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Synthesis, crystal structure and thermal decomposition mechanism of complex [Sm(*o*-MBA)$_3$phen]$_2$

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Abstract

The title complex [Sm(*o*-MBA)$_3$phen]$_2$ (*o*-MBA, *o*-methylbenzoate; phen, 1,10-phenanthroline) was prepared and characterized by single crystal X-ray diffraction, elemental analysis, IR spectra and TG-DTG techniques. The results show that the crystal is triclinic, space group P $\bar{1}$ with $a = 13.1364(10)$ Å, $b = 14.3739(11)$ Å, $c = 17.4356(13)$ Å; $\alpha = 83.1100(10)^\circ$, $\beta = 83.7760(10)^\circ$, $\gamma = 73.0520(10)^\circ$, $Z = 2$, $D_c = 1.568$ Mg/m^3, F (000) = 1476. The crystal is consisted of two similar types of binuclear molecule. Each Sm^{3+} is nine-coordinated by one bidentate chelating carboxylate group, two bidentate bridging and two tridentate chelating-bridging carboxylate groups, as well as one 1,10-phenanthroline molecule. The thermal decomposition mechanism of [Sm(*o*-MBA)$_3$phen]$_2$ has been determined on the basis of thermal analysis. The dependences of $E - \alpha$ for the first-stage decomposition process were determined by using Ozawa-iterative procedure, which show the E values varied with the extent of conversion. In addition, the lifetime equation at weight-loss of 10% was deduced as $\ln \tau = -25.5547 + 18511.68/T$ by isothermal thermogravimetric analysis.

Keywords: *o*-Methylbenzoic acid; Crystal structure; 1,10-Phenanthroline; Samarium complex; Thermal analysis

1. Introduction

The coordination complexes of rare-earth with various carboxylic acids have been an important research field in coordination chemistry and structure chemistry, due to the special structures and interesting luminescence properties [1–3]. Benzoic acid and its derivatives are always widely used in the coordination complexes of rare-earth because of their versatile coordination modes. In previous work, a series of rare-earth complexes with benzoic acid or its derivatives and 1,10-phenanthroline have been reported [4–10]. Herein we report the synthesis and crystal structural of samarium *o*-methylbenzoate with 1,10-phenanthroline, and characterize the complex by elemental analysis, thermal analysis, and IR spectra.

2. Experimental

2.1. Materials

All the regents used were Analar grade and were used without further purification.

2.2. Synthesis of complex [Sm(o-MBA)$_3$phen]$_2$

SmCl$_3$·6H$_2$O, *o*-MBA and phen were dissolved in 95% ethanol in a molar ratio of 1:3:1, respectively. The pH value of the *o*-MBA was adjusted to 6–7 by adding 1.0 M NaOH solution. The ethanol solution of two ligands were mixed and then added dropwise to the ethanolic SmCl$_3$ solution. At once a large white precipitate formed. The mixture solution was stirred for 8 h at room temperature and then deposited them for 12 h. Subsequently, the precipitate was filtered out and washed three times with deionized water and 95% ethanol. The white powdery complex [Sm(*o*-MBA)$_3$phen]$_2$ was obtained with yield of 80%. A

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colorless cubic crystal was grown by slow evaporation of its solvent for a month and its structure was established by X-ray crystallography.

2.3. *Experimental equipment and conditions*

Elemental analysis (C, H, N) were determined by a Carlo-Erba model 1106 elemental analyzer. The content of samarium was assayed using EDTA titration method. The infrared spectra in KBr discs were recorded over the range 4000–400 cm^{-1}, using Bio-Rad FTS-135 spectrometer. X-ray diffraction data collection was performed on Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K using ϕ–ω scan mode. A semi-empirical absorption correction based on SADABS scan technique was applied. 10893 Unique data ($R_{int} = 0.0142$) were used to solve the structure by direct methods using SHELXS-97 program and refined on F^2 by full-matrix least squares methods using SHELXL-97 program. All non-H atoms were refined anisotropically, and the H atoms were included in the structure-factor calculations. The crystal data and refinement details of the complex are summarized in Table 1. The TG and DTG experiments for the title compound were performed using a Perkin-Elmer's TGA7 Thermogravimetric Analyzer under a static air atmosphere. The heating rate used was 3, 5, 7, 10 °C min^{-1} from ambient to 925 °C and the sample size was 2.5 ± 0.2 mg.

