



# A new honeycomb-like molecular compound: $\text{Gd}[\text{C}_6\text{H}_3(\text{COO})_3](\text{H}_2\text{O})_3 \cdot 1.5\text{H}_2\text{O}$

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## Abstract

The reaction in gel of Gd(III) ions with  $\text{TMA}^{3-}$ , where  $\text{TMA}^{3-}$  stands for  $[\text{C}_6\text{H}_3(\text{COO})_3]^{3-}$ , has afforded single crystals of a bidimensional molecular compound formulated as  $\text{Gd}[\text{TMA}(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$  whose crystal structure is reported here:  $C2/c$ ,  $a=20.454(2)$  Å,  $b=9.973(1)$  Å,  $c=15.251(2)$  Å,  $\beta=125.68(1)^\circ$  and  $Z=8$ . The structure consists of parallel double-sheet networks based on honeycomb-like motifs based on Gd(III) ions and  $\text{TMA}^{3-}$  groups. This compound exhibits a paramagnetic behaviour in the whole temperature range (2–300K). © 1998 Elsevier Science S.A.

**Keywords:** Gd(III); Crystal structure; Double-sheet network

## 1. Introduction

In order to investigate the lanthanide contraction and the steric hindrance effects on rare-earth complexation, we have undertaken the study of lanthanide trimesate complexes (where trimesate stands for 1,3,5 phenyl trioate and will be here after symbolised by  $\text{TMA}^{3-}$ ). The trimesate anion is known for its great coordination versatility and indeed three different kinds of complexes were obtained by reaction of a trimesate ion with a given rare-earth element. To the best of our knowledge, up to now, only two lanthanide complexes with 1,3,5 phenyl trioate have been reported [1,2], namely  $[\text{ErTMA}(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$  and  $[\text{LuTMA}(\text{H}_2\text{O})_5] \cdot 4\text{H}_2\text{O}$ . The synthesis and crystal structure of a new Gd(III) compound, of formula  $\text{Gd}[\text{TMA}(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$ , is reported herein.

## 2. Experimental

### 2.1. Synthesis

Trimesic acid was purchased from Acros Organics and used without further purification. Dilute aqueous solutions

of gadolinium (III) chloride (0.25 mmol) and sodium salt of trimesic acid (0.25 mmol) were slowly added, at the same rate, to an agar–agar gel. The mixture was then kept at 30°C. After a few weeks, single crystals were obtained. Anal. Calc. (found) for  $\text{Gd}[\text{TMA}(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$ : Gd 35.3% (35.1%); C 24.3% (24.3%); H 2.7% (2.8%); O 37.7% (37.8%). The crystals are fragile and decompose by loss of water molecules at room temperature.

### 2.2. X-ray data collection and structure determination of $\text{Gd}[\text{TMA}(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$

A transparent plate-like crystal was sealed in a glass capillary and mounted on a STOE IPDS single  $\phi$ -axis diffractometer with a 2D area detector based on Imaging Plate Technology. 130 images were recorded by using the rotation method ( $0 \leq \phi \leq 260^\circ$ ) with  $\Delta\phi=2.0^\circ$  increments, an exposure time of 3 min and a crystal to plate distance of 80 mm (EXPOSE) [3]. The images were processed with the set of programs from STOE (DISPLAY, INDEX, CELL, PROFILE, INTEGRATE) [3] and the data were corrected by an empirical absorption correction (ABSOR) [3]. The structure was solved by direct method and difference Fourier techniques, and refined (on Fs) by full matrix least-squares calculations using the software package XTAL3.4 [4]. All nonhydrogen atoms have been anisotropically refined. Hydrogen atoms of the  $\text{TMA}^{3-}$

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ligand were included at idealised positions. Other pertinent crystallographic data are listed in Table 1. The positional parameters are listed in Table 2, selected bond lengths and angles in Tables 3 and 4. See also supplementary material.

