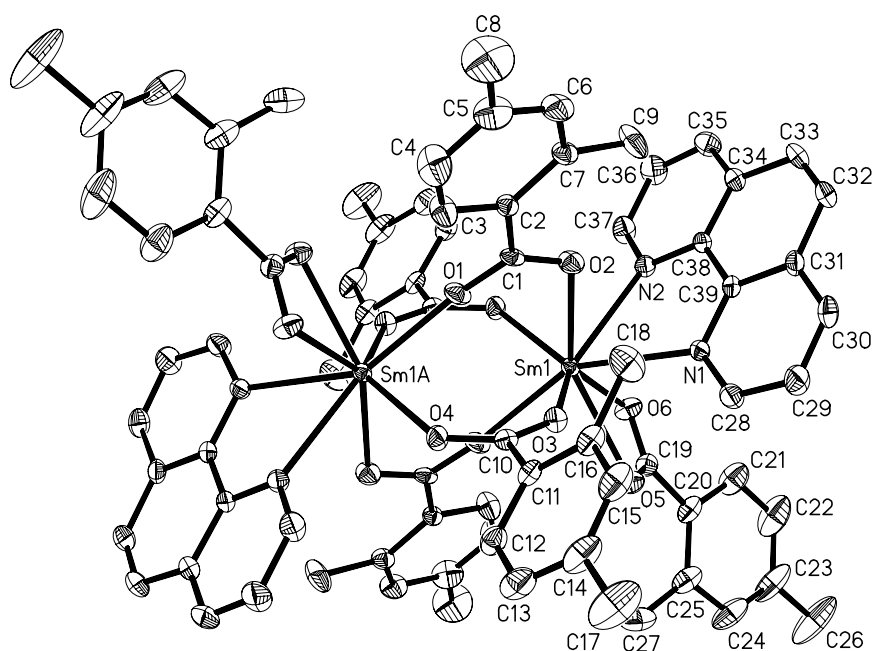


# Crystal structure of bis(1,10-phenanthroline-*N,N'*)bis(2,4-dimethylbenzoato-*O,O'*)tetrakis( $\mu$ -2,4-dimethylbenzoato-*O,O'*)disamarium(III), $\text{Sm}_2(\text{C}_9\text{H}_9\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2$

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## Abstract

$\text{C}_{78}\text{H}_{70}\text{N}_4\text{O}_{12}\text{Sm}_2$ , monoclinic,  $C12/c1$  (no. 15),  
 $a = 27.523(3)$  Å,  $b = 15.699(2)$  Å,  $c = 16.048(2)$  Å,  
 $\beta = 101.123(2)^\circ$ ,  $V = 6803.7$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.026$ ,  
 $wR_{\text{ref}}(F^2) = 0.063$ ,  $T = 294$  K.

## Source of material

0.5 mmol 2,4-dimethylbenzoic acid and 0.35 mmol 1,10-phenanthroline were dissolved in 7 ml distilled water. The pH value was adjusted to about 6-7 with 2 M NaOH solution. Then 0.35 mmol  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  dissolved in 3 ml distilled water were added. The mixture was placed in a Teflon-lined stainless vessel (25 ml). The vessel was sealed and heated at 160 °C for 24 h under autogenous pressure and then cooled down to room temperature. After being filtered, the product was washed with ethanol and then dried under ambient. Column-like crystal was collected.

## Discussion

Like other lanthanide carboxylate complexes containing 1,10-phenanthroline (phen) or 2,2'-bipyridine, the title complex is also a dimer with an inversion center. The two central Sm(III) ions are bridged by four carboxylate groups with Sm...Sm distance of 4.120 Å. In addition, each Sm(III) ion is chelated by one carboxylate group and one phen molecule. The coordination number

of Sm(III) ion is eight, including six O atoms from carboxylate groups and two N atoms from phen ligand. They adopt a distorted square antiprism, the four apical positions of the upper square are occupied by O1A, O2, O3, and O4A, and those of the lower square by O5, O6, N1, and N2 with mean deviations of 0.056 Å and 0.209 Å between the two squares, respectively. The dihedral angle between the two squares is 7.4°.

