Crystal structure of catena-{ethanol[μ -(3-methylbenzoato-*O,O'*)]bis[μ -(3-methylbenzoato-*O,O':O'*)]lanthanum(III)}, $\text{La}(\text{C}_2\text{H}_5\text{OH})(\text{C}_8\text{H}_7\text{O}_2)_3$

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Abstract

$\text{C}_{26}\text{H}_{27}\text{LaO}_7$, triclinic, $P\bar{1}$ (no. 2), $a = 8.162(3)$ Å, $b = 12.698(5)$ Å, $c = 12.832(5)$ Å, $\alpha = 77.197(6)^\circ$, $\beta = 86.326(5)^\circ$, $\gamma = 82.844(6)^\circ$, $V = 1285.8$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.091$, $T = 293$ K.

Source of material

1.5 mmol 3-Methylbenzoic acid was dissolved in appropriate amounts of ethanol and its pH was controlled in a range of 5–6 with 2 M NaOH solution. Then an ethanolic solution of LaCl_3 (0.5 mmol) was dropped. The mixture was heated under reflux with stirring for 2 h. Single crystals were obtained from the mother liquor after 4 days at room temperature.

Discussion

To our knowledge, lanthanide carboxylate complexes display a variety of structural types, such as mono-nuclear molecular, bi-nuclear units and coordination polymers. Different carboxylic acid ligands or lanthanide ion possibly affect the structures of their complexes. The molecular structure of the title complex (I) is different from complexes of the lanthanide 3-methylbenzoates $\text{Nd}(\text{C}_8\text{H}_7\text{O}_2)_3$ (II) and $\text{Tb}(\text{C}_8\text{H}_7\text{O}_2)_3$ (III) [1]. These three complexes all show infinite chain structures. Generally, complexes of lanthanide with monoacids are coordination polymers, such as $[\text{Nd}(\text{CH}_3\text{OC}_6\text{H}_4\text{COO})_3] \cdot 4\text{H}_2\text{O}$ [2] and $[\text{Eu}(\text{DMOBA})_3]_n$ (DMOBA = 2,3-dimethoxybenzoate) [3]. In complex II, the Nd^{3+} ions are linked together by three 3-methylbenzoato groups in chelating-bridging. In complex III, the Tb^{3+} ions are linked by two 3-methylbenzoato groups in chelating-bridging and one 3-methylbenzoato group in bridging mode. In the title complex, La^{3+} and

La^{3+} ions are linked by two 3-methylbenzoato units in chelating-bridging and two 3-methylbenzoato units in bridging, La^{3+} and La^{3+} ions are linked by two 3-methylbenzoato in chelating-bridging. These trimeric units are linked with each other and form infinite one-dimensional polymer chains.

The distances between two La^{3+} ions are 4.086 Å and 4.272 Å, respectively. The angle $\text{La}1\text{a} - \text{La}1 - \text{La}1\text{c}$ is 155.1° . Each La^{3+} ion is surrounded by eight O atoms from six 3-methylbenzoato and one O atom from ethanol molecule. Carboxyl group $\text{O}5 - \text{C}17 - \text{O}6$ is in a bridging mode, in which two O atoms link La^{3+} ions. Carboxyl groups $\text{O}3 - \text{C}9 - \text{O}4$ and $\text{O}1 - \text{C}1 - \text{O}2$ are in a bridging-chelating mode, in which two O atoms chelate one La^{3+} ion and one of them links another La^{3+} ion simultaneously. The distances of $\text{La} - \text{O}_{\text{carboxyl}}$ are in the range of 2.452(3) Å to 2.748(3) Å, with an average distance 2.559 Å, the longest is between La^{3+} and $\text{O}3\text{a}$ in the tridentate bridge. The distance of La^{3+} and $\text{O}7$ atom of ethanol is 2.639(4) Å. The hydrogen bonds form between ethanol and carboxyl $\text{O}4$ atom, with $d(\text{O}7 \cdots \text{O}4) = 2.851$ Å, $\angle \text{O} - \text{H} \cdots \text{O} = 153.4^\circ$. Comparing title complex with complexes II and III, the distance of metal and carboxyl oxygen atom $d(\text{La} - \text{O}) > d(\text{Nd} - \text{O}) = 2.512$ Å $>$ $d(\text{Tb} - \text{O}) = 2.424$ Å, the coordination number of central metal for complex I and II is nine, the Tb coordination number for complex III is eight. Being due to the decrease of radii of Ln^{3+} ions, $\text{La}^{3+} > \text{Nd}^{3+} > \text{Tb}^{3+}$, the distances of $\text{Ln} - \text{O}_{\text{carboxyl}}$ and coordination number of lanthanide ions decrease from La to Tb. The ethanol carbon atoms and one methyl group are disordered. They were split over two positions each with different occupancies.

Table 1. Data collection and handling.

