(COO)_3]^{3-}$, afforded single crystals suitable for crystalline resolution. The crystal structure has been solved for the Ce(III) compound and is reported here. The chemical formula is $Ce_2(CO_3)_3.8\ H_2O$ and the space group of the crystalline structure is *Pccn* with: $a=8.9421(7)$ Å, $b=9.5292(9)$ Å, $c=16.971(2)$ Å and $Z=4$. The structure consists in planes in which the lanthanides ions are connected via bidendate carboxylato groups or μ_2-oxo bridges. The isostructurality of the other compounds has been assumed on the basis of X-ray powder diagram and elementary cell determination. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide; Coordination chemistry; Crystal structure

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 so been obtained with rare earth ions ranging from Gd^{3+} to Lu^{3+} [1–5]. However, up to now there is no trimesate complex involving one of the biggest rare earth ions. Our attempts to obtain single crystals of such a complex were unsuccessful and we wish to report here the synthesis and the crystal structure of the lanthanide carbonate obtained during these attempts. This hydrolysis of the ligand TMA^{3-} is very surprising for such a strong ligand. However it is well known that the rare earth ions, and especially the biggest ones, can promote such a decomposition in water. This observation has, indeed, already been observed in other systems but is not well understood [6–10] yet. Further more, this hydrolysis has, to the best of our knowledge, not been encountered yet with carboxylic acids and it seems reasonable to imagine that in the mechanism, the state schematized in Scheme 1 occurs.



Scheme 1.

Carbonate is a strong complexing ligand for f-elements and many compounds have been already described [11–15]. Some single-crystals structures have been reported [16–19] but most of the rare earth carbonates have been studied using powder X-Ray diffraction [20–22]. However, many Ln(III) carbonates are amorphous and have not been structurally described [23] yet.

2. Experimental

2.1. Synthesis

Trimesic acid was purchased from Acros Organics and used without further purification. Dilute aqueous solutions of Ln(III) chloride (0.25 mmol) (Ln=Ce and La) and sodium salt of trimesic acid (0.25 mmol) were allowed to

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slowly diffuse through an agar–agar gel in an U-shaped tube. After a few weeks, colorless plate-like single crystals were obtained. Anal. Calc. (found) for $Ce_2(CO_3)_3.8\ H_2O$: Ce 46.4% (46.0%); C 6.0% (6.0%); H 2.7% (2.0%); O 45.0% (45.5%).

White micro-crystalline powders of $Ln_2(CO_3)_3.8\ H_2O$ with Ln=Ce or La where synthesized by bubbling CO_2 in an aqueous solution of lanthanide chloride at room temperature and standard pressure. The pH must be controlled and maintained between 5.5 and 6 during the whole operation. The obtained powders where characterized by elemental analysis and X-ray powder diagrams.

2.2. X-ray data collection and structure determination of $Ln_2(CO_3)_3.8\ H_2O$ with Ln=La or Ce

A transparent plate-like single crystal of $Ce_2(CO_3)_3.8\ H_2O$ 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. 130 images were recorded by using the rotation method ($0 \leq \phi \leq 260°$) with $\Delta\phi = 2.0°$ increments, an exposure time of 3 min and a crystal to plate distance of 60 mm (EXPOSE [24]). The images were processed with the set of programs from STOE [24] (DISPLAY, PROFILE, INDEX, CELL, INTEGRATE) and the data were corrected by an empirical absorption correction [24] (ABSORB). The structure was solved by direct method and difference Fourier techniques and refined (on F^2s) by full matrix least squares calculations using the software package SHELXS-86 [25] and SHELXL-93 [26]. All non-hydrogen atoms have been anisotropically refined. Other pertinent data are listed in Table 1. See also supplementary materials.

$La_2(CO_3)_3.8\ H_2O$ has been assumed to be isostructural to the Ce containing material on the basis of X-ray powder pattern and of a cell determination on a single crystal.