The title molecule structure is similar to that of  $\text{Eu}_2(3,4\text{-dimethylbenzoate})_6(\text{phen})_2$  [1]. However, it is different from terbium 2-methylbenzoate complex with phen,  $[\text{Tb}(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ , in which two crystallographically different binuclear molecules exist [2]. It is also unlike dysprosium 4-methylbenzoate complex with phen,  $[\text{Dy}(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ , which contains two different binuclear molecules having two different coordination modes of 4-methylbenzoate groups [3]. Carboxylate groups of 2,4-dimethylbenzoic acid adopt bidentate bridging and bidentate chelating modes. The distances between Sm and O atoms from bridged carboxylate groups range from 2.353(2) Å to 2.428(2) Å with an average distance of 2.389 Å. The distances between Sm and O atoms from chelated carboxylate groups are 2.427(2) Å and 2.513(2) Å, respectively, with an average distance of 2.4705 Å. The Sm—N bond lengths are 2.616(2) Å and 2.639(2) Å, respectively and the N—Sm—N angle is 62.23(7)°.

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**Table 1.** Data collection and handling.

Crystal:	yellow prism, size 0.10 × 0.16 × 0.20 mm
Wavelength:	Mo K <sub>α</sub> radiation (0.71073 Å)
μ:	17.76 cm <sup>-1</sup>
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
2θ <sub>max</sub> :	52.8°
N(hkl) <sub>measured</sub> , N(hkl) <sub>unique</sub> :	18960, 6951
Criterion for I <sub>obs</sub> , N(hkl) <sub>gt</sub> :	I <sub>obs</sub> > 2 σ(I <sub>obs</sub> ), 5489
N(param) <sub>refined</sub> :	439
Programs:	SHELXS-97 [4], SHELXL-97 [5]

**Table 2.** Continued.

Atom	Site	x	y	z	U <sub>iso</sub>
H(13)	8f	0.0959	0.5827	0.2693	0.066
H(15)	8f	0.0789	0.8342	0.2694	0.065
H(17A)	8f	0.0677	0.7127	0.4017	0.137
H(17B)	8f	0.0371	0.6424	0.3451	0.137
H(17C)	8f	0.0220	0.7384	0.3319	0.137
H(18A)	8f	0.1106	0.8945	0.1089	0.091
H(18B)	8f	0.1665	0.8910	0.1534	0.091
H(18C)	8f	0.1269	0.9269	0.2025	0.091
H(21)	8f	0.4412	0.9268	0.2618	0.075
H(22)	8f	0.5070	0.9321	0.3758	0.103
H(24)	8f	0.4649	0.7115	0.4595	0.081
H(26A)	8f	0.5402	0.7716	0.5325	0.190
H(26B)	8f	0.5332	0.8702	0.5401	0.190
H(26C)	8f	0.5669	0.8342	0.4798	0.190
H(27A)	8f	0.4004	0.6306	0.3867	0.099
H(27B)	8f	0.3832	0.6479	0.2892	0.099
H(27C)	8f	0.3543	0.6887	0.3543	0.099
H(28)	8f	0.2574	0.8910	0.2716	0.050
H(29)	8f	0.2249	0.9968	0.3443	0.059
H(30)	8f	0.2206	1.1342	0.2933	0.052
H(32)	8f	0.2426	1.2390	0.1873	0.051
H(33)	8f	0.2825	1.2680	0.0818	0.056
H(35)	8f	0.3337	1.2150	-0.0260	0.061
H(36)	8f	0.3705	1.1026	-0.0820	0.065
H(37)	8f	0.3606	0.9662	-0.0344	0.051

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	U <sub>iso</sub>
H(3)	8f	0.1093	0.8077	-0.1113	0.057
H(4)	8f	0.0289	0.8541	-0.1514	0.077
H(6)	8f	0.0715	1.0882	-0.0764	0.056
H(8A)	8f	-0.0289	0.9779	-0.1875	0.148
H(8B)	8f	-0.0122	1.0670	-0.1481	0.148
H(8C)	8f	-0.0281	0.9952	-0.0910	0.148
H(9A)	8f	0.1502	1.1286	-0.0301	0.087
H(9B)	8f	0.1930	1.0718	-0.0516	0.087
H(9C)	8f	0.1773	1.0631	0.0369	0.087
H(12)	8f	0.1476	0.5966	0.1722	0.047