Crystal:	white prism, size $0.12 \times 0.20 \times 0.24$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	17.02 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6705, 4511
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3782
$N(\text{param})_{\text{refined}}$:	334
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3A)	2i		0.2743	0.2017	0.6781	0.062
H(4A)	2i		0.1104	0.3505	0.7207	0.078
H(5A)	2i		0.1010	0.5173	0.6048	0.081
H(7A)	2i		0.4394	0.3968	0.4127	0.057
H(8A)	2i		0.1839	0.6360	0.4448	0.118

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(8B)	2i		0.2278	0.5769	0.3499	0.118
H(8C)	2i		0.3692	0.6084	0.4103	0.118
H(11A)	2i		1.2884	0.3226	0.2514	0.073
H(12A)	2i		1.2073	0.4836	0.1325	0.098
H(13A)	2i		0.9329	0.5323	0.0951	0.089
H(15A)	2i		0.8146	0.2661	0.3002	0.060
H(16A)	2i		0.6523	0.5077	0.1208	0.149
H(16B)	2i		0.6048	0.4468	0.2370	0.149
H(16C)	2i		0.6211	0.3852	0.1430	0.149
H(19A)	2i		0.6569	0.1937	0.7418	0.079
H(20)	2i	0.55	0.5981	0.2855	0.8783	0.110
H(21A)	2i		0.7871	0.2763	1.0042	0.124
H(22)	2i	0.45	1.0445	0.1833	0.9924	0.101
H(23A)	2i		1.1083	0.0936	0.8533	0.079
H(24A)	2i	0.75	1.0436	0.2216	1.0761	0.178
H(24B)	2i	0.75	1.1881	0.2095	0.9915	0.178

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(24C)	2i	0.75	1.1180	0.1058	1.0609	0.178
H(24D)	2i	0.25	0.5423	0.3430	0.9502	0.173
H(24E)	2i	0.25	0.4515	0.2647	0.9011	0.173
H(24F)	2i	0.25	0.5164	0.3678	0.8268	0.173
H(7C)	2i	0.55	0.4981	0.1379	0.3066	0.071
H(7B)	2i	0.45	0.5460	0.1708	0.2833	0.071
H(25A)	2i	0.55	0.5267	-0.0210	0.2439	0.089
H(25B)	2i	0.55	0.6780	0.0282	0.1779	0.089
H(26A)	2i	0.55	0.4482	0.0666	0.0725	0.185
H(26B)	2i	0.55	0.5009	0.1758	0.0900	0.185
H(26C)	2i	0.55	0.3496	0.1261	0.1558	0.185
H(25C)	2i	0.45	0.7278	0.0880	0.1610	0.106
H(25D)	2i	0.45	0.5807	0.1823	0.1386	0.106
H(26D)	2i	0.45	0.5113	0.0268	0.0854	0.233
H(26E)	2i	0.45	0.3898	0.0534	0.1781	0.233
H(26F)	2i	0.45	0.5348	-0.0407	0.2026	0.233

