Crystal structure of di(2,2′-bipyridine)tetra[μ-(4-methylbenzoato-*O*,*O*′)]-di(4-methylbenzoato)disamarium(III), $Sm_2(C_8H_7O_2)_6(C_{10}H_8N_2)_2$

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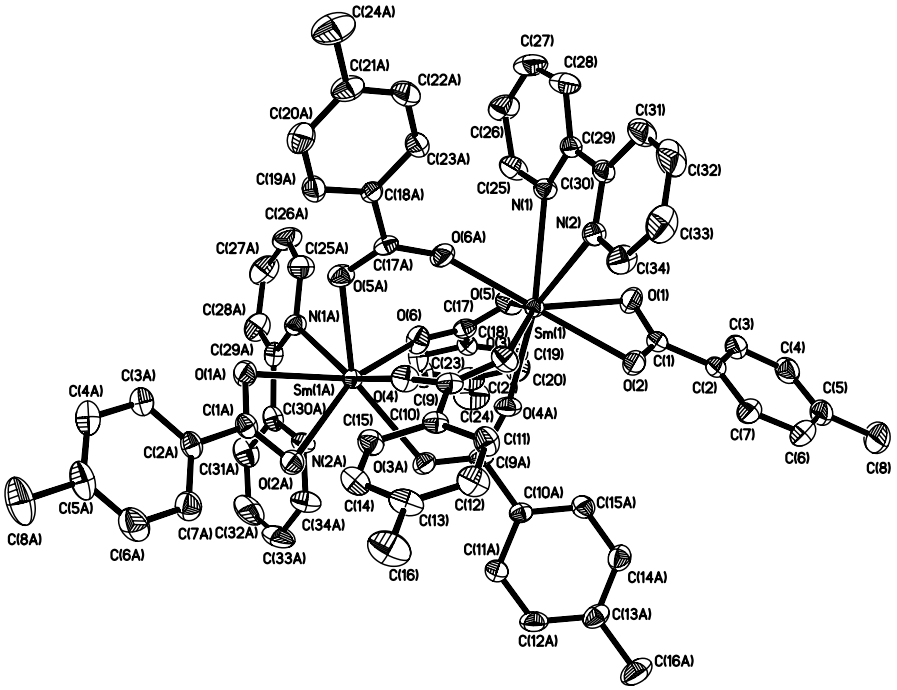

Abstract

$C_{68}H_{58}N_4O_{12}Sm_2$, monoclinic, *C*12/*c*1 (No. 15), *a* = 14.123(7) Å, *b* = 19.151(9) Å, *c* = 23.12(1) Å, β = 96.600(8)°, *V* = 6211.0 Å^3, *Z* = 4, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.053, *T* = 293 K.

Source of material

0.5 mmol $SmCl_3 \cdot 6H_2O$, 1.5 mmol 4-methylbenzoic acid and 0.5 mmol 2,2′-bipyridine were first dissolved separately in appropriate amounts of ethanol. The ethanolic solution of the 4-methylbenzoic acid was controlled to pH = 6-7 with 1M NaOH solution, then the ethanolic solution of 2,2′-bipyridine and ethanolic solution of $SmCl_3$ were successively dropped in. The mixture was heated under reflux with stirring for 2 h. Single crystals were obtained from the mother liquor after 3 weeks at room temperature.