**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Sm(1)	8f	0.290196(5)	0.838931(9)	0.079137(9)	0.02348(8)	0.01991(8)	0.02316(8)	0.00161(6)	0.00703(6)	-0.00008(6)
O(1)	8f	0.19946(8)	0.8079(1)	-0.0589(1)	0.050(1)	0.026(1)	0.041(1)	0.013(1)	0.019(1)	0.005(1)
O(2)	8f	0.22290(8)	0.9279(1)	0.0071(1)	0.030(1)	0.033(1)	0.045(1)	0.004(1)	-0.000(1)	0.004(1)
O(3)	8f	0.21936(7)	0.7834(1)	0.1283(1)	0.026(1)	0.034(1)	0.034(1)	-0.0021(9)	0.0109(9)	-0.0033(9)
O(4)	8f	0.18245(8)	0.6741(1)	0.0518(1)	0.045(1)	0.031(1)	0.029(1)	-0.005(1)	0.016(1)	-0.0049(9)
O(5)	8f	0.32773(8)	0.7898(1)	0.2265(1)	0.028(1)	0.044(1)	0.036(1)	-0.000(1)	0.004(1)	0.007(1)
O(6)	8f	0.37605(8)	0.8523(1)	0.1503(1)	0.033(1)	0.054(2)	0.033(1)	-0.002(1)	0.005(1)	0.010(1)
N(1)	8f	0.27567(9)	0.9609(2)	0.1827(2)	0.042(2)	0.024(1)	0.025(1)	-0.000(1)	0.011(1)	-0.001(1)
N(2)	8f	0.32039(9)	0.9935(2)	0.0493(2)	0.032(1)	0.029(1)	0.028(1)	-0.004(1)	0.010(1)	-0.001(1)
C(1)	8f	0.1906(1)	0.8835(2)	-0.0387(2)	0.036(2)	0.023(2)	0.028(2)	0.006(1)	0.016(1)	0.009(1)
C(2)	8f	0.1397(1)	0.9199(2)	-0.0684(2)	0.027(2)	0.026(2)	0.029(2)	0.002(1)	0.006(1)	0.000(1)
C(3)	8f	0.1019(1)	0.8646(2)	-0.1036(2)	0.039(2)	0.039(2)	0.063(2)	-0.001(2)	0.006(2)	-0.009(2)
C(4)	8f	0.0535(1)	0.8923(3)	-0.1273(3)	0.030(2)	0.070(3)	0.089(3)	-0.011(2)	0.003(2)	-0.014(3)
C(5)	8f	0.0415(1)	0.9756(3)	-0.1157(3)	0.031(2)	0.072(3)	0.069(3)	0.012(2)	0.007(2)	0.008(2)
C(6)	8f	0.0794(1)	1.0313(2)	-0.0827(2)	0.039(2)	0.045(2)	0.054(2)	0.019(2)	0.008(2)	0.004(2)
C(7)	8f	0.1285(1)	1.0063(2)	-0.0584(2)	0.033(2)	0.031(2)	0.037(2)	0.008(1)	0.007(1)	0.003(1)
C(8)	8f	-0.0118(2)	1.0068(4)	-0.1376(4)	0.036(2)	0.120(5)	0.135(5)	0.027(3)	0.003(3)	0.004(4)
C(9)	8f	0.1656(1)	1.0735(2)	-0.0226(3)	0.052(2)	0.028(2)	0.091(3)	0.008(2)	0.006(2)	-0.013(2)
C(10)	8f	0.1856(1)	0.7286(2)	0.1108(2)	0.025(2)	0.029(2)	0.027(2)	0.005(1)	0.008(1)	0.003(1)
C(11)	8f	0.1473(1)	0.7244(2)	0.1663(2)	0.026(2)	0.044(2)	0.022(2)	-0.004(1)	0.004(1)	-0.002(1)
C(12)	8f	0.1348(1)	0.6452(2)	0.1932(2)	0.038(2)	0.050(2)	0.031(2)	-0.010(2)	0.010(2)	-0.003(2)
C(13)	8f	0.1033(1)	0.6365(3)	0.2510(2)	0.047(2)	0.076(3)	0.042(2)	-0.022(2)	0.011(2)	0.009(2)
C(14)	8f	0.0830(1)	0.7087(3)	0.2813(2)	0.034(2)	0.102(4)	0.037(2)	-0.002(2)	0.016(2)	0.002(2)
C(15)	8f	0.0937(1)	0.7863(3)	0.2510(2)	0.039(2)	0.086(3)	0.040(2)	0.013(2)	0.015(2)	-0.009(2)
C(16)	8f	0.1255(1)	0.7979(2)	0.1941(2)	0.028(2)	0.055(2)	0.032(2)	0.005(2)	0.007(1)	-0.004(2)
C(17)	8f	0.0493(2)	0.6997(4)	0.3460(3)	0.063(3)	0.165(5)	0.059(3)	0.001(3)	0.044(2)	0.009(3)
C(18)	8f	0.1330(1)	0.8854(3)	0.1618(3)	0.054(3)	0.052(3)	0.082(3)	0.015(2)	0.027(2)	-0.005(2)
C(19)	8f	0.3693(1)	0.8180(2)	0.2191(2)	0.029(2)	0.035(2)	0.032(2)	0.005(1)	0.003(1)	-0.002(1)
C(20)	8f	0.4125(1)	0.8153(2)	0.2924(2)	0.028(2)	0.062(2)	0.029(2)	0.005(2)	0.006(1)	-0.004(2)
C(21)	8f	0.4456(1)	0.8831(3)	0.3017(2)	0.045(2)	0.092(3)	0.048(2)	-0.017(2)	0.005(2)	-0.003(2)
C(22)	8f	0.4853(2)	0.8861(4)	0.3700(3)	0.048(3)	0.147(5)	0.061(3)	-0.038(3)	0.004(2)	-0.020(3)
C(23)	8f	0.4927(2)	0.8214(4)	0.4293(3)	0.036(2)	0.169(6)	0.034(2)	0.003(3)	0.004(2)	-0.002(3)
C(24)	8f	0.4600(2)	0.7549(3)	0.4194(2)	0.040(2)	0.126(4)	0.037(2)	0.023(3)	0.005(2)	0.011(2)
C(25)	8f	0.4195(1)	0.7488(3)	0.3521(2)	0.038(2)	0.077(3)	0.034(2)	0.019(2)	0.010(2)	0.006(2)
C(26)	8f	0.5374(2)	0.8246(5)	0.5022(3)	0.048(3)	0.28(1)	0.044(3)	-0.008(4)	-0.007(2)	-0.007(4)
C(27)	8f	0.3864(2)	0.6721(3)	0.3449(3)	0.068(3)	0.069(3)	0.061(3)	0.019(2)	0.011(2)	0.028(2)
C(28)	8f	0.2571(1)	0.9466(2)	0.2514(2)	0.062(2)	0.031(2)	0.038(2)	-0.002(2)	0.023(2)	-0.000(2)

