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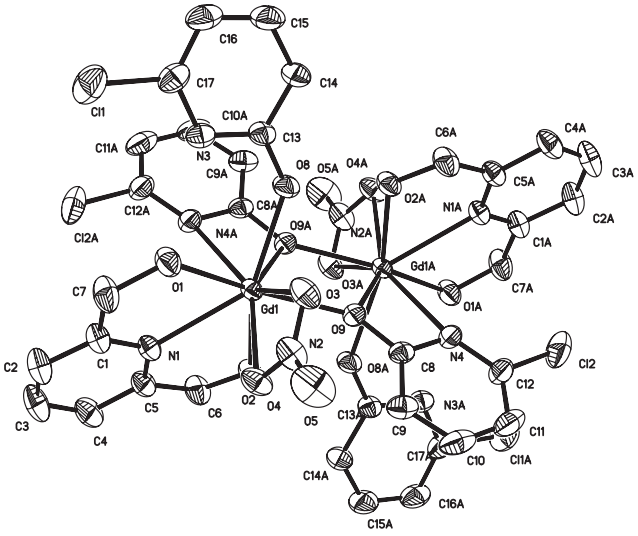
Yu Youzhu*, Guo Yuhua, Yang Liguo and Niu Yongsheng

Crystal structure of bis(2,6-dihydroxymethyl) pyridine-κ³*N*,*O*,*O*′)-bis(μ₂-6-chloropyridin-2-olato-κ³*N*,*O*:*O*)-bis(6-chloropyridin-2-olato-κ*O*)-bis(nitrato-κ²*O*,*O*′)digadolinium(III), $C_{34}H_{30}Cl_4Gd_2N_8O_{14}$



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Abstract

$C_{34}H_{30}Cl_4Gd_2N_8O_{14}$, monoclinic, $P2_1/c$ (no. 14), $a = 8.9118(5)$ Å, $b = 20.7857(11)$ Å, $c = 11.7642(6)$ Å, $\beta = 100.677(2)°$, $V = 2141.4(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0245$, $wR_{ref}(F^2) = 0.1057$, $T = 293(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless blocks
Size:	0.24 × 0.12 × 0.09 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	33.9 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	56.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	61803, 5322, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4713
$N(param)_{refined}$:	280
Programs:	Bruker programs [5, 6], SHELX [7], DIAMOND [8]

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized *via* the reaction of $Gd(NO_3)_2{\cdot}6H_2O$ (1 mmol, 0.451 g), 2,6-pyridinedimethanol (1 mmol, 0.139 g) and 6-chloro-2-pyridinol (1 mmol, 0.130 g) in 10 mL MeOH and 10 mL MeCN, followed by the addition of triethylamine (2 mmol, 0.202 g). The mixture was stirred for 12 h and filtered. Evaporation of the filtrate at ambient conditions afforded colourless block-shaped crystals within 6 days in a yield of 20%.

Experimental details

H atoms were treated as riding atoms with distances C—H = 0.96 (CH_3), 0.97 (CH_2), 0.93Å (ArH) and O—H = 0.85 Å.

Discussion

Exploration of the magnetocaloric effects (MCEs) of molecular magnetic cryogenic materials is currently an active research