### 2.3. Description of the structure of $Gd[TMA(H_2O)_3] \cdot 1.5H_2O$

The asymmetric unit along with the atomic numbering scheme is depicted in Fig. 1. It is interesting to note that, in contrast with other published structures of Ln(III) complexes with  $TMA^{3-}$  [1,2] where some of the  $TMA^{3-}$  carboxylato groups serve as monodentate or nonbonding ligands, in this compound, all  $TMA^{3-}$  carboxylato groups act as chelating bidentate ligands. The structure consists of parallel double-sheet networks based on honeycomb-like molecular motifs where one corner out of two is occupied by a Gd(III) ion and the other corner occupied by a  $TMA^{3-}$  ion, as shown in Fig. 2. Molecular bidimensional motifs spread parallel to the  $(b, \vec{a} + \vec{c})$  plane in a step like manner (see Fig. 3).  $TMA^{3-}$  anions belonging to equivalent molecular motifs are superimposed along the  $\vec{c}$  axis direction whereas  $TMA^{3-}$  belonging to nonequivalent molecular motifs are rotated by  $180^\circ$  around the  $\vec{c}$  axis direction and slightly shifted along the  $\vec{b}$  axis direction. The shortest distance between two Gd atoms (5.880 Å) involves Gd atoms belonging to two different double

Table 2  
Atomic positional and isotropic displacement parameters

Atom	$x/a$	$y/b$	$z/c$	$U$
Gd	-0.13827(2)	0.50946(4)	0.26212(3)	0.0178(2)
O111	-0.8797(4)	0.7493(6)	-0.7348(5)	0.035(3)
O112	-0.9789(3)	0.6564(6)	-0.8816(5)	0.035(3)
O311	-0.7417(3)	0.5718(6)	-0.5864(4)	0.029(3)
O312	-0.7229(3)	0.4098(5)	-0.6670(5)	0.027(3)
O511	-0.8701(4)	0.2617(6)	-0.7372(5)	0.041(3)
O512	-0.9818(3)	0.3697(5)	-0.8483(5)	0.027(3)
C11	-0.9479(5)	0.7577(8)	-0.8240(7)	0.024(4)
C31	-0.6957(5)	0.4883(8)	-0.5871(7)	0.024(4)
C51	-0.9433(5)	0.2608(8)	-0.8106(6)	0.024(4)
C1	-0.9896(5)	0.8898(8)	-0.8624(6)	0.020(4)
C2	-1.0706(5)	0.8940(8)	-0.9487(7)	0.024(4)
C3	-0.6099(5)	0.4850(8)	-0.4927(6)	0.023(4)
C4	-1.0682(5)	0.1346(8)	-0.9495(7)	0.022(4)
C5	-0.9885(5)	0.1311(8)	-0.8596(6)	0.022(4)
C6	-0.9490(4)	1.0101(8)	-0.8167(6)	0.023(4)
O1	-0.7093(4)	0.1440(6)	-0.6859(6)	0.042(4)
O2	-0.6164(4)	-0.0865(7)	-0.5793(5)	0.041(4)
O3	-0.6066(5)	-0.007(1)	-0.8678(6)	0.069(5)
O4	-0.7522(4)	0.9203(8)	-0.5913(6)	0.049(4)
O5	-3/4	1/4	1/2	0.12(1)

layers while the shortest distances between Gd atoms within one layer lie in the range 9.736–9.973 Å. Crystallisation water molecules bridge adjacent bilayers, via a hydrogen bond network. The Gd atom is nine-coordinated by six oxygen atoms from three carboxylato groups of

Table 1  
Experimental data for the X-ray diffraction study of  $GdTMA \cdot 4.5H_2O$

Molecular formula	$GdC_9O_{10.5}H_{12}$
Formula weight	445
Crystal dimensions (mm)	0.2*0.2*0.1
Temperature (K)	293
Crystal system	monoclinic
Space group	$C2/c$ ( $n^215$ )
$a$ (Å)	20.454(2)
$b$ (Å)	9.973(1)
$c$ (Å)	15.251(2)
$\beta$ ( $^\circ$ )	125.68(1)
$V$ (Å <sup>3</sup> )	2527.1(6)
$Z$	8
$D_{calc}$ (g cm <sup>-3</sup> )	2.341
$F(000)$	1712
$\mu$ (cm <sup>-1</sup> )	53.0
Radiation	monochromated Mo $K\alpha$ ( $\lambda=0.71073$ Å)
$hkl$ range	$0 \leq h \leq 23$ ; $0 \leq k \leq 11$ ; $-15 \leq l \leq 14$
$\theta$ Range ( $^\circ$ )	$2.38 \leq \theta \leq 24.23$
Data collected	21012
Independent data	1894 ( $R_{int}=0.057$ )
Observed data ( $F_{obs}^2 \geq 3\sigma(F_{obs}^2)$ )	1441
Parameters refined	187
$R^a$ (%)	3.4
$R_w^b$ (%)	3.6
Goodness of fit	5.606
Final shift/error	$3.10^{-4}$
Residual density ( $e$ Å <sup>-3</sup> )	+0.86 -0.91 (maximum in the vicinity of Gd)

<sup>a</sup>  $R = \Sigma |K|F_o| - |F_c| / \Sigma K|F_o|$ .