Table 1
Crystallographic data and structure refinement for [Sm(o-MBA)$_3$phen]$_2$

Empirical formula	$C_{72}H_{58}N_4O_{12}Sm_2$
Formula weight	1471.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	$a = 13.1364(10)$ Å $\alpha = 83.1100(10)°$ $b = 14.3739(11)$ Å $\beta = 83.7760(10)°$ $c = 17.4356(13)$ Å $\gamma = 73.0520(10)°$
Volume	3117.1(4) Å^3
Z, calculated density	2, 1.568 Mg/m^3
Absorption coefficient	1.933 mm^{-1}
F(000)	1476
Crystal size	0.34 × 0.26 × 0.18 mm
Theta range for data collection	1.63–25.03°
Limiting indices	$-15 \le h \le h$ 14, $-17 \le k \le 11$, $-19 \le l \le 20$
Reflections collected/unique	16606/10893 [R(int) = 0.0142]
Completeness to theta = 25.03	98.9%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000000 and 0.742728
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10893/6/905
Goodness-of-fit on F^2	1.083
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0246$, $wR2 = 0.0673$
R indices (all data)	$R1 = 0.0328$, $wR2 = 0.0699$
Largest diff. peak and hole	0.374 and −0.456 e Å^{-3}

3. Results and discussion

3.1. *Elemental analysis*

The analysis data of the element content are shown in Table 2. It can be seen the experimental data are in a good accord with the theoretical values.

3.2. *Infrared spectra*

The band of the COOH group for o-methylbenzoic acid ligand at 1684 cm^{-1}, completely disappears in the spectra of the complex. However, the appearance of slight bands at 1591, 1531, 1519 and 1490 cm^{-1}, 1402 cm^{-1}, 1347 cm^{-1} were assigned to asymmetric and symmetric vibrations of the COO^- group, indicating that the carboxyl group is coordinated to Sm(III) ion in three coordination modes [11], which was confirmed by X-ray diffraction analysis. In addition, IR spectra of the complex show that the bands of $\nu_{C=N}$ (1646 cm^{-1}), $\delta_{C–C}$(854 cm^{-1}) and $\delta_{C–H}$(740 cm^{-1}) for phen ligand are observed to move lower wavenumbers at 1613, 846 and 731 cm^{-1}, respectively, suggesting the coordination of the nitrogen atoms of the 1,10-phenanthroline to Sm^{3+} ion [12].

3.3. *Crystal structure*

The final atomic coordinates and thermal parameters for the title complex are presented in Table 3. Selected bond lengths and angles are listed in Table 4. In the asymmetric part, the two different Sm(o-MBA)$_3$phen units are combined through inversion with the corresponding units of the closest asymmetric species respectively, and thus the crystal of the title complex has two similar types of binuclear molecules [5], as shown in Fig. 1a and b. The carboxylate groups are bonded to the samarium(III) ion in three modes: bidentate chelating, bidentate bridging, tridentate chelating-bridging. Each Sm^{3+} ion is coordinated to one bidentate chelating carboxylate group, two bidentate bridging and two tridentate chelating-bridging carboxylate groups, as well as one 1,10-phenanthroline molecule, giving the coordination number of 9. The coordination polyhedron adopts a distorted monocapped square antiprism geometry. The oxygen atom from the tridentate chelating-bridging carboxylate is at the capped position.

In the Fig. 1a and b, the Sm–Sm distances are 4.045(4) and 4.019 (4) Å. The average Sm–O distances are 2.465 and 2.456 Å. The mean bond lengths of Sm–N are 2.628 and 2.656 Å, respectively. It can be concluded that the differences are probably caused by steric effects of the different position of the methyl

Table 2
Elemental analysis data of [Sm(o-MBA)$_3$phen]$_2$ (%)

Complex [Sm(o-MBA)$_3$phen]$_2$	Mass fraction (%)			
	C	H	N	Sm
Experimental data	58.88	3.93	4.28	20.01
Theoretical values	58.69	3.94	3.80	20.43

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the molecules (a) and (b)