2.3. Description of the structure of $Ln_2(CO_3)_3.8\ H_2O$ with Ln=La or Ce

The asymmetric unit, along with the atomic numbering scheme is depicted in Fig. 1. Each Ce atom is eight coordinated. Actually, Ce1 is coordinated by four oxygen atoms from carbonato groups and four from coordination water molecules which form a slightly distorted square antiprism, while Ce2 is coordinated by six oxygen atoms from carbonato groups and two from coordination water molecules which form a distorted dodecahedron. Ce1 atom is linked to four carbonato groups (two bridging and two μ_2-oxo) in a square plane manner while Ce2 atom is linked to five carbonato groups (two bridging, two μ_2-oxo and a bidentate) in a square based pyramid manner. The three different coordination modes observed are depicted in Scheme 2. Modes 1, 2 and 3 are respectively bidentate, bridging and μ_2-oxo.

The structure consists in parallel sheet networks as can be seen in Figs. 2 and 3. The carbonato groups which acts as chelating bidentate ligands for Ce2 points toward the

Table 1
Experimental data for the X-ray diffraction study of $Ce_2(CO_3)_3.8\ H_2O$

Molecular formula	$Ce_2C_3O_{17}H_{16}$
Formula weight	604.40
Crystal dimensions (mm)	0.1*0.05*0.05
Temperature (K)	298
Crystal system	orthorhombic
Space group	*Pccn* (n°56)
a (Å)	8.9421(7)
b (Å)	9.5292(9)
c (Å)	16.971(2)
V (Å^3)	1446.2(2)
Z	4
Dcalc (g cm^{-3})	2.776
F(000)	1144
μ (cm^{-1})	0.631
Radiation	Mo Kα
hkl Range	$0=h=10$; $0=k=12$; $0=l=22$
θ Range (°)	$3.12=\theta=27.98$
Data collected	1624
Observed data ($F_{obs} \geq 2\sigma$(Fobs2))	985
Parameters refined	102
R^a (%)	3.10
$R_w^{b,c}$ (%)	8.15
Goodness of fit	1.068
Final shift/error	0.001
Residual density (e Å^{-3})	0.258 (maximum in the vicinity of Ce)

[a] $R = \Sigma \| Fo| - |Fc\| / \Sigma |Fo|$.

[b] $R_w = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$.

[c] $1/[\sigma^2(Fo^2) + (0.0443*P)^2 + 0.00*P]$ where $P = (Fo^2 + 2*Fc^2)/3$.