***Corresponding author: Yu Youzhu,** College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P.R.China, e-mail: 119yyz@163.com
Guo Yuhua, Yang Liguo and Niu Yongsheng: College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P.R.China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Gd1	0.55276(2)	0.08864(2)	0.96047(2)	0.03763(8)
O9	0.5688(3)	0.01364(12)	1.10928(19)	0.0423(5)
O2	0.3094(3)	0.08983(11)	1.0269(3)	0.0510(6)
H20	0.2806	0.0581	1.0584	0.076*
O1	0.6603(3)	0.17281(14)	0.8670(3)	0.0621(7)
H21	0.7063	0.1610	0.8164	0.093*
O8	0.7341(3)	0.02795(13)	0.8862(2)	0.0522(6)
O4	0.6221(3)	0.16803(14)	1.1177(3)	0.0583(7)
O3	0.8104(3)	0.11123(15)	1.0830(3)	0.0626(7)
N2	0.7640(4)	0.15354(16)	1.1443(3)	0.0594(8)
N1	0.3797(3)	0.18415(14)	0.9016(3)	0.0467(6)
C5	0.2331(4)	0.18277(19)	0.9138(3)	0.0519(8)
C6	0.1813(4)	0.1244(2)	0.9692(4)	0.0624(10)
H6A	0.1176	0.1369	1.0240	0.075*
H6B	0.1211	0.0973	0.9107	0.075*
C4	0.1344(5)	0.2332(2)	0.8764(4)	0.0682(12)
H4	0.0339	0.2323	0.8880	0.082*
O5	0.8452(4)	0.1784(2)	1.2265(4)	0.0987(13)
C3	0.1880(6)	0.2846(2)	0.8219(5)	0.0795(15)
H3	0.1229	0.3183	0.7940	0.095*
C7	0.5954(5)	0.2344(2)	0.8384(5)	0.0711(13)
H7A	0.6039	0.2453	0.7596	0.085*
H7B	0.6507	0.2665	0.8895	0.085*
C1	0.4305(5)	0.23477(18)	0.8497(4)	0.0551(9)
C2	0.3362(6)	0.2858(2)	0.8088(5)	0.0714(12)
H2	0.3738	0.3206	0.7728	0.086*
N3	0.8119(4)	0.09280(14)	0.7529(3)	0.0515(8)
C17	0.8964(5)	0.0994(2)	0.6706(4)	0.0608(10)
C13	0.8161(4)	0.03491(18)	0.8073(3)	0.0468(7)
C9	0.6179(4)	0.0517(2)	1.3046(3)	0.0573(9)
H9	0.6148	0.0948	1.2833	0.069*
N4	0.5869(4)	−0.05927(16)	1.2498(2)	0.0504(7)
C14	0.9084(5)	−0.0146(2)	0.7775(4)	0.0624(10)
H14	0.9132	−0.0540	0.8155	0.075*
C15	0.9911(6)	−0.0046(3)	0.6926(4)	0.0767(14)
H15	1.0516	−0.0376	0.6725	0.092*
C16	0.9863(5)	0.0535(3)	0.6361(4)	0.0740(13)
H16	1.0416	0.0609	0.5776	0.089*
C8	0.5927(4)	0.00358(18)	1.2208(3)	0.0444(7)
C12	0.6148(6)	−0.0740(3)	1.3623(4)	0.0643(11)
C11	0.6496(5)	−0.0298(3)	1.4494(3)	0.0758(15)
H11	0.6738	−0.0425	1.5265	0.091*
C10	0.6472(5)	0.0344(3)	1.4182(4)	0.0730(13)
H10	0.6656	0.0660	1.4751	0.088*
Cl1	0.8813(2)	0.17484(8)	0.60444(13)	0.0956(4)
Cl2	0.6057(3)	−0.15475(9)	1.39553(13)	0.1154(6)

field, and the strong impetus for rapid development originates from the potential applications of such materials as energy-efficient and environmentally friendly cryogenic refrigerators [1, 2]. The Gd^{3+} with seven unpaired 4f electrons was preferentially selected to construct molecular units with high MCE because the intrinsic nature of Gd^{3+} fulfils the requirements of improving MCEs, such as having a large spin ground state S, negligible magnetic anisotropy and low-lying excited spin states [3, 4]. Many applications in daily-life such as fridges and air-conditioners are applications for the possible use gadolinium or gadolinium-based alloys. To enlarge gadolinium based molecular magnetic cryogenic materials we report here the synthesis and crystal structure of a new dinuclear gadolinium complex.

The structure of this complex is centrosymmetric and contains two Gd^{3+} atoms, two 2,6-pyridinedimethanol groups, four 6-chloro-2-pyridinol groups and two nitrate groups. Consequently, the two Gd^{3+} atoms are in the same coordination environment and each Gd^{3+} ion is nona-coordinated by N and O of the three different ligands (*cf.* the figure). Each $Gd(C_7H_9O_2N)(C_5H_3ONCl)_2(NO_3)$ unit is bridged by two 6-chloropyridin-2-olato ligand to give a Gd-Gd separation of 3.956 Å. The Gd(1)—Gd(1A)—O(9)—O(9A) bridging unit is planar. The Gd(1)—O(9)—Gd(1A) and O(9)—Gd(1)—O(9A) angles in the bridge are 111.49° and 68.51°, respectively. The distances of O(9)—Gd(1) and O(9)—Gd(1A) are 2.329 Å and 2.457 Å, respectively. The crystal packing doesn't exhibit hydrogen bonds or classical interactions.

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