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Crystal structure of *catena*-poly[$\{\mu_2$ -3-carboxy-2,3-bis((4-methylbenzoyl)oxy)propanoato- $\kappa^2 O:O'\}$ tris(methanol- $\kappa^1 O$)lanthanum(III)], $C_{63}H_{63}LaO_{27}$

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Abstract

$C_{63}H_{63}LaO_{27}$, trigonal, $R3$ (no. 146), $a = 27.5427(11)$ Å, $c = 7.7330(4)$ Å, $V = 5080.3(5)$ Å³, $Z = 3$, $R_{gt}(F) = 0.037$, $wR_{ref}(F^2) = 0.096$, $T = 100$ K.

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A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Synchrotron radiation (0.710 Å)
μ :	0.70 mm ⁻¹
Diffractometer, scan mode:	mar555
θ_{max} , completeness:	30.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	9418, 9418, 0.000
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 9415
$N(param)_{refined}$:	279
Programs:	Data processing [1], Bruker [2], SHELX [3, 4]

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the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents are analytically pure and used without further purification. The D-H₂DTTA (Systematic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
La1	0.666667	0.333333	−0.08427 (2)	0.01006 (8)
O1	0.71133 (13)	0.40985 (13)	0.1242 (5)	0.0173 (6)
O2	0.75601 (13)	0.50115 (13)	0.0516 (4)	0.0180 (6)
O3	0.71745 (13)	0.40974 (13)	−0.3031 (5)	0.0174 (6)
O4	0.73019 (14)	0.49588 (13)	0.7414 (4)	0.0177 (6)
H4	0.739982	0.491713	0.840649	0.026*
O5	0.79391 (12)	0.53204 (12)	0.3805 (4)	0.0149 (5)
O6	0.86356 (14)	0.52462 (15)	0.2513 (5)	0.0243 (7)
O7	0.68455 (12)	0.49212 (12)	0.4194 (4)	0.0153 (5)
O8	0.60451 (15)	0.43367 (17)	0.5607 (6)	0.0281 (8)
O9	0.77891 (12)	0.37914 (14)	−0.0984 (5)	0.0186 (6)
H9A	0.794461	0.396249	−0.193391	0.028*
C1	0.74035 (16)	0.46078 (16)	0.1547 (6)	0.0138 (7)
C2	0.75774 (16)	0.47381 (16)	0.3473 (6)	0.0130 (6)
H2	0.776879	0.452735	0.383763	0.016*
C3	0.70500 (16)	0.45470 (16)	0.4578 (6)	0.0136 (6)
H3	0.676166	0.416091	0.420511	0.016*
C4	0.71816 (16)	0.45269 (15)	0.6492 (5)	0.0129 (7)
C5	0.84698 (17)	0.55309 (17)	0.3202 (6)	0.0163 (7)
C6	0.88150 (17)	0.61460 (17)	0.3537 (6)	0.0171 (7)
C7	0.93618 (19)	0.64297 (19)	0.2884 (7)	0.0230 (9)
H7	0.949318	0.623926	0.216837	0.028*
C8	0.9712 (2)	0.69925 (19)	0.3290 (7)	0.0250 (9)
H8	1.008506	0.718208	0.285846	0.030*
C9	0.9526 (2)	0.72843 (18)	0.4319 (7)	0.0237 (9)
C10	0.8978 (2)	0.6992 (2)	0.4966 (8)	0.0289 (11)
H10	0.884736	0.718272	0.568217	0.035*
C11	0.8620 (2)	0.6427 (2)	0.4581 (8)	0.0238 (10)
H11	0.824885	0.623568	0.502381	0.029*
C12	0.9909 (2)	0.7903 (2)	0.4693 (9)	0.0344 (12)
H12A	0.978898	0.812356	0.400511	0.052*
H12B	1.029500	0.801064	0.438960	0.052*
H12C	0.988853	0.797431	0.592500	0.052*
C13	0.63190 (18)	0.4757 (2)	0.4750 (6)	0.0196 (8)
C14	0.6127 (2)	0.5142 (2)	0.4117 (7)	0.0257 (9)
C15	0.6493 (2)	0.5645 (2)	0.3285 (8)	0.0300 (11)
H15	0.687625	0.575245	0.314185	0.036*
C16	0.6295 (3)	0.5990 (3)	0.2666 (10)	0.0393 (14)
H16	0.654810	0.633295	0.211321	0.047*
C17	0.5736 (3)	0.5841 (3)	0.2844 (10)	0.0436 (16)
C18	0.5380 (3)	0.5346 (4)	0.3688 (13)	0.054 (2)
H18	0.499884	0.524632	0.385021	0.064*
C19	0.5562 (3)	0.4989 (3)	0.4307 (10)	0.0449 (17)
H19	0.530552	0.464553	0.485253	0.054*
C20	0.5524 (4)	0.6213 (4)	0.2119 (14)	0.064 (3)
H20A	0.583977	0.659361	0.195870	0.095*
H20B	0.525386	0.622131	0.292657	0.095*
H20C	0.534045	0.606340	0.100358	0.095*
C21	0.8222 (2)	0.3919 (2)	0.0253 (8)	0.0293 (11)
H21A	0.833783	0.428471	0.078056	0.044*
H21B	0.854460	0.393081	−0.032546	0.044*
H21C	0.808206	0.362994	0.115298	0.044*

