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Crystal structure of bis(μ_2 -3,5-dichloro-2-oxidobenzoato- $\kappa^4 O, O': O', O''$)-hexakis(μ_2 -pivalato- $\kappa^2 O: O'$)-bis(pivalato- $\kappa^2 O, O'$)-tetrakis(1,10-phenanthroline- $\kappa^2 N, N'$)tetragadolinium(III), $C_{102}H_{108}Cl_4Gd_4N_8O_{22}$

<https://doi.org/10.1515/ncrs-2018-0204>

Received June 10, 2018; accepted September 30, 2018; available online October 16, 2018

Abstract

$C_{102}H_{108}Cl_4Gd_4N_8O_{22}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.4271(18)$ Å, $b = 12.779(2)$ Å, $c = 20.102(3)$ Å, $\alpha = 76.6197(17)^\circ$, $\beta = 86.9059(18)^\circ$, $\gamma = 71.4460(18)^\circ$, $V = 2706.7(8)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0350$, $wR_{ref}(F^2) = 0.1350$, $T = 296(2)$ K.

CCDC no.: 1870691

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

Source of material

All reagents and solvents employed were commercially available and used as received without further purification. A mixture of Gd_2O_3 (0.5 mmol, 0.181 g), pivalic acid (1 mmol,

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.59 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	78962, 13226, 0.035
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 10890
$N(param)_{refined}$:	643
Programs:	Bruker [1, 2], SHELX [3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Gd1	1.01386(2)	0.60784(2)	0.86982(2)	0.03253(7)
Gd2	0.80556(2)	0.82433(2)	0.68839(2)	0.03499(8)
C1	0.6317(5)	1.1127(4)	0.6538(3)	0.0523(12)
H1	0.5721	1.0806	0.6738	0.063*
C2	0.6029(6)	1.2302(5)	0.6396(3)	0.0624(15)
H2	0.5265	1.2749	0.6512	0.075*
C3	0.6859(8)	1.2780(5)	0.6092(4)	0.076(2)
H3	0.6666	1.3565	0.5993	0.092*
C4	0.8016(7)	1.2117(5)	0.5921(3)	0.0611(15)
C5	0.8940(9)	1.2564(6)	0.5584(4)	0.081(2)
H5	0.8777	1.3345	0.5459	0.097*