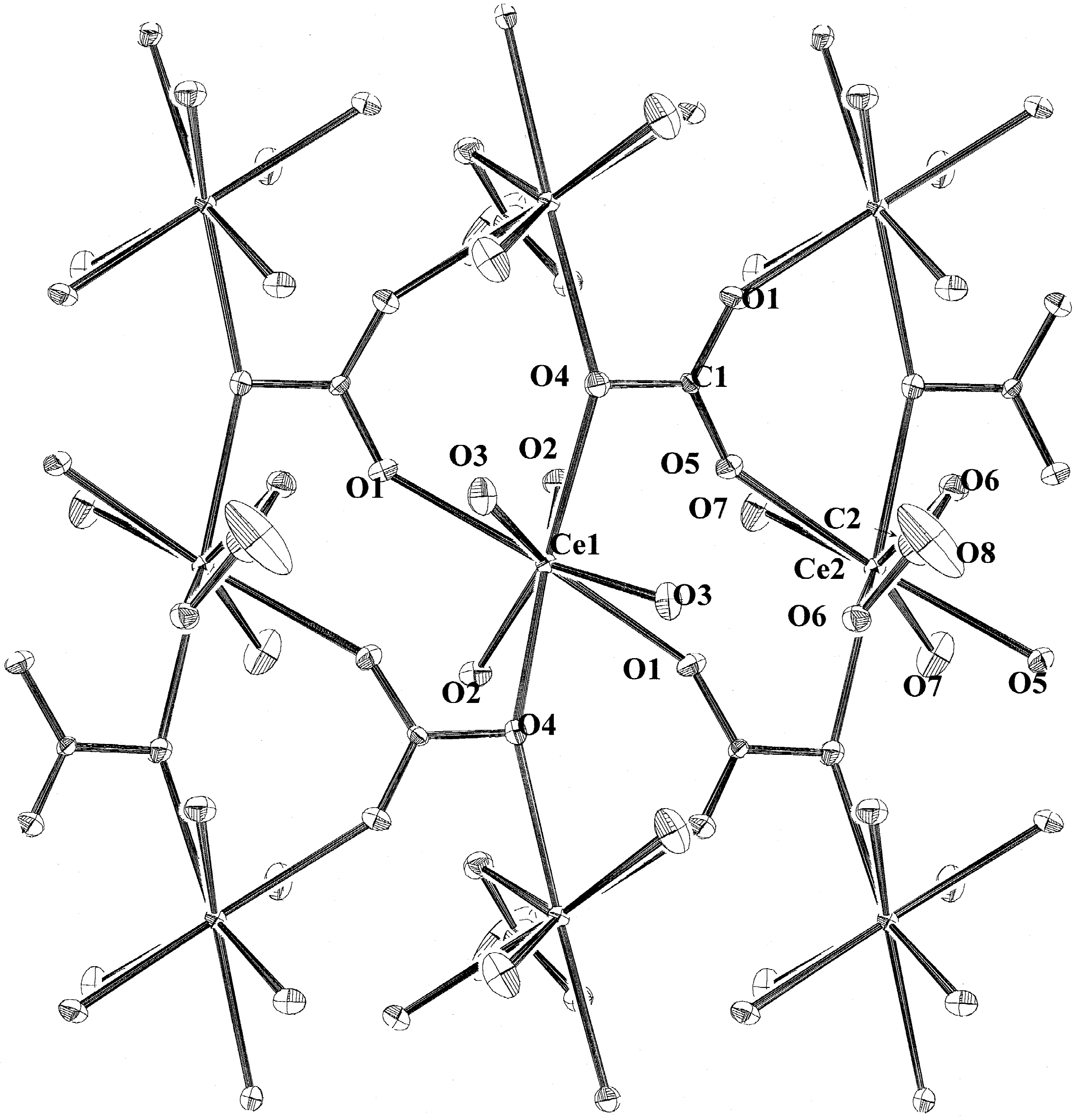
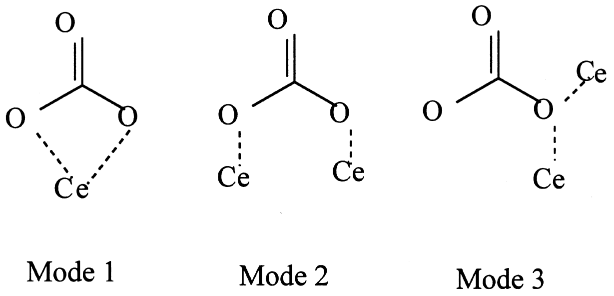


Fig. 1. Extended asymmetric unit of $Ce_2(CO_3)_3.8\ H_2O$.

inter-plane space which is filled with crystallization water molecules (see Figs. 3 and 4). These water molecules bridge adjacent layers via an hydrogen bond network involving the oxygen atom of the bidentate carbonato group and the Ce2's coordination water molecules (see Table 2). The O8 atom which belongs to the Ce2's bidentate carbonato groups exhibit a fairly large atomic displacement effect. This is due to the fact that it points toward the inter-plane space and it is involved in the hydrogen bond network. Each Ce1 atom is bounded to four Ce2 atoms. The μ_2-oxo bridges Ce1–O–Ce2 lead to rather short intra-plane intermetallic distances. Actually, the shortest intra-plane Ce–Ce distances lie in the range 4.5–4.8 Å while the shortest inter-plane distances are roughly 8.5 Å as shown in Table 3. When Ce1 is bounded to Ce2 via a μ_2-oxo bridge the free oxygen atom belonging to the bidentate carbonato group is pointing toward the upper interplane space while when Ce1 is bounded to Ce2 via a chelating carbonato group, the free oxygen atom is pointing in the lower interplane space. Two out of the four



Scheme 2.

