Instrumental Achievements

Crystal Structure of Gadolinium 3,5-Dinitrobenzoate Dihydrate

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Rare earth carboxylates may have chelating, bridging and chelating-bridging modes of coordination simultaneously or separatively.[1-5] The title compound, catena-poly[[tetraaqua-1κ^2O,2κ^2O-tetrakis(μ-3,5-dinitrobenzoato-*O*:*O*′)digadolinium]-bis(μ-3,5-dinitrobenzoato-*O*:*O*′)] dihydrate $[Gd_2(H_2O)_4(C_7H_3N_2O_6)_6]\cdot 2H_2O$, was synthesized in order to study the structure and to determine the mode of coordination around Gd.

In a mole ratio of 1:1, 3,5-dinitrobenzoic acid and $NaHCO_3$ were added into hot distilled water and stirred by a magnetic stirrer until complete dissolution. A solution containing Gd^{3+} was prepared by dissolving an appropriate quantity (1:3 mol of 3,5-dinitrobenzoic acid) of the $Gd(NO_3)_3\cdot 6H_2O$ (prepared from metallic Gd) in 10 ml of water. Within two weeks, crystals were obtained by slow evaporation of the filtered final solution. A chemical diagram of the title compound is shown in Fig. 1.

The coordination around a Gd ion is eightfold (Fig. 2). Six carboxylate O atoms [O1, O3, O5, O2^i, O4, O6;

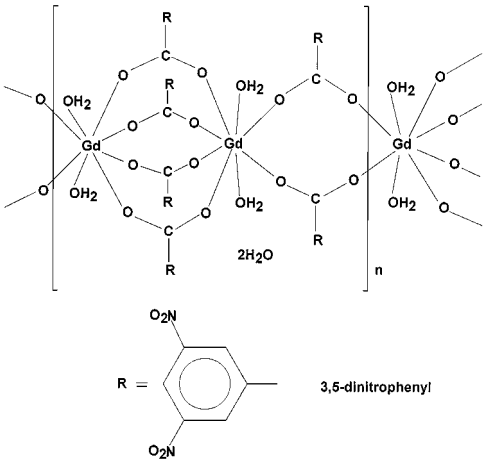

Fig. 1 Chemical diagram of the polymeric structure.

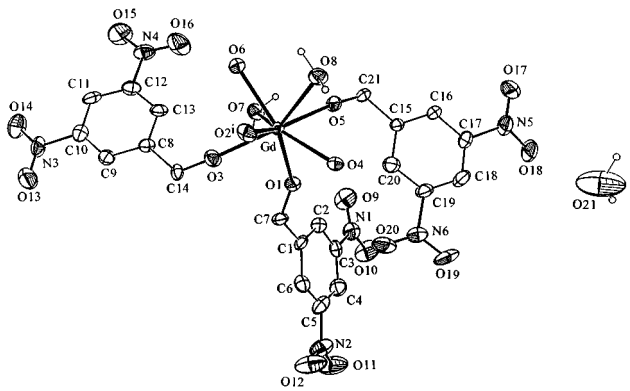

Fig. 2 ORTEP drawing of the asymmetric unit of the title compound with the atom numbering scheme. Geometrically placed H atoms have been omitted for clarity.

Table 1 Crystal and experimental data

Formula:	$[Cd_{21}(H_2O)_4(C_7H_3N_2O_6)_6]\cdot 2H_2O$
Formula weight:	1689.26
Crystal system:	triclinic
Space group:	$P\bar{1}$ Z=1
a:	9.2741(12)Å
b:	11.4833(11)Å
c:	13.7452(13)Å
α:	107.109(3)°
β:	90.499(3)°
γ:	93.824(2)°
V:	1395.3(3)Å^3
D_x:	2.010 g/cm^3
μ:	2.490 mm^{-1} (Int. Tables for X-ray Crystallography)
$2\theta_{max}$:	55.6° with Mo K_α
T:	295 K
Colorless	
F(0 0 0):	830
Crystal size:	0.35×0.12×0.10 mm
Radiation:	Mo K_α
R:	0.041
Rw:	0.040
(Δ/σ):	0.0004
$(\Delta\rho)_{max}$:	1.34 eÅ^{-3} (0.96 Å from Gd)
$(\Delta\rho)_{min}$:	–0.25 eÅ^{-3}
No. of reflections used:	4121
No. of parameters:	469
Goodness-of-fit:	1.01
Measurement:	Enraf Nonius CAD-4 diffractometer
Program system:	CAD-4 EXPRESS Software
Structure determination:	SIR(88)-MolEN
Treatment of hydrogen atoms:	The water H atoms were found from a difference map. H atoms bonded to C atoms were placed geometrically 0.95 Å from their parent atoms and a riding model was used for all H atoms.
Refinement:	full matrix least-squares (MolEN)