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C6	1.0074(8)	1.1861(7)	0.5441(4)	0.081(2)
H6	1.0653	1.2173	0.5208	0.097*
C7	1.0363(6)	1.0661(5)	0.5645(3)	0.0585(14)
C8	1.1519(6)	0.9913(7)	0.5549(4)	0.073(2)
H8	1.2142	1.0193	0.5348	0.087*
C9	1.1733(6)	0.8786(7)	0.5748(4)	0.0691(17)
H9	1.2487	0.8282	0.5667	0.083*
C10	1.0823(5)	0.8401(6)	0.6070(3)	0.0606(14)
H10	1.1001	0.7621	0.6224	0.073*
C11	0.9460(5)	1.0191(4)	0.5978(2)	0.0460(11)
C12	0.8261(5)	1.0922(4)	0.6100(2)	0.0466(11)
C13	1.2532(6)	0.7060(5)	0.7800(3)	0.0661(16)
H13	1.1911	0.7750	0.7770	0.079*
C14	1.3664(8)	0.7072(8)	0.7475(4)	0.087(2)
H14	1.3810	0.7751	0.7276	0.105*
C15	1.4526(6)	0.6059(7)	0.7467(3)	0.0698(17)
H15	1.5260	0.6037	0.7239	0.084*
C16	1.4317(5)	0.5058(6)	0.7795(3)	0.0561(14)
C17	1.5189(5)	0.3960(7)	0.7803(4)	0.073(2)
H17	1.5919	0.3913	0.7565	0.088*
C18	1.4988(6)	0.3021(7)	0.8135(4)	0.074(2)
H18	1.5566	0.2326	0.8116	0.089*
C19	1.3875(5)	0.3049(5)	0.8532(3)	0.0581(15)
C20	1.3627(7)	0.2062(5)	0.8926(4)	0.0728(19)
H20	1.4178	0.1348	0.8924	0.087*
C21	1.2620(7)	0.2156(5)	0.9295(4)	0.0731(19)
H21	1.2467	0.1516	0.9563	0.088*
C22	1.1784(6)	0.3245(5)	0.9273(3)	0.0583(14)
H22	1.1080	0.3305	0.9535	0.070*
C23	1.2985(4)	0.4098(4)	0.8535(2)	0.0429(10)
C24	1.3194(4)	0.5114(4)	0.8148(2)	0.0433(10)
C25	0.5636(4)	0.8822(4)	0.7874(2)	0.0402(9)
C26	0.4374(5)	0.9451(5)	0.7922(3)	0.0500(12)
C27	0.3779(5)	0.9504(4)	0.8530(3)	0.0548(13)
H27	0.2951	0.9927	0.8535	0.066*
C28	0.4428(5)	0.8922(4)	0.9134(3)	0.0493(12)
C29	0.5653(5)	0.8273(4)	0.9125(3)	0.0435(11)
H29	0.6079	0.7873	0.9534	0.052*
C30	0.6246(4)	0.8220(4)	0.8509(2)	0.0385(9)
C31	0.7567(4)	0.7483(4)	0.8549(2)	0.0353(8)
C32	1.3123(7)	0.6301(7)	0.9779(4)	0.077(2)
H32A	1.3317	0.5710	0.9532	0.115*
H32B	1.3867	0.6445	0.9871	0.115*
H32C	1.2560	0.6979	0.9511	0.115*
C33	1.2527(5)	0.5933(4)	1.0454(3)	0.0436(10)
C34	1.3435(6)	0.4902(6)	1.0900(4)	0.080(2)
H34A	1.3061	0.4687	1.1328	0.120*
H34B	1.4162	0.5079	1.0984	0.120*
H34C	1.3657	0.4286	1.0672	0.120*
C35	1.2109(7)	0.6912(6)	1.0818(4)	0.0683(17)
H35A	1.1545	0.7559	1.0525	0.102*
H35B	1.2814	0.7103	1.0924	0.102*
H35C	1.1705	0.6691	1.1233	0.102*
C36	1.1364(4)	0.5658(3)	1.0332(2)	0.0351(8)
C37	1.0141(5)	0.5618(4)	0.7139(2)	0.0488(12)
C38	1.0378(8)	0.4709(4)	0.6732(3)	0.100(3)
C39	1.1446(10)	0.3658(8)	0.7023(5)	0.152(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H39A	1.1374	0.3446	0.7510	0.228*
H39B	1.2212	0.3815	0.6918	0.228*
H39C	1.1428	0.3049	0.6824	0.228*
C40	1.0114(9)	0.5166(7)	0.5969(2)	0.092(3)
H40A	1.0640	0.5612	0.5783	0.139*
H40B	0.9266	0.5629	0.5894	0.139*
H40C	1.0269	0.4545	0.5749	0.139*
C41	0.9391(15)	0.4147(16)	0.6965(11)	0.245(9)
H41A	0.9543	0.3492	0.6776	0.368*
H41B	0.8594	0.4673	0.6811	0.368*
H41C	0.9411	0.3920	0.7455	0.368*
C42	0.6127(15)	0.6213(11)	0.5573(7)	0.168(5)
H42A	0.5911	0.5993	0.5183	0.252*
H42B	0.5513	0.6182	0.5916	0.252*
H42C	0.6916	0.5706	0.5756	0.252*
C43	0.4938(10)	0.8280(12)	0.5341(6)	0.139(4)
H43A	0.4451	0.8268	0.4970	0.208*
H43B	0.5033	0.9016	0.5276	0.208*
H43C	0.4531	0.8114	0.5764	0.208*
C44	0.6191(6)	0.7402(6)	0.5361(3)	0.0606(14)
C45	0.6734(9)	0.7598(10)	0.4680(4)	0.108(3)
H45A	0.7582	0.7129	0.4702	0.162*
H45B	0.6690	0.8380	0.4535	0.162*
H45C	0.6285	0.7411	0.4359	0.162*
C46	0.6928(5)	0.7598(4)	0.5905(2)	0.0462(11)
C47	0.9450(4)	0.8906(4)	0.8120(2)	0.0376(9)
C48	0.9313(5)	0.9908(4)	0.8432(3)	0.0499(11)
C56	0.9875(14)	1.0700(10)	0.7953(7)	0.151(4)
H56A	0.9281	1.1180	0.7601	0.226*
H56B	1.0588	1.0268	0.7748	0.226*
H56C	1.0114	1.1158	0.8202	0.226*
C57	0.9943(12)	0.9602(10)	0.9107(5)	0.136(4)
H57A	1.0001	1.0274	0.9221	0.204*
H57B	1.0757	0.9083	0.9089	0.204*
H57C	0.9480	0.9252	0.9449	0.204*
C58	0.7993(9)	1.0473(9)	0.8492(7)	0.133(4)
H58A	0.7673	1.0033	0.8866	0.199*
H58B	0.7570	1.0546	0.8075	0.199*
H58C	0.7869	1.1212	0.8573	0.199*
N1	0.7395(4)	1.0449(3)	0.6402(2)	0.0455(9)
N2	0.9697(4)	0.9052(4)	0.6183(2)	0.0463(9)
N3	1.2300(4)	0.6123(4)	0.8145(2)	0.0468(9)
N4	1.1942(4)	0.4180(3)	0.8904(2)	0.0447(9)
O1	0.7013(4)	0.7024(4)	0.65036(19)	0.0638(11)
O2	0.7413(4)	0.8384(3)	0.57340(18)	0.0543(9)
O3	0.9712(4)	0.6635(3)	0.6843(2)	0.0575(10)
O4	1.0311(4)	0.5272(3)	0.77567(18)	0.0586(10)
O5	0.6159(3)	0.8873(3)	0.72860(18)	0.0554(9)
O6	1.0135(3)	0.7941(3)	0.8424(2)	0.0594(10)
O7	0.9124(3)	0.4801(3)	0.91644(19)	0.0526(9)
O8	1.0907(3)	0.5954(3)	0.97422(17)	0.0512(8)
O9	0.8137(3)	0.7176(3)	0.91082(17)	0.0500(8)
O10	0.8111(3)	0.7148(3)	0.80256(14)	0.0364(6)
O11	0.8905(5)	0.9084(3)	0.75734(19)	0.0648(11)
Cl1	0.35431(15)	1.01983(18)	0.71626(10)	0.0838(5)
Cl2	0.36942(16)	0.90342(14)	0.99040(9)	0.0761(5)