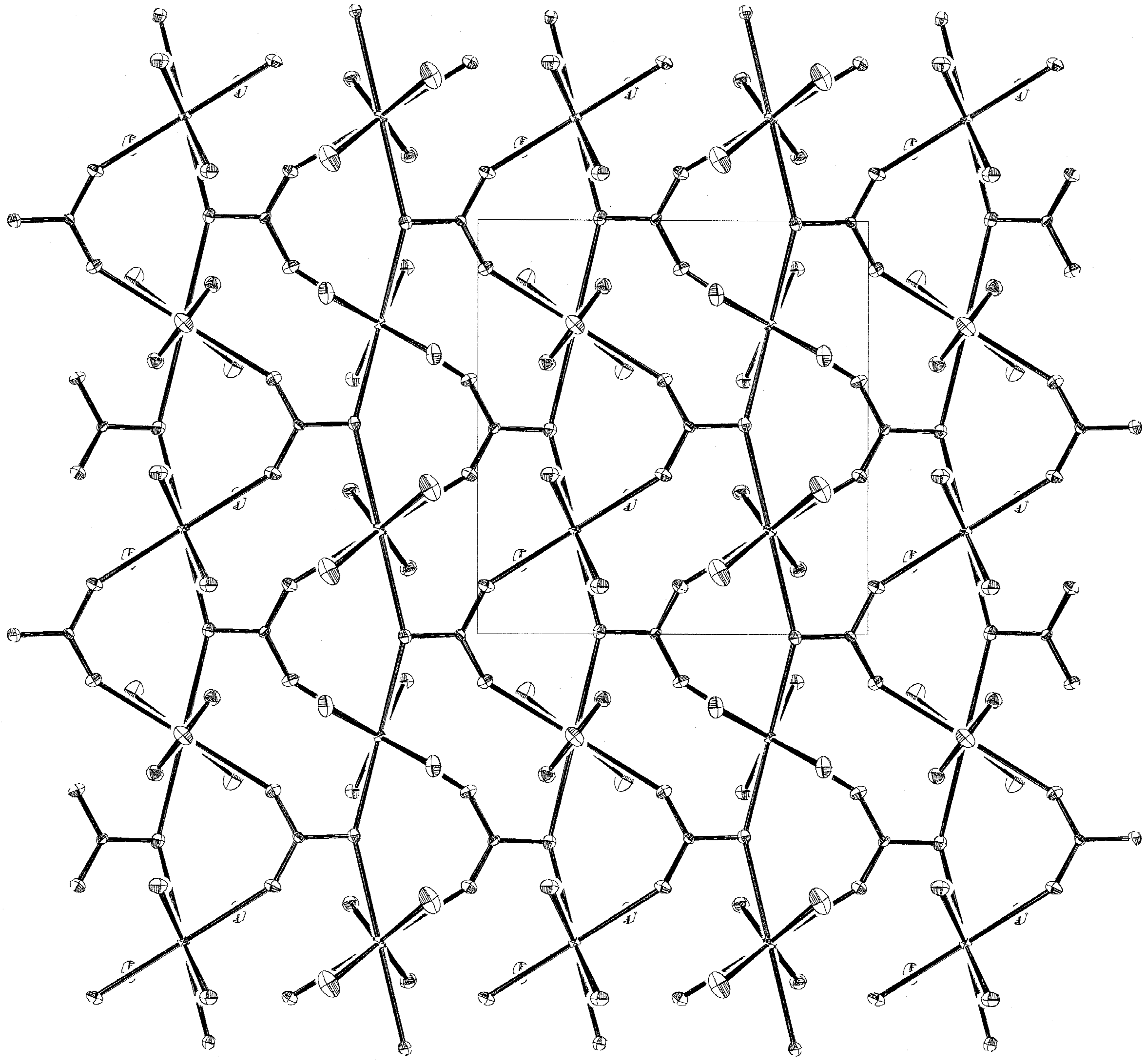


Fig. 2. Molecular layer of $Ce_2(CO_3)_3.8\ H_2O$.

coordination water molecules linked to the Ce1 atom are pointing toward an interplane space while the other two are pointing toward the opposite direction.

