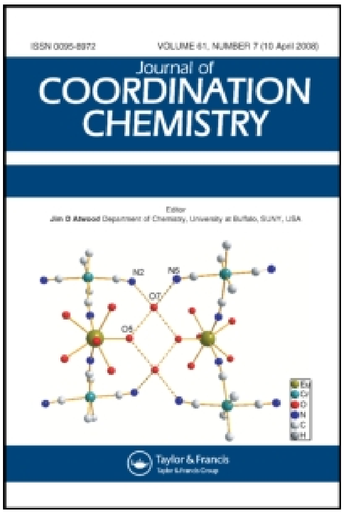

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The crystal structure of a Terbium(III) complex with 1,1-Cyclobutanedicarboxylic acid

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THE CRYSTAL STRUCTURE OF A TERBIUM(III) COMPLEX WITH 1,1-CYCLOBUTANEDICARBOXYLIC ACID

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A complex of 1,1-cyclobutanedicarboxylic acid with terbium was obtained as a pentahydrate. The salt crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 15.885(3)$, $b = 8.489(2)$, $c = 19.189(4)$ Å, $\beta = 106.02(3)^\circ$ and $Z = 4$. The structure was solved by direct methods and refined to $R = 0.0537$. The complex forms polymeric chains in which terbium(III) ions are linked by carboxylate bridges. Each terbium cation is surrounded by carboxylate oxygen atoms and two or three water oxygen atoms, giving coordination number 9. The structure is stabilized by a system of hydrogen bonds.

Keywords: Terbium(III); 1,1-Cyclobutanedicarboxylate; X-ray anaysis

INTRODUCTION

Some lanthanide complexes play an appreciable role in biology and medicine. There is increasing interest in the application of lanthanides in the investigation of the properties and function of biochemical systems and in determination of biologically active substances [1,2]. Recently, lanthanides have been used in agriculture as additives to fertilizers to promote plant growth [3]. Lanthanides react with biologically active compounds, replacing calcium (they can also replace Zn(II), Mg(II), Mn(II), Fe(II) and Fe(III)), and due to their spectroscopic properties they can serve as probes, providing information about these materials and biochemical processes occurring in them. Fluorescent rare earth complexes are used as labels in immunoassays. Eu(II) and Tb(II) are particularly important and to be used in the analysis of drugs [1,3–5]. Therapeutic applications of lanthanides have been studied. Lanthanides inhibit biological functions and are toxic to microbes and cancer cells. Moreover, they promote hydrolysis of nucleic acids, block nerve signal transmission, influence lipid peroxidation, stabilize oxyhemoglobin and induce hemolysis or stabilize and destabilize the

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cytoskeleton [3,6–9]. The reason for our interest in 1,1-cyclobutanedicarboxylic acid is its use (carboplatin) in cancer treatment [10–12].

In a systematic investigation of lanthanide complexes with 1,1-cyclobutanedicarboxylic acid [13], single crystals of a terbium(III) complex were obtained and the preliminary results presented at ICCC [14].

EXPERIMENTAL

A complex salt, terbium(III) 1,1-cyclobutanedicarboxylate pentahydrate, was made by adding a hot aqueous solution of 1,1-cyclobutanedicarboxylic acid to freshly precipitated rare earth hydroxide. During recrystallization from aqueous solution single crystals were obtained after a few weeks, filtered, washed with ethanol and dried at room temperature. Chemical analysis confirms the composition $[Tb_2(C_6H_6O_4)_3 \cdot 5H_2O]$. The crystal system, space group and approximate unit cell dimensions were determined from Weissenberg photographs. Intensities were measured on a Kuma KM-4 diffractometer using MoKα radiation. Crystallographic data and the refinement details are given in Table I. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXS-97 and refined by the full-matrix least-square methods using SHELXL-97 [15,16]. Positions of all hydrogen atoms were determined from difference Fourier maps. Several cycles of refinement of coordinates and thermal parameters (anisotropic for nonhydrogen and isotropic for hydrogen atomic) reduced the R value to 0.0537. Scattering factors were those incorporated in SHELXL97. Final atomic and selected bonding parameters are listed in Tables II and III.