Discussion

The title complex $Sm_2(C_8H_7O_2)_6(C_{10}H_8N_2)_2$ (**I**) is a dimeric molecule. The Sm^{3+} ion is coordinated by six oxygen atoms and two nitrogen atoms. Two of 4-methylbenzoato and two 2,2′-bipyridine chelate to Sm^{3+} ions, four of 4-methylbenzoato in bidentate bridging link two Sm^{3+} ions, in resulting the Sm(1)—Sm(1A) distance of 4.298 Å. The structure of the title complex is isomorphous with $Eu_2(C_8H_7O_2)_6(C_{10}H_8N_2)_2$ (**II**) [1], but different from the structure of the complex $Nd_2(C_9H_9O_4)_6(C_{10}H_8N_2)_2$ (**III**) [2] in coordination modes of the carboxyl group, crystal system and space group. This may be caused by difference of steric effect of groups on the phenyl ring. O(5)–C(17)–O(6) and O(3)–C(9)–O(4) groups are in bidentate bridging mode, in which O atoms coordinate to two Sm^{3+} ions. Their Sm—O bond lengths range from 2.316(2) Å to 2.445(2) Å. The O(1)–C(1)–O(2) groups are in bidentate chelating mode, and the correspondig Sm—O bond lengths are significantly longer, being 2.445(2) and 2.499(2) Å, respectively. This is common for lanthanide compounds with carboxylic acid. This is because a carboxylate group O(1)–C(1)–O(2) with a metal ion forms an unstable four membered ring. The average length of all Sm—O bonds in **I** is 2.404(2) Å, the O–Sm–O angles vary considerably, 52.34(8)° – 156.511(8)°, and the O(1)–Sm(1)–O(2) angle is the smallest. The 2,2′-bipyridine ligand chelates with two nitrogen to the samarium ion. The mean value of Sm—N distance is 2.639(3) Å, in agreement with those in the similar complex, such as in complex **III**.

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Table 1. Data collection and handling.

Crystal:	white prism, size 0.20 × 0.22 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.38 cm^{-1}
Diffractometer, scan mode:	Bruker CCD, φ/ω
$2\theta_{max}$:	52.88°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23984, 6299
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5052
$N(param)_{refined}$:	391
Programs:	SHELXS-97[3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	8*f*	0.7823	0.2120	0.0419	0.060
H(4)	8*f*	0.8348	0.1671	–0.0416	0.073
H(6)	8*f*	0.8632	–0.0199	0.0331	0.087
H(7)	8*f*	0.8032	0.0228	0.1149	0.070
H(8A)	8*f*	0.8392	0.0307	–0.0964	0.145
H(8B)	8*f*	0.9257	–0.0033	–0.0580	0.145
H(8C)	8*f*	0.9344	0.0727	–0.0821	0.145
H(11)	8*f*	0.6733	–0.0099	0.3377	0.058
H(12)	8*f*	0.6648	–0.1076	0.3944	0.069
H(14)	8*f*	0.4285	–0.0349	0.4516	0.063
H(15)	8*f*	0.4327	0.0613	0.3924	0.055
H(16A)	8*f*	0.5753	–0.1366	0.5056	0.119
H(16B)	8*f*	0.5712	–0.1849	0.4506	0.119
H(16C)	8*f*	0.4766	–0.1571	0.4718	0.119
H(19)	8*f*	0.5061	0.2863	0.0489	0.058

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(20)	8*f*	0.4173	0.3149	–0.0372	0.073
H(22)	8*f*	0.1966	0.3605	0.0476	0.079
H(23)	8*f*	0.2831	0.3304	0.1339	0.067
H(24A)	8*f*	0.1738	0.3447	–0.0607	0.136
H(24B)	8*f*	0.2652	0.3379	–0.0929	0.136
H(24C)	8*f*	0.2395	0.4098	–0.0663	0.136
H(25)	8*f*	0.6263	0.3824	0.2088	0.070
H(26)	8*f*	0.6789	0.4900	0.2429	0.081
H(27)	8*f*	0.8297	0.4985	0.2928	0.086
H(28)	8*f*	0.9176	0.3985	0.3128	0.074
H(31)	8*f*	0.9971	0.3032	0.3223	0.078
H(32)	8*f*	1.0634	0.1981	0.3511	0.099
H(33)	8*f*	0.9741	0.0972	0.3368	0.090
H(34)	8*f*	0.8193	0.1057	0.2944	0.072