0.102 g), 3,5-dichlorosalicylic acid (1 mmol, 0.207 g) and 1,10-phenanthroline (0.5 mmol, 0.090 g) were mixed in water (10 mL) and heated at 433 K for 2 d in a sealed 15 mL Teflon-lined stainless steel vessel under autogenous pressure. After cooling to room temperature at a rate of $10\text{ K} \cdot \text{h}^{-1}$, colorless block crystals were isolated, washed with methanol and then dried in air, obtaining crystals in 37% yield.

Experimental details

All the non-H atoms were refined anisotropically. H atoms were subsequently treated as riding atoms with distances $C-H = 0.96\text{ (CH}_3\text{)}$ and 0.93 Å (ArH) .

Comment

In recent years, magnetocaloric effect (MCE), has received interest due to the possibility of replacing the expensive and increasingly rare helium-3 in ultralow-temperature refrigeration [5]. A molecule exhibiting a large MCE usually has a large spin ground state, negligible magnetic anisotropy, low-lying excited spin states and dominant ferromagnetic exchange [6]. In this regard, Gd^{3+} with seven unpaired 4f electrons was preferentially selected because of its intrinsic nature [7]. The case was further supported by some reported gadolinium-containing clusters [8–11]. So far, a lot of investigations of MCE of pure gadolinium-clusters have been reported, nevertheless, only a few substances have been shown to display a sufficiently large MCE to be potentially useful [5]. It is still a big challenge in discovering and synthesising gadolinium-clusters with high MCE at present. The reported title structure is part of our continuing interest in magnetic materials.

3,5-Dichlorosalicylic acid contains hydroxyl and carboxyl groups, which is suitable for selection as the ligand to transition metal coordination polymers and complexes. The CCDC database shows that no rare earth complex based on 3,5-dichlorosalicylic acid and the corresponding deprotonated 3,5-dichloro-6-hydroxybenzoate has been reported by now. Pivalate has been proved to be a good ligand for the synthesis of rare earth clusters [12–14]. Armed with the aforementioned information, we report here the synthesis and crystal structure of a new Gd_4 complex.

The complex, crystallized as $[Gd_4(C_7H_2Cl_2O_3)_2(C_5H_9O_2)_8(Phen)_4]$, belongs to the triclinic system. The structure of this complex is centrosymmetric with half of the complex forming the asymmetric unit (*cf.* the figure). Each $Gd_2(C_7H_2Cl_2O_3)(C_5H_9O_2)_4(Phen)_2$ unit is bridged by two μ_2 -type of pivalate ligands to give a Gd(1)-Gd(1A) separation of 5.366 Å . Gd(1)-Gd(2) were bridged by one 3,5-dichlorosalicylic acid and two pivalate ligands with the Gd1-Gd1' distance 4.234 Å ($' = 2-x, 1-y, 2-z$). Each Gd^{3+} ion is octa-coordinated and among the four Gd^{3+} atoms there are two kinds of coordination environments. For Gd(1) atom, the coordination sites are six

O atoms of 3,5-dichloro-2-oxidobenzoate and pivalate and ligands, two N atoms of phen. For Gd(2) the coordination environment consists of one pivalate ligand adopting a κ^2O,O coordination mode, which is different from μ_2 modes of other pivalate ligands. The four Gd^{3+} atoms are not in a straight line. The crystal packing doesn't exhibit classical hydrogen bonds.

Acknowledgements: This work was supported by Henan province key project of science and technology (No. 182102210200).

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