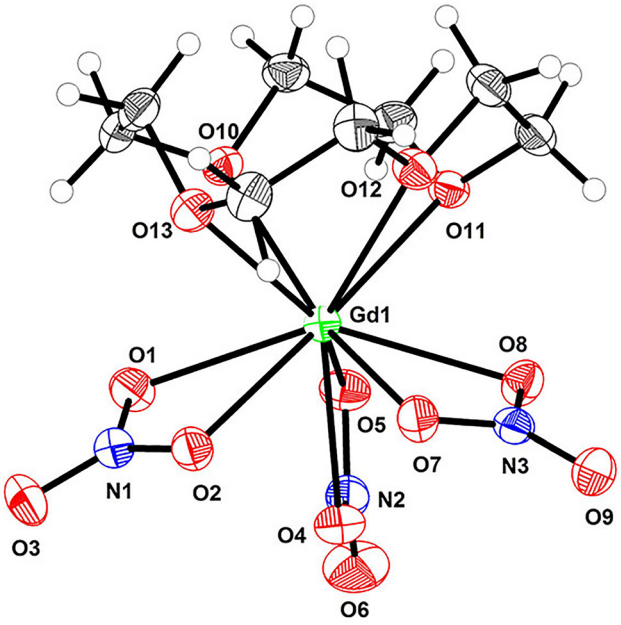
Feng Gao* and Zi-Hang Cheng

Crystal structure of [(1,4,7,10-tetraoxacyclododecane-κ^4O,O',O'',O''')-tris(nitrato-κ^2O,O')gadolinium(III)], $C_8H_{16}N_3O_{13}Gd$



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Abstract

$C_8H_{16}N_3O_{13}Gd$, monoclinic, $P2_1/c$ (no. 14), a = 12.1159(16) Å, b = 8.5454(11) Å, c = 15.251(2) Å, β = 91.848(2)°, V = 1578.2(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0257, $wR_{ref}(F^2)$ = 0.0555, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Feng Gao**, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, Jiangsu 221116, P. R. China, E-mail: gf2016@jsnu.edu.cn. https://orcid.org/0000-0003-3020-8489

Zi-Hang Cheng, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, Jiangsu 221116, P. R. China

Table 1: Data collection and handling.

Crystal:	White block
Size:	0.19 × 0.18 × 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.28 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9137, 3560, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3124
$N(param)_{refined}$:	226
Programs:	Bruker [1], SHELX [2], Diamond [3]

Source of material

The title complex has been synthesized as following: 1,4,7,10-tetraoxacyclododecane (8.81 mg, 0.05 mmol) and $Gd(NO_3)_3{\cdot}6H_2O$ (22.57 mg, 0.05 mmol) were dissolved in 15 mL acetonitrile. The reaction mixture was stirred and heated at 85 °C for 15 h, and then slowly cooled to room temperature. Colorless block crystals of [(1,4,7,10-tetraoxacyclododecane- κ^4O,O',O'',O''')-tris(nitrato-κ^2O,O')gadolinium(III)] were obtained by evaporation of the mother liguid after several days. Yield: 18.51 g, 69.89%.

Experimental details

All hydrogen atoms were placed in geometrically calculated positions. Their U_{iso} values were set to 1.2U_{eq} or 1.5U_{eq} of the parent atoms.

Comment

Macrocyclic crown ether molecules with adjustable cavity sizes and selective metal binding properties have attracted extensive attention in the fields of molecular recognition [4], biological analysis [5], functional materials [6], and so