TABLE I Crystal data and structure refinement details

Formula	$Tb_2(C_6H_6O_4)_3 \cdot 5H_2O$
M	834.24
Crystal system	monoclinic
Space group	$P2_1/n$
T (K)	100(1)
Wavelength (Å)	0.71073
a (Å)	15.885(3)
b (Å)	8.489(2)
c (Å)	19.189(4)
β (°)	106.02(3)
Volume (Å^3)	2487.1 (9)
Z	4
F (000)	1608
Absorption coefficient (mm^{-1})	5.722
Density (Mg/m^3)	2.228
Crystal size (mm)	$0.05 \times 0.18 \times 0.18$
Reflections measured	16 556/5846 [R(int) = 0.0399]
θ range for data collection (°)	3.75 to 28.39
Index ranges	$-19 \le h \le 20$, $-11 \le k \le 11$, $-25 \le l \le 18$
Data [$I > 2\sigma(I)$]/parameters	5477/335
Goodness-of-fit on F^2	1.244
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0537$, $wR2 = 0.1247$
R indices (all data)	$R1 = 0.0579$, $wR2 = 0.1262$
Extinction coefficient	0.00038(10)
Largest diff. peak and hole (eÅ^{-3})	4.631 and −2.181

TABLE II Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for nonhydrogen atoms with esd values in parentheses

Atom	x/a	y/b	z/c	U^*_{eq}
Tb(1)	0.35077(3)	0.22283(5)	0.20482(2)	0.00735(13)
Tb(2)	0.42334(3)	0.18293(5)	0.01393(2)	0.00726(13)
O(11)	0.2488(4)	0.4380(8)	0.1255(3)	0.0127(13)
O(12)	0.3138(4)	0.2618(7)	0.0755(3)	0.0090(12)
O(13)	0.3626(5)	0.4275(8)	−0.0359(4)	0.0140(13)
O(14)	0.3073(5)	0.6675(8)	−0.0309(4)	0.0145(14)
O(21)	0.5003(4)	0.1158(8)	0.2591(3)	0.0123(13)
O(22)	0.4512(4)	0.1198(8)	0.1409(3)	0.0105(12)
O(23)	0.5564(4)	0.0412(8)	0.0607(3)	0.0104(12)
O(24)	0.6506(4)	−0.1380(8)	0.1153(4)	0.0138(13)
O(31)	0.4400(4)	0.4426(8)	0.1934(4)	0.0125(13)
O(32)	0.4578(5)	0.7039(8)	0.1911(4)	0.0145(14)
O(33)	0.3184(4)	0.4136(8)	0.2829(3)	0.0111(13)
O(34)	0.2981(4)	0.6673(8)	0.3044(4)	0.0121(13)
OW1	0.3655(5)	0.0917(8)	0.3187(4)	0.0151(14)
OW2	0.3244(4)	−0.0589(8)	0.1702(4)	0.0133(13)
OW3	0.5220(4)	0.2743(8)	−0.0517(4)	0.0125(13)
OW4	0.5182(4)	0.3781(8)	0.0864(4)	0.0124(13)
OW5	0.3165(5)	−0.0231(8)	0.0174(4)	0.0144(14)
C(11)	0.2624(6)	0.3810(10)	0.0693(5)	0.0091(16)
C(12)	0.3037(6)	0.5206(11)	−0.0266(5)	0.0105(17)
C(13)	0.2259(6)	0.4476(11)	−0.0059(5)	0.0105(17)
C(14)	0.1730(6)	0.3170(12)	−0.0576(5)	0.0152(19)
C(15)	0.0882(7)	0.3918(14)	−0.0450(6)	0.023(2)
C(16)	0.1412(7)	0.5422(12)	−0.0170(5)	0.0169(19)
C(21)	0.5134(6)	0.0937(10)	0.1976(5)	0.0090(16)
C(22)	0.6035(6)	−0.0216(11)	0.1191(5)	0.0098(16)
C(23)	0.6037(6)	0.0471(11)	0.1929(5)	0.0108(17)
C(24)	0.6735(6)	0.1852(11)	0.2115(5)	0.0133(18)
C(25)	0.7396(6)	0.0664(12)	0.2582(5)	0.0157(19)
C(26)	0.6623(6)	−0.0457(11)	0.2577(5)	0.0092(16)
C(31)	0.4472(6)	0.5800(11)	0.2226(5)	0.0082(16)
C(32)	0.3452(6)	0.5556(11)	0.2956(4)	0.0100(17)
C(33)	0.4410(6)	0.5837(11)	0.3013(5)	0.0102(17)
C(34)	0.4879(6)	0.7235(11)	0.3479(5)	0.0147(18)
C(35)	0.5643(8)	0.6114(14)	0.3827(7)	0.031(3)
C(36)	0.5067(7)	0.4679(11)	0.3518(5)	0.0152(19)