<sup>b</sup>  $R_w = [\Sigma w(K|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ ,  $w = 1$ .

Table 3  
Selected bond distances (Å)

Atom 1	Atom 2	Distance
Gd	O2	2.388(8)
Gd	O3	2.42(1)
Gd	O1	2.43(1)
Gd	O311	2.433(5)
Gd	O512	2.436(6)
Gd	O112	2.474(5)
Gd	O111	2.492(6)
Gd	O312	2.520(6)
Gd	O511	2.521(6)

Table 4  
Selected bond angles (°)

Atom 1	Atom 2	Atom 3	Angle
O311	Gd	O512	142.4(2)
O311	Gd	O112	125.6(2)
O311	Gd	O111	73.9(2)
O311	Gd	O312	52.6(2)
O311	Gd	O511	101.4(2)
O512	Gd	O112	72.7(2)
O512	Gd	O111	116.0(2)
O512	Gd	O312	121.9(2)
O512	Gd	O511	52.0(2)
O112	Gd	O111	51.7(2)
O112	Gd	O312	160.1(3)
O112	Gd	O511	124.8(2)
O111	Gd	O312	120.6(2)
O111	Gd	O511	152.4(3)
O312	Gd	O511	71.3(2)

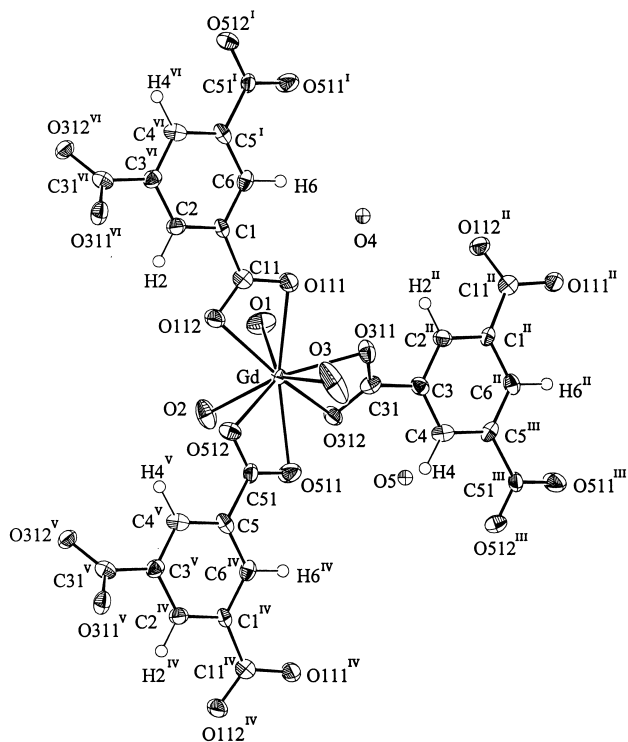


Fig. 1. Asymmetric unit. Indexed atoms are obtained by one of the following operations: I ( $1-x, y+1, z$ ); II ( $1/2+x, 1/2-y, z-1/2$ ); III ( $1/2+x, -1/2-y, z-1/2$ ); IV ( $x, y-1, z$ ); V ( $x-1/2, -y-1/2, 1/2+z$ ); VI ( $x-1/2, 1/2-y, 1/2+z$ ).