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2150 (3)	0.0683 (5)	0.8344 (2)	0.0464 (9)
H1A	0.238265	0.159960	0.802414	0.056*
H1B	0.171167	0.002318	0.794967	0.056*
C2	0.3129 (3)	−0.0193 (4)	0.8703 (2)	0.0452 (9)
H2A	0.289357	−0.118617	0.894207	0.054*
H2B	0.363277	−0.040588	0.823607	0.054*
C3	0.4604 (3)	0.1653 (4)	0.9131 (3)	0.0446 (9)
H3A	0.494431	0.118259	0.862814	0.054*
H3B	0.515171	0.168480	0.960948	0.054*
C4	0.4249 (3)	0.3284 (4)	0.8907 (3)	0.0488 (9)
H4A	0.488732	0.396588	0.888566	0.059*
H4B	0.387058	0.330010	0.833631	0.059*
C5	0.3040 (3)	0.5322 (4)	0.9385 (3)	0.0484 (9)
H5A	0.289981	0.543813	0.875891	0.058*
H5B	0.354320	0.614405	0.958013	0.058*
C6	0.1972 (3)	0.5438 (4)	0.9865 (3)	0.0478 (9)
H6A	0.213240	0.562389	1.048305	0.057*
H6B	0.154382	0.631480	0.963627	0.057*
C7	0.0854 (3)	0.3759 (4)	0.8897 (2)	0.0468 (9)
H7A	0.137814	0.401297	0.845033	0.056*
H7B	0.020242	0.440473	0.880469	0.056*
C8	0.0554 (3)	0.2062 (4)	0.8852 (2)	0.0432 (9)
H8A	−0.003240	0.184354	0.925306	0.052*
H8B	0.029104	0.179720	0.826316	0.052*
N1	0.0385 (2)	0.2260 (4)	1.1361 (2)	0.0445 (7)
N2	0.2477 (2)	−0.0985 (4)	1.1524 (2)	0.0500 (8)
N3	0.4323 (2)	0.2910 (4)	1.15552 (19)	0.0416 (7)
O1	0.0535 (2)	0.1205 (3)	1.07887 (17)	0.0475 (6)
O2	0.1189 (2)	0.3152 (3)	1.15316 (17)	0.0458 (6)
O3	−0.0491 (2)	0.2402 (4)	1.1724 (2)	0.0652 (8)
O4	0.2455 (2)	0.0343 (3)	1.18962 (17)	0.0529 (7)
O5	0.2501 (2)	−0.0965 (3)	1.06848 (17)	0.0495 (6)
O6	0.2471 (3)	−0.2192 (3)	1.1934 (2)	0.0807 (11)
O7	0.3427 (2)	0.3662 (3)	1.15219 (17)	0.0462 (6)
O8	0.4366 (2)	0.1695 (3)	1.10788 (17)	0.0469 (6)
O9	0.5103 (2)	0.3309 (3)	1.20228 (19)	0.0595 (8)
O10	0.15143 (18)	0.1138 (3)	0.90865 (15)	0.0389 (5)
O11	0.36878 (18)	0.0713 (3)	0.93827 (14)	0.0378 (5)
O12	0.35169 (19)	0.3813 (3)	0.95729 (16)	0.0430 (6)
O13	0.13402 (19)	0.4023 (3)	0.97613 (16)	0.0429 (6)
Gd1	0.24495 (2)	0.18484 (2)	1.04876 (2)	0.03249 (6)

on. In our previous work, Dy(III), Tb(III), Ho(III), Er(III) complexes based on 1,4,7,10-tetraoxacyclododecane crown ether ligand have been synthesized and structurally characterized [7]. Herein, we prepared the corresponding Gd(III) crown ether complex and determined its structure.

In the title complex (see the figure), the central Gd(III) ion is ten fold coordinated by four O atoms (O10, O11, O12, O13) from the 1,4,7,10-tetraoxacyclododecane crown ether ligand, and six oxygen atoms (O1, O2, O4, O5, O7, O8) from three bidentate coordinating nitrate groups, forming a half-sandwich coordination geometry. The Gd–O bond lengths range from 2.424(3) to 2.560(2) Å. The average Gd–O (crown ether) distance of 2.509 Å is slightly larger than the average Gd–O (nitrate) distance of 2.471 Å. For all three nitrate groups, the average coordinated N–O distance is 1.269 Å, also larger than the average terminal N–O bond length (1.212 Å).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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