3. Conclusion and outlook

The crystal structure reported here could be of great interest as far as 4f–4f magnetic interactions are concerned. The vicinity of the lanthanide ions could indeed lead to original magnetic properties. In order to investigate this point we are trying to synthesize other iso-structural materials containing smaller rare earth ions.

It could also be of some interest to deeply study the hydrolysis phenomenon that gave rise to the single crystals. Indeed, we have recently observed once more this behavior in another system.

4. Supplementary material

Anisotropic thermal parameters (Table S1), complete lists of bond length and angles (Tables S2 and S3), complete list of atomic co-ordinates (Table S4) and listing of calculated and observed structure factors may be obtained on request from the authors.

Further details of the crystal structure determination can be ordered from FACHINFORMATIONSZENTRUM KARLSRUHE, 76344 eggenstein-leopoldshafen, under the depository number CSD-410859.

Acknowledgements

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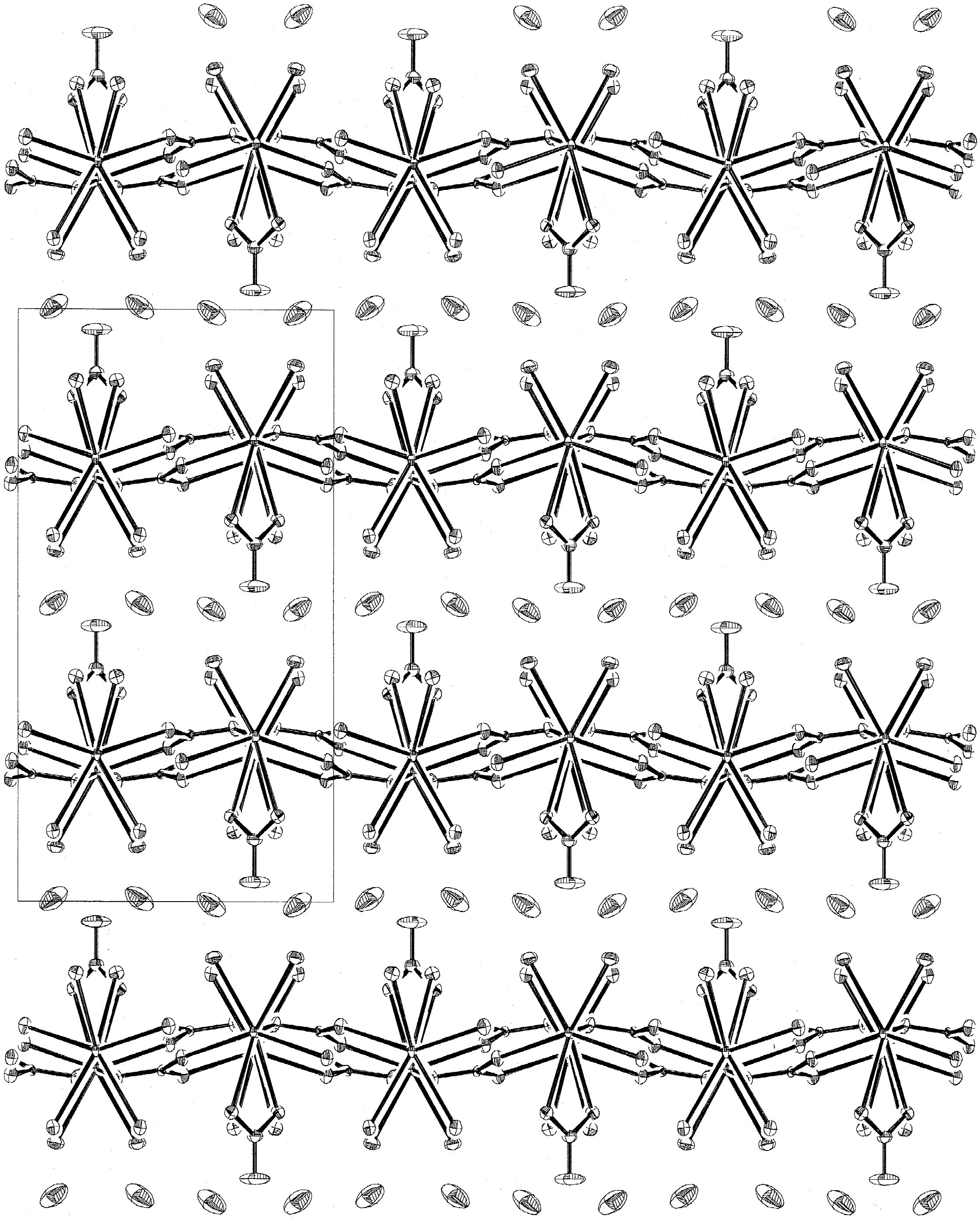