Table 3. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(29)	8 <i>f</i>	0.2369(1)	1.0101(2)	0.2955(2)	0.071(3)	0.046(2)	0.040(2)	−0.002(2)	0.032(2)	−0.006(2)
C(30)	8 <i>f</i>	0.2351(1)	1.0914(2)	0.2662(2)	0.050(2)	0.041(2)	0.040(2)	0.002(2)	0.016(2)	−0.017(2)
C(31)	8 <i>f</i>	0.2554(1)	1.1102(2)	0.1944(2)	0.038(2)	0.029(2)	0.031(2)	−0.001(1)	0.001(1)	−0.009(1)
C(32)	8 <i>f</i>	0.2577(1)	1.1949(2)	0.1630(2)	0.056(2)	0.026(2)	0.044(2)	0.007(2)	0.008(2)	−0.008(2)
C(33)	8 <i>f</i>	0.2809(1)	1.2120(2)	0.1000(2)	0.068(3)	0.021(2)	0.051(2)	0.002(2)	0.008(2)	−0.004(2)
C(34)	8 <i>f</i>	0.3042(1)	1.1448(2)	0.0585(2)	0.049(2)	0.026(2)	0.035(2)	−0.006(1)	0.004(2)	−0.002(1)
C(35)	8 <i>f</i>	0.3307(2)	1.1599(2)	−0.0062(2)	0.073(3)	0.033(2)	0.049(2)	−0.017(2)	0.015(2)	0.008(2)
C(36)	8 <i>f</i>	0.3521(2)	1.0934(2)	−0.0400(2)	0.074(3)	0.048(2)	0.050(2)	−0.020(2)	0.034(2)	−0.000(2)
C(37)	8 <i>f</i>	0.3460(1)	1.0111(2)	−0.0106(2)	0.048(2)	0.042(2)	0.043(2)	−0.009(2)	0.023(2)	−0.007(2)
C(38)	8 <i>f</i>	0.3003(1)	1.0605(2)	0.0854(2)	0.033(2)	0.023(2)	0.027(2)	−0.004(1)	0.001(1)	−0.002(1)
C(39)	8 <i>f</i>	0.2759(1)	1.0424(2)	0.1556(2)	0.034(2)	0.025(2)	0.024(2)	−0.003(1)	0.003(1)	−0.004(1)

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