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
La(1)	2i		0.75451(3)	0.02341(2)	0.46801(2)	0.0280(2)	0.0348(2)	0.0421(2)	-0.0054(1)	0.0040(1)	-0.0109(1)
O(1)	2i		0.6138(4)	0.2142(3)	0.4537(3)	0.042(2)	0.040(2)	0.075(2)	-0.003(2)	0.019(2)	-0.012(2)
O(2)	2i		0.4627(3)	0.0951(2)	0.5527(3)	0.031(2)	0.033(2)	0.056(2)	-0.005(1)	-0.001(1)	-0.015(1)
O(3)	2i		1.0036(4)	0.1244(2)	0.4263(3)	0.035(2)	0.035(2)	0.055(2)	-0.009(1)	0.009(2)	-0.006(1)
O(4)	2i		1.2624(4)	0.1422(3)	0.3757(3)	0.035(2)	0.059(2)	0.053(2)	-0.013(2)	0.000(2)	-0.003(2)
O(5)	2i		0.8196(4)	0.0783(3)	0.6310(3)	0.042(2)	0.068(2)	0.055(2)	-0.004(2)	0.002(2)	-0.030(2)
O(6)	2i		1.0836(4)	0.0486(3)	0.6737(3)	0.038(2)	0.071(2)	0.057(2)	-0.006(2)	0.006(2)	-0.032(2)
C(1)	2i		0.4890(5)	0.1942(4)	0.5136(4)	0.034(3)	0.038(3)	0.054(3)	-0.005(2)	-0.005(2)	-0.013(2)
C(2)	2i		0.3749(5)	0.2847(4)	0.5415(4)	0.031(2)	0.034(2)	0.056(3)	-0.002(2)	-0.003(2)	-0.018(2)
C(3)	2i		0.2747(6)	0.2701(4)	0.6332(4)	0.048(3)	0.048(3)	0.059(3)	0.000(2)	0.003(3)	-0.017(2)
C(4)	2i		0.1748(7)	0.3587(5)	0.6576(5)	0.060(4)	0.066(4)	0.071(4)	0.008(3)	0.008(3)	-0.031(3)
C(5)	2i		0.1708(8)	0.4592(5)	0.5882(6)	0.060(4)	0.051(4)	0.097(5)	0.016(3)	-0.011(4)	-0.038(3)
C(6)	2i		0.2667(6)	0.4755(4)	0.4957(5)	0.046(3)	0.038(3)	0.083(4)	0.002(2)	-0.018(3)	-0.018(3)
C(7)	2i		0.3707(6)	0.3873(4)	0.4740(4)	0.038(3)	0.042(3)	0.065(3)	-0.006(2)	-0.004(2)	-0.016(2)
C(8)	2i		0.2614(8)	0.5841(5)	0.4181(6)	0.068(4)	0.039(3)	0.125(6)	0.000(3)	-0.032(4)	-0.008(3)
C(9)	2i		1.1110(6)	0.1753(4)	0.3666(4)	0.043(3)	0.038(3)	0.040(2)	-0.011(2)	0.004(2)	-0.016(2)
C(10)	2i		1.0593(6)	0.2778(4)	0.2876(4)	0.052(3)	0.038(3)	0.038(2)	-0.008(2)	0.001(2)	-0.010(2)
C(11)	2i		1.1772(7)	0.3431(5)	0.2373(4)	0.061(3)	0.061(4)	0.057(3)	-0.025(3)	0.005(3)	0.003(3)
C(12)	2i		1.129(1)	0.4389(5)	0.1660(5)	0.109(6)	0.061(4)	0.066(4)	-0.036(4)	0.016(4)	0.012(3)
C(13)	2i		0.9639(9)	0.4683(5)	0.1442(5)	0.107(5)	0.054(4)	0.051(3)	0.003(4)	0.001(4)	0.002(3)
C(14)	2i		0.8454(8)	0.4054(5)	0.1934(4)	0.076(4)	0.059(4)	0.052(3)	0.012(3)	0.002(3)	-0.007(3)
C(15)	2i		0.8940(6)	0.3096(4)	0.2658(4)	0.056(3)	0.045(3)	0.046(3)	-0.002(3)	0.008(2)	-0.007(2)
C(16)	2i		0.6643(9)	0.4394(6)	0.1716(6)	0.088(5)	0.101(6)	0.091(5)	0.029(5)	-0.012(4)	0.002(4)
C(17)	2i		0.9343(6)	0.0837(4)	0.6884(4)	0.043(3)	0.043(3)	0.044(3)	-0.008(2)	0.005(2)	-0.015(2)
C(18)	2i		0.8918(6)	0.1361(4)	0.7818(4)	0.057(3)	0.047(3)	0.044(3)	-0.012(3)	0.010(2)	-0.016(2)
C(19)	2i		0.7365(8)	0.1922(5)	0.7910(5)	0.070(4)	0.067(4)	0.061(4)	-0.006(3)	0.018(3)	-0.024(3)
C(20)	2i		0.701(1)	0.2457(6)	0.8735(6)	0.115(6)	0.084(5)	0.077(5)	0.003(5)	0.027(5)	-0.038(4)
C(21)	2i		0.814(1)	0.2410(6)	0.9480(6)	0.157(8)	0.092(6)	0.070(5)	-0.017(6)	0.039(5)	-0.047(4)
C(22)	2i		0.967(1)	0.1856(6)	0.9417(5)	0.115(6)	0.097(5)	0.053(4)	-0.026(5)	0.009(4)	-0.037(4)
C(23)	2i		1.0046(8)	0.1324(5)	0.8579(4)	0.069(4)	0.077(4)	0.056(3)	-0.012(3)	0.007(3)	-0.028(3)
C(24)	2i	0.75	1.090(1)	0.180(1)	1.0250(8)	0.15(1)	0.16(1)	0.072(7)	-0.033(9)	-0.022(7)	-0.064(7)
C(24')	2i	0.25	0.538(2)	0.311(2)	0.889(3)	0.18(4)	0.08(2)	0.09(2)	0.00(2)	0.00(2)	-0.03(2)
O(7)	2i		0.5915(4)	0.1057(3)	0.2918(3)	0.053(2)	0.065(2)	0.056(2)	-0.003(2)	-0.003(2)	-0.009(2)
C(25)	2i	0.55	0.571(2)	0.047(1)	0.2105(9)	0.09(1)	0.070(9)	0.065(9)	0.010(8)	-0.015(8)	-0.025(7)
C(26)	2i	0.55	0.457(3)	0.110(2)	0.124(1)	0.20(2)	0.13(2)	0.045(8)	-0.01(2)	-0.04(1)	-0.011(9)
C(25')	2i	0.45	0.613(2)	0.110(2)	0.1797(8)	0.10(1)	0.10(2)	0.06(1)	0.00(1)	-0.002(9)	-0.001(9)
C(26')	2i	0.45	0.502(4)	0.030(2)	0.160(2)	0.22(3)	0.17(3)	0.11(2)	-0.06(3)	-0.02(2)	-0.07(2)

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