$^*U_{\mathrm{eq}} = (1/3)\sum_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$.

RESULTS AND DISCUSSION

Crystals $Tb_2(C_6H_6O_4)_3 \cdot 5H_2O$ (Fig. 1) contain a centrosymmetric polymer, whose infinite chains run parallel to the *ac* axis. Terbium ions are coordinated by oxygen atoms of carboxylate groups and water molecules, achieving coordination number 9. Seven oxygen atoms from four 1,1-cyclobutanedicarboxylate ligands and two water oxygen coordinate Tb(1) · Tb–O$_{\mathrm{(carboxylate)}}$ distances vary in the range 2.357(6)–2.630(7) Å while Tb–O$_{\mathrm{(water)}}$ bond lengths are 2.406(7) and 2.486(7) Å. In the coordination sphere of Tb(2) there are three water oxygen atoms and six carboxylate oxygen atom of three different 1,1-cyclobutanedicarboxylate anions. Tb–O$_{\mathrm{(carboxylate)}}$ distances fall in the range 2.376(7)–2.463(7) Å, and Tb–O$_{\mathrm{(water)}}$ in the range 2.382(6)–2.451(7) Å. Each Tb(1) center is connected to two other Tb(1) and one Tb(2) ions. Carboxylate groups which bind two Tb(l) ions adopt *syn-anti* bidentate bridging modes [torsion

TABLE III Selected bondlengths (Å) and angles (°)

Tb(1)–O(33)	2.357(6)	Tb(2)–O(13)	2.376(7)
Tb(1)–O(34)^{i}	2.369(6)	Tb(2)–O(23)	2.382(6)
Tb(l)–O(31)	2.389(7)	Tb(2)–OW3	2.394(6)
Tb(1)–OW1	2.406(7)	Tb(2)–OW4	2.407(6)
Tb(1)–O(12)	2.409(6)	Tb(2)–O(22)	2.414(6)
Tb(1)–O(22)	2.428(6)	Tb(2)–OW5	2.451(7)
Tb(1)–OW2	2.486(7)	Tb(2)–O(12)	2.452(6)
Tb(1)–O(21)	2.488(7)	Tb(2)–O(23)^{ii}	2.455(6)
Tb(1)–O(11)	2.630(7)	Tb(2)–O(24)^{ii}	2.463(7)
O(11)–C(ll)	1.254(11)	O(24)–C(22)	1.254(11)
O(12)–C(11)	1.285(10)	O(24)–Tb(2)^{ii}	2.463(7)
O(13)–C(12)	1.274(11)	O(31)–C(31)	1.285(11)
O(14)–C(12)	1.253(11)	O(32)–C(31)	1.247(11)
O(2 I)–C(21)	1.267(11)	O(33)–C(32)	1.279(11)
O(22)–C(21)	1.270(11)	O(34)–C(32)	1.248(11)
O(23)–C(22)	1.280(11)	O(34)–Tb(1)^{iii}	2.369(6)
O(23)–Tb(2)^{ii}	2.455(6)		
C(11)–C(13)	1.509(12)	C(23)–C(24)	1.586(13)
C(12)–C(13)	1.530(12)	C(24)–C(25)	1.550(13)
C(I 3)–C(16)	1.530(13)	C(25)–C(26)	1.552(13)
C(13)–C(14)	1.567(13)	C(31)–C(33)	1.541(12)
C(14)–C(15)	1.567(14)	C(32)–C(33)	1.515(12)
C(I5)–C(16)	1.542(15)	C(33)–C(34)	1.547(13)
C(21)–C(23)	1.515(12)	C(33)–C(36)	1.561(13)
C(22)–C(23)	1.530(12)	C(34)–C(35)	1.541(15)
C(23)–C(26)	1.548(12)	C(35)–C(36)	1.541(15)
O(11)–C(11)–O(12)	118.7(8)	O(24)–C(22)–O(23)	119.4(8)
O(14)–C(12)–O(13)	124.0(9)	O(32)–C(31)–O(31)	124.2(8)
O(21)–C(21)–O(22)	118.9(8)	O(34)–C(32)–O(33)	124.2(9)