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Sm(1)	5893(1)	3657(1)	10385(1)	34(1)	Sm(2)	−454(1)	1339(1)	5376(1)	36(1)
O(1)	5555(2)	2149(2)	11011(1)	60(1)	O(7)	2046(2)	2783(2)	5264(2)	54(1)
O(2)	6944(2)	1955(2)	10174(1)	53(1)	O(8)	−499(2)	3048(2)	5324(2)	54(1)
O(3)	5024(2)	3103(2)	9413(2)	75(1)	O(9)	−625(3)	1887(2)	3986(1)	89(1)
O(4)	4306(2)	4675(2)	9463(1)	47(1)	O(10)	−158(2)	302(2)	4133(1)	47(1)
O(5)	5758(2)	5811(2)	8885(1)	50(1)	O(11)	1377(2)	903(2)	4905(1)	49(1)
O(6)	6629(2)	4252(2)	9176(1)	50(1)	O(12)	1891(2)	−663(2)	4668(1)	50(1)
N(1)	7878(2)	3567(2)	10581(2)	49(1)	N(3)	640(2)	1466(2)	6551(2)	43(1)
N(2)	6424(2)	3514(2)	11812(2)	48(1)	N(4)	−1456(2)	1498(2)	6768(2)	50(1)
C(1)	8612(3)	3530(3)	9989(2)	68(1)	C(37)	1639(3)	1487(3)	6461(2)	54(1)
C(2)	9647(4)	3523(4)	10069(3)	95(2)	C(38)	2227(3)	1523(3)	7069(3)	67(1)
C(3)	9938(4)	3583(4)	10765(4)	93(2)	C(39)	1762(4)	1538(3)	7799(2)	68(1)
C(4)	9216(3)	3612(3)	11412(3)	69(1)	C(40)	702(3)	1535(3)	7932(2)	55(1)
C(5)	9461(4)	3666(3)	12177(3)	87(2)	C(41)	120(4)	1575(3)	8691(2)	72(1)
C(6)	8775(4)	3645(3)	12784(3)	81(2)	C(42)	−899(4)	1603(3)	8788(2)	68(1)
C(7)	7709(4)	3585(3)	12696(2)	67(1)	C(43)	−1474(3)	1583(3)	8148(2)	56(1)
C(8)	6964(5)	3496(3)	13314(3)	84(2)	C(44)	−2562(4)	1643(3)	8225(2)	73(1)
C(9)	5990(5)	3426(4)	13178(2)	85(1)	C(45)	−3063(3)	1629(4)	7596(2)	76(1)
C(10)	5746(3)	3443(3)	12416(2)	66(1)	C(46)	−2481(3)	1555(3)	6874(2)	67(1)
C(11)	7414(3)	3570(2)	11950(2)	49(1)	C(47)	−948(3)	1518(2)	7402(2)	45(1)
C(12)	8172(3)	3586(2)	11298(2)	50(1)	C(48)	154(3)	1500(2)	7286(2)	44(1)
C(13)	6276(3)	1612(2)	10596(2)	45(1)	C(49)	−426(3)	1096(3)	3718(2)	54(1)
C(14)	6335(3)	545(3)	10589(2)	54(1)	C(50)	−672(10)	1033(6)	2880(4)	45(3)
C(15)	7147(4)	−5(3)	10123(3)	75(1)	C(51)	−1726(8)	1029(8)	2769(5)	35(2)
C(16)	7209(5)	−970(3)	10037(4)	101(2)	C(52)	−1967(8)	990(6)	1986(6)	66(3)
C(17)	6460(5)	−1369(4)	10415(4)	102(2)	C(53)	−1165(13)	975(10)	1371(6)	70(4)
C(18)	5673(5)	−841(3)	10879(3)	89(2)	C(54)	−289(19)	983(14)	1512(9)	85(5)
C(19)	5579(4)	119(3)	10988(2)	68(1)	C(55)	106(7)	1008(5)	2308(4)	44(2)
C(20)	4686(5)	625(4)	11529(3)	117(2)	C(56)	1292(8)	1056(13)	2478(9)	74(4)
C(21)	4400(3)	3887(3)	9172(2)	56(1)	C(57)	1492(3)	3363(2)	5239(2)	39(1)
C(22)	3864(7)	3888(11)	8500(3)	45(2)	C(58)	1971(2)	4446(2)	5091(2)	40(1)
C(23)	4385(6)	3832(8)	7762(4)	50(3)	C(59)	1294(3)	4989(2)	4769(2)	48(1)
C(24)	3835(7)	3802(7)	7132(3)	83(4)	C(60)	1660(3)	6002(3)	4649(2)	63(1)
C(25)	2764(7)	3828(9)	7240(5)	73(4)	C(61)	2698(4)	6455(3)	4838(3)	73(1)
C(26)	2242(6)	3884(10)	7978(6)	82(4)	C(62)	3371(3)	5923(3)	5152(3)	75(1)
C(27)	2792(7)	3914(11)	8608(4)	66(4)	C(63)	3042(3)	4912(3)	5289(2)	58(1)
C(28)	2252(7)	3937(9)	9457(5)	58(3)	C(64)	3820(3)	4386(3)	5673(3)	100(2)
C(29)	6503(3)	5060(3)	8774(2)	43(1)	C(65)	2058(2)	149(3)	4679(2)	42(1)
C(30)	7306(2)	5104(3)	8101(2)	43(1)	C(66)	3143(3)	237(3)	4371(2)	50(1)
C(31)	7816(3)	4252(3)	7770(2)	63(1)	C(67)	3196(3)	1131(3)	4022(2)	65(1)
C(32)	8526(4)	4241(4)	7117(2)	80(1)	C(68)	4162(5)	1263(5)	3678(3)	96(2)
C(33)	8729(4)	5083(4)	6810(2)	78(1)	C(69)	5065(4)	459(6)	3716(3)	109(2)
C(34)	8238(3)	5941(3)	7127(2)	64(1)	C(70)	5014(4)	−419(5)	4094(3)	101(2)
C(35)	7531(3)	5983(3)	7789(2)	50(1)	C(71)	4072(3)	−562(4)	4418(2)	68(1)
C(36)	7088(3)	6939(3)	8139(3)	72(1)	C(72)	4104(4)	−1539(4)	4836(3)	95(2)

