

catena-Poly[bis[di aquaisonicotinogadolinium(III)]-bis(μ_3 -pyridine-3,4-dicarboxylato)]

Zheng-Bo Han* and Yong-Ke He

School of Chemical Science and Engineering,
 Liaoning University, Shenyang 110036, People's
 Republic of China

Correspondence e-mail: ceshzb@lnu.edu.cn

The title gadolinium(III) coordination polymer, $[\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_2]_n$, has a pyridine-3,4-dicarboxylate-bridged ribbon structure. The isonicotinate anion chelates to the water-coordinated metal atom, which shows ninefold coordination. The isonicotinate unit arises from the decarboxylation of pyridine-3,4-dicarboxylic acid under the hydrothermal conditions of the synthesis.

Received 16 July 2006
 Accepted 25 August 2006

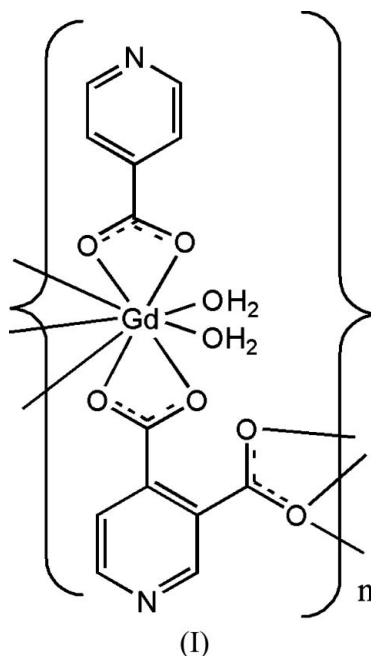
Key indicators

Single-crystal X-ray study
 $T = 293 \text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
 Disorder in main residue
 $R \text{ factor} = 0.040$
 $wR \text{ factor} = 0.090$
 Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

In our previous work, two lanthanide coordination polymers, $[\text{Nd}(\text{pydc})_2 \cdot \text{H}_2\text{O}]_n$ and $[\text{Eu}(\text{pydc})(\text{ina})(\text{H}_2\text{O})_2]_n$ (pydc = pyridine-3,4-dicarboxylate, ina = isonicotinate), were synthesized by treating Nd^{III} or Eu^{III} nitrates with pyridine-3,4-dicarboxylic acid under hydrothermal conditions (Han *et al.*, 2005). Unexpectedly, decarboxylation occurred, and the pydc group was transformed into an ina group in the hydrothermal synthesis of the Eu^{III} coordination polymer. This study has been extended to the other Ln^{III} coordination polymers as the basis for investigating *in situ* decarboxylation. We report here the synthesis and structure of the title gadolinium(III) analogue, (I).



In complex (I), the Gd^{III} ion is coordinated by nine O atoms, five from three pydc ligands, two from one chelating ina group and two from two aqua ligands. The coordination environment around the Gd^{III} ion is a tricapped trigonal prism

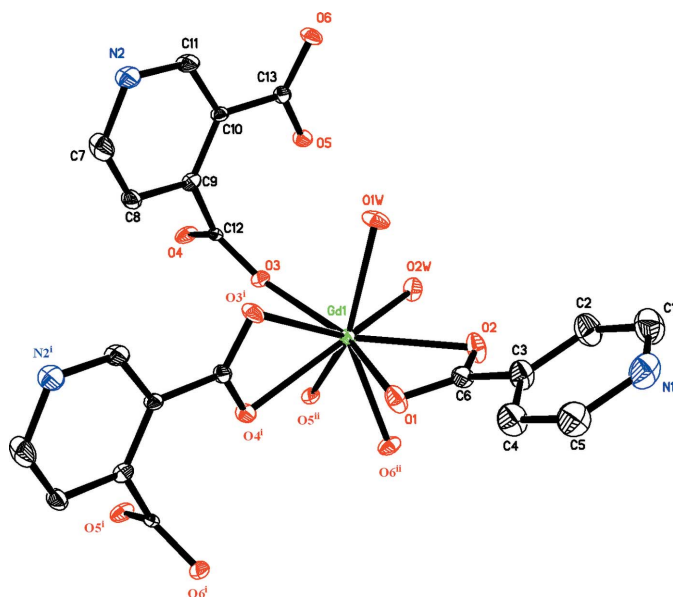


Figure 1
The coordination environment of the metal atom in (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. [Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$.]

(Fig. 1). Pairs of Gd atoms are bridged by two μ_2 -carboxylate O atoms of the pydc groups to form dinuclear $Gd_2(\text{pydc})_2$ subunits, which are interconnected through the chelating carboxylate groups of the pydc ligands to form an infinite one-dimensional ribbon; the Gd...Gd distances are 5.954 (3) and 6.433 (3) Å. These chains are further linked *via* hydrogen bonds (Table 2) between pyridyl N atoms, carboxylate O atoms and aqua ligands to form a three-dimensional supra-molecular network.