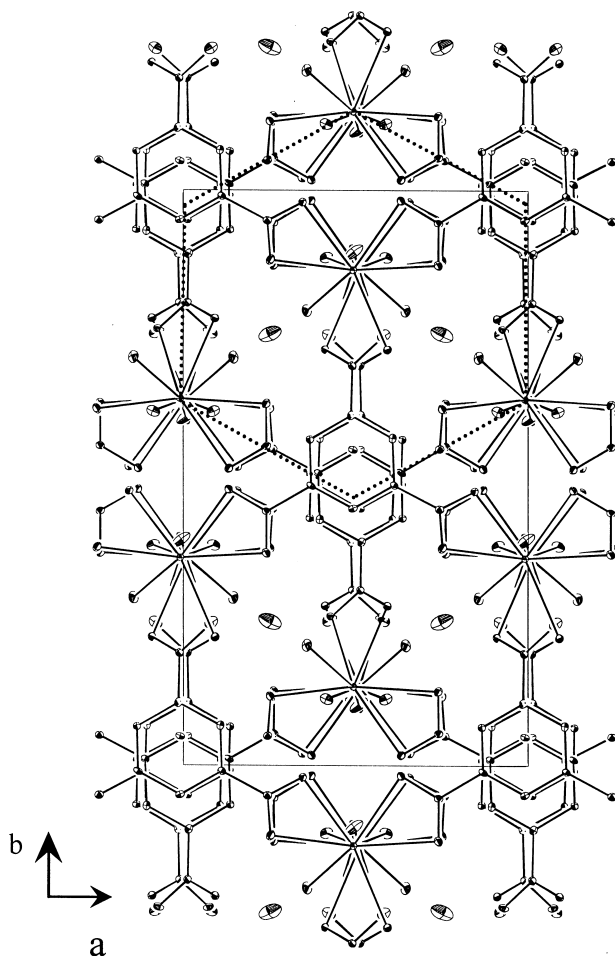


Fig. 2. Molecular honeycomb-like motif: projection along the  $c$  axis of the cell content.

three  $\text{TMA}^{3-}$  ligands as well as three water molecules, to form a distorted tricapped trigonal prism.

### 3. Magnetic measurements

Magnetic measurements were carried out with a Quantum Design SQUID magnetometer. The sample was prepared in a way to prevent the dehydration of the compound. The temperature dependence of the magnetic susceptibility was measured and the result represented in the form  $\chi_M T$  versus  $T$  curve,  $\chi_M$  being the molar magnetic susceptibility and  $T$  the temperature.  $\chi_M T$  is essentially constant in the whole temperature range (2–300K); the magnetic susceptibility follows the Curie law expected for an isolated Gd(III) ion.

### 4. Conclusion and outlook

This single crystal structure represents our first published result arising from our studies of lanthanides

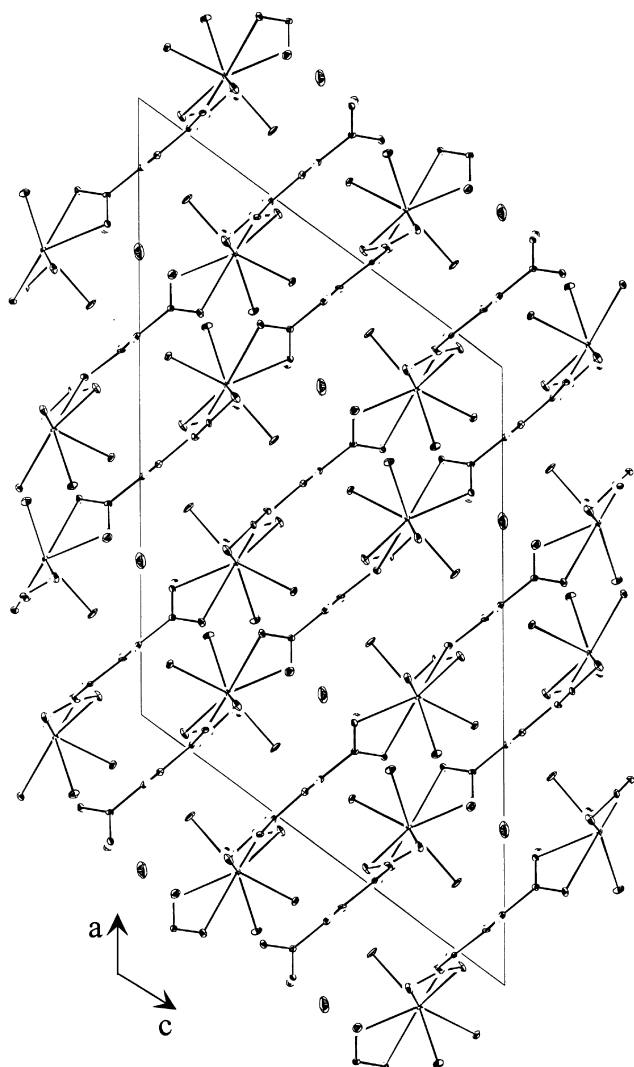


Fig. 3. Representation of the packing of the double-sheet layers: projection along the  $b$  axis of the cell content.

complexes with trimesic acid. At this stage, it seems that the reaction medium is of great importance to the coordinating ability of carboxylato groups and therefore on the dimensionality of the materials.

## 5. Supplementary material

Positional and isotropic thermal parameters of hydrogen atoms (Table S1), anisotropic thermal parameters (Table S2) and listing of calculated, observed structure factors (Table S3) and complete lists of bond lengths and angles (Tables S4 and S5) may be obtained on request from the authors.

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