substituent on the benzene ring (see Fig. 1). In contrast with the complex $[Eu(o\text{-MBA})_3phen]_2$[4] and $[Tb(o\text{-MBA})_3phen]_2$[5], they all have two types of binuclear molecules in their crystals. The coordination modes of the title complex are same to the former, but unlike the latter in which the Tb^{3+} is eight-coordinated and there is no tridentate chelating-bridging carboxylate group.

3.4. Thermal decomposition mechanism

Fig. 2 shows the TG-DTG curves of the title complex at a heating rate of 5 °C min^{-1} under a static air atmosphere. The thermalanalytical data are listed in Table 5. As was observed from the DTG curve, the thermal decomposition process of $[Sm(o\text{-MBA})_3phen]_2$ can be divided into two stages. The first weight loss of 28.01% between 256.26 and 484.63 °C, corresponding to the release of 2 mol phen and 4 mol CH_3. The IR spectra of the residue at 484 °C shows that the absorption band of C=N disappears at 1613 cm^{-1}. Average band length of Sm–N distance is longer than that of Sm–O, therefore, Sm–N bond is less stable and easy to be broken down. The second weight loss of 48.23% was in the range of 484.63–704.33 °C, in which $C_{44}H_{30}O_9$ was removed. As shown in the IR spectra of the residue at 704 °C, the bands of the asymmetric vibrations at 1607–1537 cm^{-1} and of the symmetric vibrations at 1489–1285 cm^{-1} disappeared, and IR spectra of the residue are same to that of the sample Sm_2O_3. Therefore, by 704.33 °C, the

Table 4
Selected bond lengths (Å) and angles (°) for the molecules(a) and (b)