Experimental

A mixture of $Gd(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.226 g), pyridine-3,4-dicarboxylic acid (0.5 mmol, 0.087 g), NaOH (1 mmol, 0.04 g), and water (10 ml) was placed in a 23 ml Teflon reactor, which was then heated at 453 K for 6 d. The reactor was cooled to room temperature at a rate of 5 K h^{-1} (yield 72%). CHN analysis for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_8\text{Gd}$ (found/calculated): C 32.65 (32.50), H 2.38 (2.31), N 5.62% (5.83%).

Crystal data

$[\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_2]$
 $M_r = 480.49$
 Monoclinic, $P2_1/n$
 $a = 5.9541$ (19) Å
 $b = 25.047$ (8) Å
 $c = 11.215$ (4) Å
 $\beta = 100.775$ (7)°
 $V = 1643.0$ (9) Å³

$Z = 4$
 $D_x = 1.943$ Mg m^{-3}
 Mo $K\alpha$ radiation
 $\mu = 4.08$ mm^{-1}
 $T = 293$ (2) K
 Block, colourless
 $0.37 \times 0.23 \times 0.12$ mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.314, T_{\max} = 0.634$

6192 measured reflections
 3112 independent reflections
 2803 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.090$
 $S = 1.05$
 3112 reflections
 264 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 7.8772P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.15 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.10 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------------------------------|-------------|--|-------------|
| Gd1—O2W | 2.349 (4) | Gd1—O1 | 2.452 (4) |
| Gd1—O1W | 2.352 (4) | Gd1—O2 | 2.476 (5) |
| Gd1—O3 | 2.375 (4) | Gd1—O6 ⁱ | 2.498 (4) |
| Gd1—O5 ⁱ | 2.409 (4) | Gd1—O3 ⁱⁱ | 2.643 (4) |
| Gd1—O4 ⁱⁱ | 2.449 (4) | | |
| O2W—Gd1—O1W | 76.47 (17) | O5 ⁱ —Gd1—O2 | 129.05 (15) |
| O3—Gd1—O5 ⁱ | 80.79 (15) | O4 ⁱⁱ —Gd1—O2 | 75.04 (15) |
| O3—Gd1—O4 ⁱⁱ | 115.28 (14) | O1—Gd1—O2 | 52.51 (15) |
| O5 ⁱ —Gd1—O4 ⁱⁱ | 82.01 (15) | O1—Gd1—O6 ⁱ | 73.74 (16) |
| O3—Gd1—O1 | 152.25 (15) | O2—Gd1—O6 ⁱ | 116.48 (15) |
| O5 ⁱ —Gd1—O1 | 79.66 (15) | O5 ⁱ —Gd1—O3 ⁱⁱ | 74.25 (13) |
| O4 ⁱⁱ —Gd1—O1 | 81.18 (16) | O4 ⁱⁱ —Gd1—O3 ⁱⁱ | 50.70 (13) |
| O3—Gd1—O2 | 150.15 (15) | | |

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------|------------|--------------|--------------|----------------|
| O1W—H1WB...N2 ⁱⁱⁱ | 0.847 (19) | 1.86 (3) | 2.688 (7) | 166 (5) |
| O1W—H1WA...O1 ^{iv} | 0.849 (19) | 1.94 (3) | 2.773 (6) | 167 (7) |
| O2W—H2WA...N1 ^v | 0.84 (2) | 1.88 (4) | 2.72 (3) | 173 (12) |
| O2W—H2WA...N1 ^v | 0.84 (2) | 1.97 (5) | 2.79 (3) | 166 (12) |
| O2W—H2WB...O4 ^{vi} | 0.84 (2) | 2.39 (7) | 2.939 (6) | 123 (6) |
| O2W—H2WB...O5 ^{vi} | 0.84 (2) | 2.22 (4) | 2.983 (6) | 150 (8) |

Symmetry codes: (iii) $-x, -y + 1, -z$; (iv) $x - 1, y, z$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x, -y + 1, -z + 1$.

Water H atoms were located in a difference Fourier map and refined with distance restraints of O—H = 0.85 (2) and H...H = 1.39 (1) Å. The remaining H atoms were placed in calculated positions in the riding-model approximation, with C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The pyridine ring of the isonicotinate group is disordered; the occupancy was fixed as exactly 0.5. Distance restraints of C—C and C—N = 1.390 (5), and C...C and C...N = 2.780 (5) Å, were applied to the molecule. The highest peak is 1.15 e Å^{-3} at 0.91 Å from Gd1 and the deepest hole is $-1.11 \text{ e } \text{Å}^{-3}$ at 0.98 Å from Gd1.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

The authors thank the Liaoning University Programme for Excellent Talents for supporting this work (grant No. RC-05-11).

References

- Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Han, Z.-B., Li, X.-F., Cheng, X.-N. & Chen, X.-M. (2005). *Z. Anorg. Allg. Chem.* **631**, 937–942.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.