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Gd	0.22914(5)	0.01314(4)	0.49093(4)	1.574(7)
O1	0.1430(6)	0.0456(4)	0.6618(4)	2.3(1)
O2	-0.0929(6)	-0.0094(5)	0.6541(4)	2.4(1)
O3	0.0497(6)	-0.1460(4)	0.4671(4)	2.5(1)
O4	0.1745(6)	0.2251(4)	0.5359(4)	2.6(1)
O5	0.4329(6)	0.1088(5)	0.5883(4)	2.5(1)
O6	0.3383(6)	-0.1343(4)	0.3577(4)	2.5(1)
O7	0.3261(6)	-0.1367(4)	0.5667(4)	2.6(1)
O8	0.3784(6)	0.1298(5)	0.3923(4)	2.6(1)
O9	0.3433(7)	0.0707(6)	1.0145(5)	4.4(2)
O10	0.2247(8)	0.1675(6)	1.1429(4)	4.8(2)
O11	-0.2767(8)	0.2288(7)	1.0947(5)	5.7(2)
O12	-0.3551(7)	0.2194(6)	0.9459(5)	5.4(2)
O13	-0.2792(7)	-0.6607(5)	0.3170(5)	4.5(2)
O14	-0.1104(8)	-0.7844(5)	0.2906(5)	4.4(2)
O15	0.3868(7)	-0.6255(5)	0.3598(6)	5.8(2)
O16	0.4362(7)	-0.4326(6)	0.4238(5)	4.6(2)
O17	0.8185(7)	0.5485(6)	0.8573(5)	4.8(2)
O18	0.6703(8)	0.6452(5)	0.9690(5)	4.4(2)
O19	0.1637(8)	0.5260(6)	0.9228(6)	6.9(2)
O20	0.0880(6)	0.3574(6)	0.8134(5)	4.4(2)
O21	0.4774(9)	0.9353(9)	0.7915(6)	9.1(3)
N1	0.2387(8)	0.1232(6)	1.0517(5)	3.1(2)
N2	-0.2629(9)	0.2070(6)	1.0034(5)	3.9(2)
N3	-0.1531(8)	-0.6823(5)	0.3164(5)	2.9(2)
N4	0.3518(8)	-0.5211(6)	0.3902(5)	3.2(2)
N5	0.7001(8)	0.5619(6)	0.8950(5)	3.3(2)
N6	0.1816(8)	0.4321(6)	0.8568(6)	3.6(2)
C1	0.0158(9)	0.0788(6)	0.8145(6)	2.0(2)
C2	0.1331(9)	0.0822(7)	0.8777(6)	2.4(2)
C3	0.1161(9)	0.1252(6)	0.9826(6)	2.0(2)
C4	-0.009(1)	0.1690(7)	1.0255(6)	2.8(2)
C5	-0.124(1)	0.1650(7)	0.9606(6)	2.9(2)
C6	-0.1144(9)	0.1203(7)	0.8568(6)	2.2(2)
C7	0.0224(8)	0.0336(6)	0.7001(6)	2.0(2)
C8	0.0096(8)	-0.3628(6)	0.4164(5)	1.8(2)
C9	-0.0906(9)	-0.4606(7)	0.3831(6)	2.2(2)
C10	-0.0443(9)	-0.5765(6)	0.3496(5)	2.1(2)
C11	0.1007(9)	-0.6007(7)	0.3504(6)	2.5(2)
C12	0.1957(9)	-0.4996(7)	0.3863(6)	2.2(2)
C13	0.1544(9)	-0.3820(7)	0.4187(6)	2.1(2)
C14	-0.0417(9)	-0.2352(6)	0.4514(5)	1.7(2)
C15	0.5025(8)	0.2770(6)	0.7323(5)	1.5(2)
C16	0.6135(9)	0.3608(6)	0.7803(6)	2.1(2)
C17	0.5800(9)	0.4693(7)	0.8494(6)	2.5(2)
C18	0.443(1)	0.4954(7)	0.8748(6)	3.0(2)
C19	0.3361(9)	0.4104(7)	0.8290(6)	2.4(2)
C20	0.3601(9)	0.3010(7)	0.7567(6)	2.5(2)
C21	0.5324(8)	0.1640(6)	0.6484(6)	1.9(2)