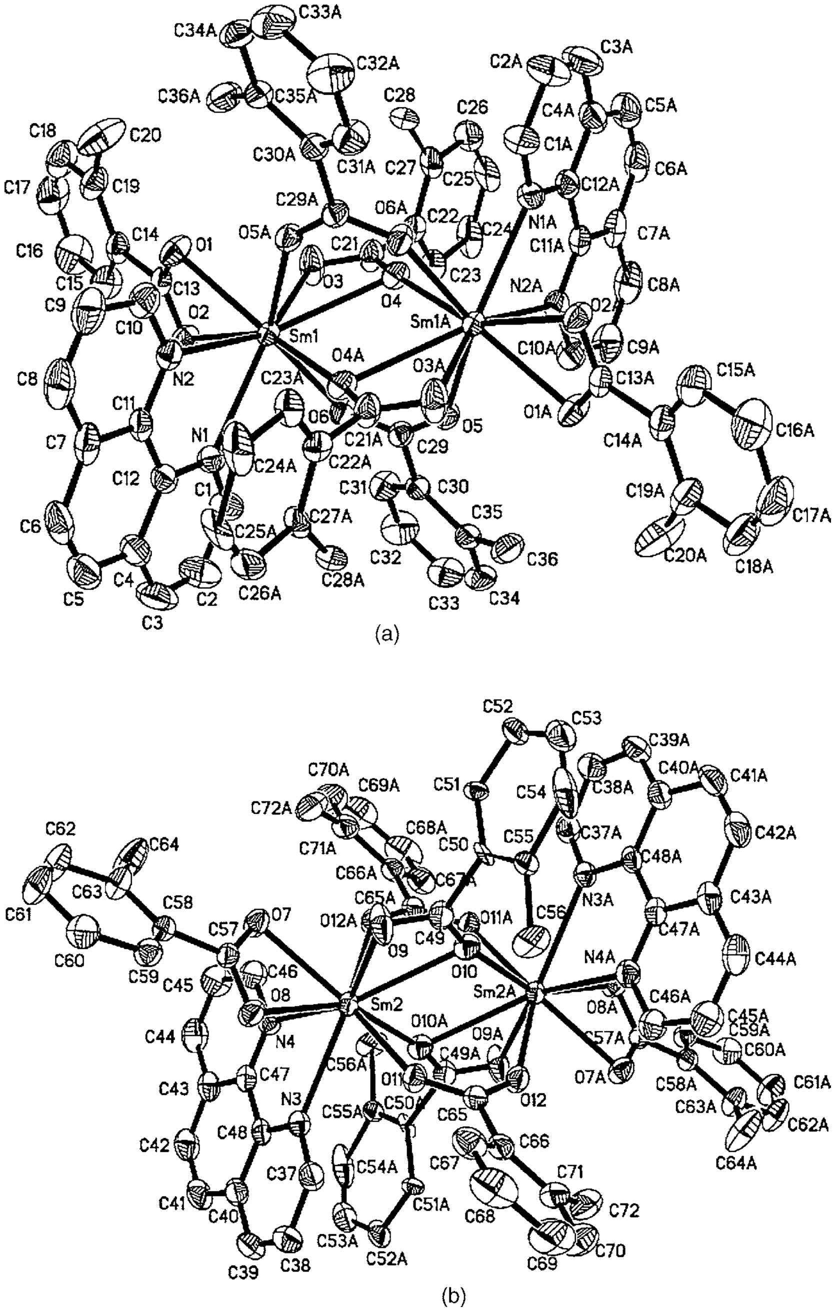
Sm(1)—O(5)#1	2.362(2)	Sm(2)—O(10)#2	2.346(2)
Sm(1)—O(4)#1	2.378(2)	Sm(2)—O(12)#2	2.373(2)
Sm(1)—O(6)	2.390(2)	Sm(2)—O(11)	2.381(2)
Sm(1)—O(1)	2.446(2)	Sm(2)—O(8)	2.431(2)
Sm(1)—O(3)	2.465(2)	Sm(2)—O(9)	2.471(2)
Sm(1)—O(2)	2.483(2)	Sm(2)—O(7)	2.486(2)
Sm(1)—O(4)	2.729(2)	Sm(2)—O(10)	2.706(2)
Sm(1)—N(2)	2.625(3)	Sm(2)—N(4)	2.634(3)
Sm(1)—N(1)	2.631(3)	Sm(2)—N(3)	2.679(3)
O(1)—C(13)	1.255(4)	O(7)—C(57)	1.251(4)
O(2)—C(13)	1.257(4)	O(8)—C(57)	1.269(4)
O(3)—C(21)	1.241(4)	O(9)—C(49)	1.227(4)
O(4)—C(21)	1.264(4)	O(10)—C(49)	1.254(4)
O(5)—C(29)	1.246(4)	O(11)—C(65)	1.261(4)
O(6)—C(29)	1.259(4)	O(12)—C(65)	1.252(4)
O(5)#1—Sm(1)—O(6)	133.53(8)	O(10)#2—Sm(2)—O(11)	77.31(8)
O(4)#1—Sm(1)—O(6)	76.21(8)	O(12)#2—Sm(2)—O(11)	134.42(7)
O(5)#1—Sm(1)—O(1)	75.77(8)	O(10)#2—Sm(2)—O(8)	152.14(8)
O(4)#1—Sm(1)—O(1)	144.52(8)	O(12)#2—Sm(2)—O(8)	128.53(8)
O(6)—Sm(1)—O(1)	139.26(8)	O(11)—Sm(2)—O(8)	91.26(8)
O(5)#1—Sm(1)—O(3)	90.78(10)	O(10)#2—Sm(2)—O(9)	123.95(8)
O(4)#1—Sm(1)—O(3)	124.20(8)	O(12)#2—Sm(2)—O(9)	87.53(10)
O(6)—Sm(1)—O(3)	76.38(9)	O(11)—Sm(2)—O(9)	79.77(10)
O(1)—Sm(1)—O(3)	75.68(9)	O(8)—Sm(2)—O(9)	77.59(9)