Fig. 3. Representation of the packing of the sheet layers: Projection along the $\vec{b}$ axis.

Table 2
O–O distances in Å in the hydrogen bond network

4.847
5.868
3.560
4.732
2.795
3.012

Table 3
Intermetallic distances in Å

	Inter-plane distances	Intra-plane distances (Å)
Ce1–Ce1	8.486	6.534
Ce2–Ce2	8.486	6.619
Ce1–Ce2	10.055	4.501
Ce2–Ce1		4.795

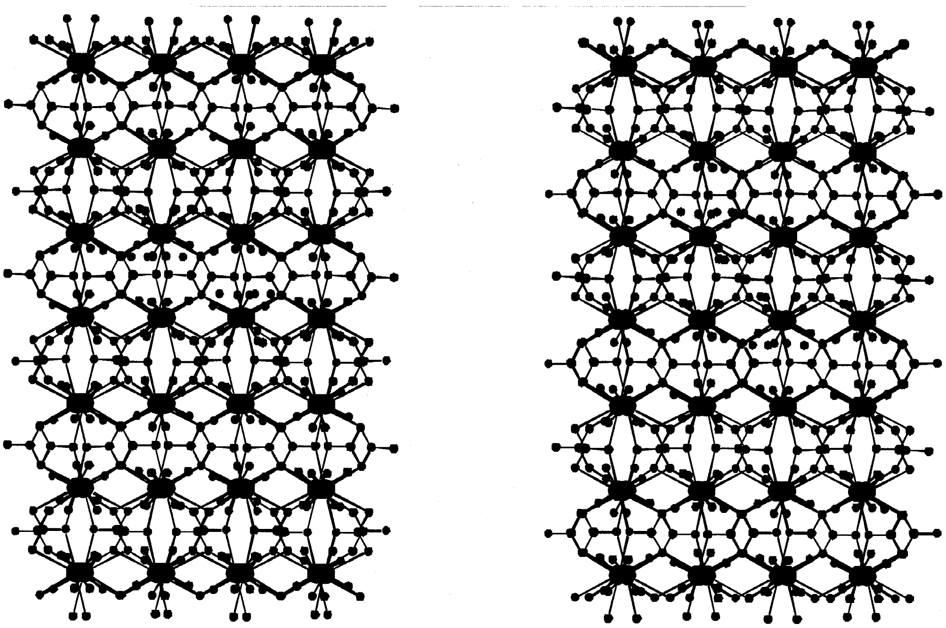

Fig. 4. Stereoscopic ball-and-stick representation of the structure of $Ce_2(CO_3)_3.8\ H_2O$.

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