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	8*f*	0.64272(1)	0.205775(8)	0.226227(7)	0.02852(8)	0.02929(8)	0.03280(8)	–0.00072(7)	0.00103(5)	–0.00072(7)
C(1)	8*f*	0.7479(2)	0.1512(2)	0.1398(2)	0.033(2)	0.043(2)	0.048(2)	–0.005(2)	0.006(2)	–0.008(2)
C(2)	8*f*	0.7862(2)	0.1218(2)	0.0869(1)	0.033(2)	0.048(2)	0.046(2)	–0.007(2)	0.007(1)	–0.011(2)
C(3)	8*f*	0.7971(2)	0.1648(2)	0.0400(2)	0.045(2)	0.056(2)	0.051(2)	–0.004(2)	0.011(2)	–0.003(2)
C(4)	8*f*	0.8300(3)	0.1380(2)	–0.0098(2)	0.054(2)	0.080(3)	0.051(2)	–0.012(2)	0.014(2)	–0.007(2)
C(5)	8*f*	0.8556(3)	0.0689(3)	–0.0129(2)	0.052(2)	0.088(3)	0.062(3)	–0.015(2)	0.019(2)	–0.030(2)
C(6)	8*f*	0.8458(3)	0.0268(2)	0.0344(2)	0.076(3)	0.059(3)	0.087(3)	–0.002(2)	0.025(3)	–0.028(2)
C(7)	8*f*	0.8104(3)	0.0525(2)	0.0838(2)	0.064(2)	0.050(2)	0.063(2)	–0.004(2)	0.020(2)	–0.010(2)
C(8)	8*f*	0.8921(3)	0.0395(3)	–0.0674(2)	0.088(3)	0.128(4)	0.081(3)	–0.016(3)	0.038(3)	–0.049(3)
C(9)	8*f*	0.5572(2)	0.0998(2)	0.3206(1)	0.038(2)	0.032(2)	0.041(2)	–0.000(1)	–0.010(1)	0.003(1)
C(10)	8*f*	0.5541(2)	0.0365(2)	0.3587(1)	0.034(2)	0.035(2)	0.037(2)	–0.000(1)	–0.006(1)	0.002(1)
C(11)	8*f*	0.6231(2)	–0.0148(2)	0.3602(2)	0.040(2)	0.051(2)	0.054(2)	0.007(2)	0.006(2)	0.011(2)
C(12)	8*f*	0.6182(3)	–0.0734(2)	0.3946(2)	0.049(2)	0.045(2)	0.075(3)	0.011(2)	–0.005(2)	0.016(2)
C(13)	8*f*	0.5459(3)	–0.0824(2)	0.4296(2)	0.050(2)	0.049(2)	0.054(2)	–0.009(2)	–0.011(2)	0.015(2)
C(14)	8*f*	0.4776(2)	–0.0305(2)	0.4283(2)	0.045(2)	0.058(2)	0.054(2)	–0.008(2)	0.004(2)	0.009(2)
C(15)	8*f*	0.4804(2)	0.0278(2)	0.3931(1)	0.037(2)	0.047(2)	0.052(2)	0.002(2)	0.001(2)	0.002(2)
C(16)	8*f*	0.5419(3)	–0.1460(2)	0.4679(2)	0.085(3)	0.066(3)	0.085(3)	–0.007(2)	–0.006(3)	0.037(2)
C(17)	8*f*	0.4591(2)	0.2830(2)	0.1570(1)	0.049(2)	0.026(2)	0.040(2)	0.001(1)	0.003(2)	0.004(1)
C(18)	8*f*	0.4042(2)	0.3050(2)	0.1008(1)	0.037(2)	0.036(2)	0.037(2)	–0.000(1)	0.004(1)	0.006(1)
C(19)	8*f*	0.4434(2)	0.3009(2)	0.0490(1)	0.044(2)	0.060(2)	0.044(2)	0.004(2)	0.010(2)	0.003(2)
C(20)	8*f*	0.3899(3)	0.3182(2)	–0.0026(2)	0.074(3)	0.074(3)	0.034(2)	0.001(2)	0.009(2)	0.003(2)
C(21)	8*f*	0.2965(3)	0.3406(2)	–0.0042(2)	0.064(3)	0.058(2)	0.047(2)	–0.003(2)	–0.017(2)	0.009(2)