name: 2,3-bis((4-methylbenzoyl)oxy)succinic acid; 69.5 mg, 0.18 mmol) was dissolved in 2.5 mL methanol, and added to a 25 mL round bottom flask. An aqueous solution (2.50 mL) of $La(NO_3)_3 \cdot 6H_2O$ (51.9 mg, 0.12 mmol) was added slowly to the solution. Then a KOH solution (0.2 mol/L) was carefully added to the mixture and adjust the pH value of the solution to about 6.5. After stirring for 7 h at room temperature, the filtrate was kept undisturbed for seven days. Colorless block crystals were obtained in a yield of 26%, based on D- H_2DTTA .

Experimental details

Single crystal X-ray diffraction data of the complex were collected on beam line 3W1A of the Beijing Synchrotron Radiation Facility (BSRF), using A MARCCD-165 detector ($\lambda = 0.71000 \text{ \AA}$) at a working voltage of 2.5 GeV, and the single crystals with regular shape, suitable size, and bright without cracks were selected under the polarization stereoscopic microscope. Data were collected by the MARCCD diffractometer and processed using HKL 2000 [1]. Multi-scan program SADABS was used for absorption correction [2]. The structures was solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXS-97 [3] and SHELXL-2014/7 [4]. Coordinates of hydrogen atoms were refined without any constraints or restraints. Their U_{iso} values were set to $1.2U_{eq}$ of the parent atoms.

Comment

In the past few decades, the design and application of lanthanide coordination polymers (Ln-CPs) have attracted extensive attention [5], not only the diversity of their structures, but also their wide applications in catalysis, magnetism and fluorescence detection [6]. More importantly, Ln(III) ions often endow the CPs with unique luminescent properties (characteristic sharp emission, high color purity, and long excited-state luminescence lifetimes) as a result of transitions within the partially-filled 4f shells of the trivalent Ln(III) ions [7]. Compared with other metal ions, Ln(III) ions have the characteristics of variable high coordination number, strong spin orbit coupling, and large magnetic moment, and have important functions such as magnetic, fluorescence sensing, nuclear magnetic resonance imaging [8], so Ln-CPs are the potential material for environmental or biomedical applications [9]. However, Ln-CPs are sensitive to temperature, pH, and

pressure during synthetic process, which makes it difficult to grow crystals [10].

Rational selection of ligands is considered to be a very suitable method for the synthesis of structurally diverse Ln-CPs [11]. Tartaric acid, which is relatively inexpensive and readily available, plays an important role in many areas of chemistry [12]. D-H₂DTTA ((+)-di-*p*-toluoyl-d-tartaric acid) is a flexible dicarboxylic acid with two equal chiral carbon atoms. Abundant carboxyl groups can provide variable coordination modes, which contribute to the construction of metal-organic complexes. In recent years, many Ln-CPs based on D-H₂DTTA have been reported. Zhang Yuxiao et al. reported two novel isostructural Ln-CPs [Ln(DTTA)(DMF)₃NO₃] (Ln = Eu, Tb) [13]. Our group synthesized a series of Ln-CPs, [Ln(HDTTA)₃(CH₃OH)₃]_n (Ln = Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho), and studied their optical and magnetic properties [14–17].

X-ray single crystal diffraction results show that the title complex belongs to the trigonal crystal system with the space group *R*3̄. The asymmetric unit consists of one third of a La³⁺, a HDTTA[−] ion and a coordinated methanol molecule. La³⁺ is a nine-coordinated cation, and the coordinated atoms are respectively from six carboxyl oxygen atoms of HDTTA[−] and three oxygen atoms of methanol molecules, presenting the coordination pattern of three-capped triangular prism. The bond length of La–O ranges from 2.441(3) to 2.694(3) Å, and the bond angle of O–La–O ranges from 81.15(12) to 132.64(10)°. The complex forms an infinite one-dimensional chain structure along the *c*-axis by bridging La³⁺ with carboxyl groups at both ends of the ligand.

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