Symmetry code: $^{i}-x+1/2,\ y-1/2,\ -z+1/2$; $^{ii}-x+1,\ -y,\ -z$, $^{iii}-x+1/2,\ y+1/2,\ -z+1/2$.

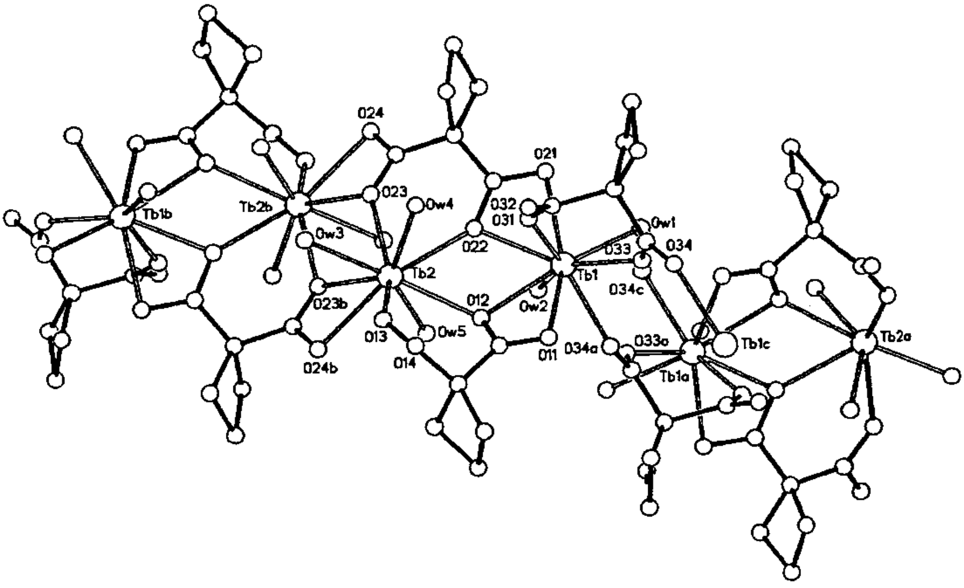

FIGURE 1 The structure of terbium(III) 1,1-cyclobutanedicarboxylate pentahydrate showing the atom numbering scheme.

angles: Tb(1)–O(33)–C(32)–C(33) −40.45°, Tb(1c)–O(34)–C(32)–C(33) 173.46°; Tb(1)–O(34a)–C(32a)–C(33a) 173.46°, Tb(1a)–O(33a)–C(32a)–C(33a) −40.45°]. This is a common carboxylate bridge in polymeric structures [17–20]. Tb(1) and Tb(2) are connected through O(12) and O(22) atoms. Two carboxylic groups (with O(23) and O(23b) atoms) create a bridge between Tb(2) and Tb(2b) ions. Distances between terbium ions are alternatively long [Tb(1)...Tb(1), 5.860 Å] and short [Tb(2)···Tb(2), 4.072 Å, Tb(1)···Tb(2), 4.146 Å].