C(22)	8*f*	0.2591(3)	0.3450(2)	0.0475(2)	0.043(2)	0.085(3)	0.067(3)	0.016(2)	–0.002(2)	0.018(2)
C(23)	8*f*	0.3110(2)	0.3273(2)	0.0994(2)	0.047(2)	0.072(3)	0.050(2)	0.016(2)	0.015(2)	0.013(2)
C(24)	8*f*	0.2384(3)	0.3601(3)	–0.0613(2)	0.104(4)	0.095(4)	0.063(3)	–0.004(3)	–0.035(3)	0.016(3)
C(25)	8*f*	0.6853(3)	0.3853(2)	0.2312(2)	0.043(2)	0.048(2)	0.082(3)	–0.005(2)	–0.002(2)	0.009(2)
C(26)	8*f*	0.7169(3)	0.4506(2)	0.2504(2)	0.087(3)	0.030(2)	0.085(3)	0.000(2)	0.011(3)	0.005(2)
C(27)	8*f*	0.8050(3)	0.4552(2)	0.2805(2)	0.096(3)	0.042(2)	0.075(3)	–0.026(2)	0.006(3)	–0.008(2)
C(28)	8*f*	0.8571(3)	0.3960(2)	0.2924(2)	0.062(2)	0.056(3)	0.065(3)	–0.024(2)	0.000(2)	–0.005(2)
C(29)	8*f*	0.8190(2)	0.3318(2)	0.2738(1)	0.042(2)	0.045(2)	0.036(2)	–0.010(2)	0.011(2)	–0.005(2)
C(30)	8*f*	0.8679(2)	0.2653(2)	0.2913(1)	0.033(2)	0.057(2)	0.039(2)	–0.005(2)	0.002(1)	–0.008(2)
C(31)	8*f*	0.9614(3)	0.2624(2)	0.3168(2)	0.039(2)	0.087(3)	0.067(3)	–0.007(2)	–0.005(2)	–0.009(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(32)	8*f*	1.0006(3)	0.2001(3)	0.3338(2)	0.037(2)	0.120(4)	0.086(3)	0.019(3)	–0.011(2)	–0.004(3)
C(33)	8*f*	0.9482(3)	0.1404(3)	0.3255(2)	0.067(3)	0.079(3)	0.075(3)	0.036(3)	–0.009(2)	0.005(3)
C(34)	8*f*	0.8557(3)	0.1462(2)	0.3000(2)	0.055(2)	0.052(2)	0.069(3)	0.014(2)	–0.009(2)	–0.001(2)
N(1)	8*f*	0.7335(2)	0.3265(1)	0.2426(1)	0.041(2)	0.034(2)	0.045(2)	–0.003(1)	0.004(1)	0.002(1)
N(2)	8*f*	0.8153(2)	0.2069(2)	0.2826(1)	0.035(1)	0.042(2)	0.047(2)	0.006(1)	–0.002(1)	–0.001(1)
O(1)	8*f*	0.7316(2)	0.2154(1)	0.1418(1)	0.071(2)	0.041(2)	0.062(2)	0.002(1)	0.031(1)	–0.003(1)
O(2)	8*f*	0.7322(2)	0.1117(1)	0.1809(1)	0.055(1)	0.042(1)	0.049(1)	0.002(1)	0.016(1)	–0.003(1)
O(3)	8*f*	0.6309(2)	0.1114(1)	0.2963(1)	0.043(1)	0.045(1)	0.051(1)	–0.001(1)	0.003(1)	0.014(1)
O(4)	8*f*	0.4842(2)	0.1379(1)	0.3150(1)	0.045(1)	0.043(1)	0.058(2)	0.010(1)	–0.006(1)	0.010(1)
O(5)	8*f*	0.5487(2)	0.2813(1)	0.1601(1)	0.042(1)	0.050(2)	0.055(1)	–0.001(1)	–0.008(1)	0.011(1)
O(6)	8*f*	0.4124(2)	0.2684(1)	0.1987(1)	0.067(2)	0.051(2)	0.038(1)	0.009(1)	0.015(1)	0.012(1)

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