$B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles (°)

Gd	Gd^{i}	4.2547(15)			
Gd	Gd^{ii}	5.0620(16)			
Gd	O1	2.419(5)			
Gd	O2^{i}	2.339(6)			
Gd	O3	2.334(5)			
Gd	O4	2.419(5)			
Gd	O5	2.321(6)			
Gd	O6	2.383(5)			
Gd	O7	2.469(5)			
Gd	O8	2.530(6)			
O1	C7	1.257(9)			
O2	C7	1.233(9)			
O3	C14	1.251(9)			
O4	C14	1.254(10)			
O5	C21	1.239(9)			
O6	C21	1.265(9)			
O1- Gd -O3		78.22(18)	O5- Gd- O7		73.07(19)
O1- Gd -O5		78.48(19)	O5- Gd -O8		70.90(19)
O1- Gd -O7		70.07(18)	O5- Gd -O6		100.22(19)
O1- Gd -O8		138.26(18)	O6- Gd -O7		72.90(18)
O1- Gd -O2^{i}		126.94(19)	O6- Gd -O8		73.01(18)
O1- Gd -O4		78.44(17)	O7- Gd -O8		123.97(18)
O1- Gd -O6		141.62(18)	Gd- O1 -C7		135.3(5)
O2^{i}- Gd -O3		73.34(19)	Gd^{i}- O2 -C7		141.7(5)
O2^{i}- Gd -O5		142.3(2)	Gd- O3 -C14		176.8(5)
O2^{i}- Gd -O7		137.4(2)	Gd^{ii}- O4 -C14		110.8(4)
O2^{i}- Gd -O8		72.39(19)	Gd- O5 -C21		173.5(5)
O2^{i}- Gd -O4		80.43(19)	Gd^{i}- O6 -C21		129.0(5)
O2^{i}- Gd -O6		76.68(19)	O1- C7 - O2		127.1(7)
O3- Gd -O5		144.1(2)	O1- C7 - C1		117.1(7)
O3- Gd -O7		73.51(18)	O2- C7 - C1		115.9(7)
O3- Gd -O8		141.26(19)	O3- C14- O4		123.6(7)
O3- Gd -O4		122.41(19)	O3- C14- C8		118.8(7)
O3- Gd -O6		82.03(19)	O4- C14- C8		117.6(6)
O4- Gd -O5		78.6(2)	O5- C21- O6		124.2(7)
O4- Gd -O7		140.92(18)	O5- C21-C15		119.3(7)
O4- Gd -O8		68.36(18)	O6- C21-C15		116.4(7)
O4- Gd -O6		139.48(18)			

Symmetry codes: (i) –*x*, –*y*, 1–*z*; (ii) 1–*x*, –*y*, 1–*z*

symmetry code: (i) –*x*, –*y*, 1–*z*] and two water O atoms (O7, O8) constitute the coordination sphere. In the coordination sphere the shortest bond length (2.321(6)Å] is between the central Gd ion and the carboxylate oxygen, O5; the longest Gd–O distance [2.530(6)Å] involves the water oxygen O8. The Gd–$O_{carboxylate}$ distances, ranging from 2.321(6) to 2.419(5)Å, are shorter than the Gd–O_{water} [2.469(5) and 2.530(6)Å] distances. Linear polymeric chains are formed, because the gadolinium ions are bridged alternately by two and four carboxylate groups. Within the polymeric chains, only the bridging mode of coordination is observed.

The two different Gd–Gd distances of 4.2547(15) and 5.0620(16)Å are a consequence of alternate bridging by four and two ligands, respectively. This structure is extremely similar to the polymeric chains observed in cerium 3,5-dinitrobenzoato dihydrate[6] and catena-{(tetraaqua)hexakis(3,5-dinitrobenzenato)-disamarium} monohydrate.[7] Table 1 gives the crystal and experimental data, while a final atomic parameters are given in Table 2. The bond distances and angles are given in Table 3.

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