The carboxylate groups occur as terdentate bridging–chelating, bidentate bridging and monodentate groups. As a result, the ligand acts as a terdentate [one group is bidentate bridging, the second one is monodentate], a tetradentate [one carboxylate group is terdentate bridging–chelating, the second monodentate] and a hexadentate [two groups are terdentate bridging–chelating]. The mode of coordination of the carboxylate groups influences the O–C–O angles. These angles are 124.0(9)° in monodentate groups, 124.2(9)° in bidentates and from 118.7(8)° to 119.4(8)° in terdentates in comparison to 123.5° to 123.9° in free acid structures [21].

In the crystal structure a system of hydrogen bonds occurs. Carboxylate groups of 1,1-cyclobutanedicarboxylic ligands take part in hydrogen bonds as proton acceptors and water molecules include one, two or three hydrogen bonds as proton donors. OW1 molecules act as a proton donor in the $\mathrm{O{-}H\cdots O_{carboxyl}}$ bonds and OW1 and OW3 participate in two hydrogen bonds as proton donors to carboxylic oxygen atom. The water molecules OW4 and OW5 are involved in three hydrogen bonds as proton donors to carboxylate groups and other water molecules. O(2) and O(3) at $-x+5$, $-y+1$, $-z$ also act as proton acceptors. Hydrogen bond geometry is given in Table IV.

Moreover, the chains in the crystal structure are arranged towards in such a way that the cyclobutane rings interact. C···C distances between the rings of different chains are smaller than the sum of van der Waals radii and are in the range 3.394–3.691 Å. This indicates that neighboring chains are connected via van der Waals interactions as well.

The $\mathrm{C_{carboxy}{-}C_{ring}}$ bond lengths and all other C–C distances in the rings are similar to those in 1,1-cyclobutanedicarboxylic acid [21]. The cyclobutane ring, as in the free acid, is puckered with internal rotation (torsion) angles of approximately 14°, 17.5° and 15.5° for tercoordinated, tetracoordinated and hexacoordinated ligands respectively [21,22].

TABLE IV Hydrogen bondlengths (Å) and angles (°) cyclobutanedicarboxylate

$D\cdots H\cdots A$	$D{-}H$	$H\cdots A$	$D\cdots A$	$<DH\cdots A$
OW1–H(1W1)···O(11)$^{\mathrm{i}}$	0.93	1.85	2.686(9)	148
OW2–H(IW2)···O(33)$^{\mathrm{i}}$	1.01	1.72	2.673(9)	157
OW2–H(2W2)···O(32)$^{\mathrm{iv}}$	0.91	1.98	2.870(10)	169
OW3–H(1W3)···O(32)$^{\mathrm{v}}$	0.97	1.85	2.786(9)	161
OW3–H(2W3)···O(14)$^{\mathrm{v}}$	0.83	1.99	2.781(10)	160
OW4–H(1W4)···O(13)$^{\mathrm{v}}$	0.87	2.02	2.874(9)	165
OW4–H(2W4)···O(31)	0.94	2.22	2.733(9)	114
OW4–H(2W4)···OW3$^{\mathrm{v}}$	0.94	2.36	3.053(10)	130
OW5–H(1W5)···O(14)$^{\mathrm{iv}}$	0.90	2.02	2.776(9)	142
OW5–H(2W5)···OW2	0.88	2.04	2.915(9)	173
OW5–H(2W5)···O(22)	0.88	2.55	2.979(9)	111.1

Symmetry codes: $^{\mathrm{i}}-x+1/2,\ y-1/2,\ -z+1/2$; $^{\mathrm{iv}}x,\ y-1,\ z$; $^{\mathrm{v}}-x+1,\ -y+1,\ -z$.

Supplementary Material

A list of atomic positions, thermal parameters, observed and calculated structure factors and completed tables of bond distances and angles are available from the authors on request.

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