O(5)#1—Sm(1)—O(2)	127.96(8)	O(10)#2—Sm(2)—O(7)	144.77(7)
O(4)#1—Sm(1)—O(2)	153.95(8)	O(12)#2—Sm(2)—O(7)	75.68(8)
O(6)—Sm(1)—O(2)	90.96(8)	O(11)—Sm(2)—O(7)	137.82(8)
O(1)—Sm(1)—O(2)	52.54(7)	O(8)—Sm(2)—O(7)	52.85(7)
O(3)—Sm(1)—O(2)	72.76(9)	O(9)—Sm(2)—O(7)	72.03(9)
O(5)#1—Sm(1)—N(2)	76.07(9)	O(10)#2—Sm(2)—N(4)	81.99(8)
O(4)#1—Sm(1)—N(2)	79.42(8)	O(12)#2—Sm(2)—N(4)	75.62(8)
O(6)—Sm(1)—N(2)	132.26(9)	O(11)—Sm(2)—N(4)	134.05(8)
O(1)—Sm(1)—N(2)	74.38(9)	O(8)—Sm(2)—N(4)	88.39(9)
O(3)—Sm(1)—N(2)	149.43(9)	O(9)—Sm(2)—N(4)	144.12(10)
O(2)—Sm(1)—N(2)	93.55(9)	O(7)—Sm(2)—N(4)	73.18(9)
O(5)#1—Sm(1)—N(1)	134.62(9)	O(10)#2—Sm(2)—N(3)	78.23(8)
O(4)#1—Sm(1)—N(1)	79.97(8)	O(12)#2—Sm(2)—N(3)	131.69(8)
O(6)—Sm(1)—N(1)	73.28(8)	O(11)—Sm(2)—N(3)	74.02(8)
O(1)—Sm(1)—N(1)	107.59(9)	O(8)—Sm(2)—N(3)	74.20(8)
O(3)—Sm(1)—N(1)	134.45(10)	O(9)—Sm(2)—N(3)	140.62(10)
O(2)—Sm(1)—N(1)	74.60(8)	O(7)—Sm(2)—N(3)	109.82(8)
N(2)—Sm(1)—N(1)	62.40(9)	N(4)—Sm(2)—N(3)	61.74(8)
O(5)#1—Sm(1)—O(4)	68.45(7)	O(10)#2—Sm(2)—O(10)	74.78(8)
O(4)#1—Sm(1)—O(4)	75.49(8)	O(12)#2—Sm(2)—O(10)	69.01(7)
O(6)—Sm(1)—O(4)	69.50(7)	O(11)—Sm(2)—O(10)	69.62(7)
O(1)—Sm(1)—O(4)	111.38(8)	O(8)—Sm(2)—O(10)	125.21(8)
O(3)—Sm(1)—O(4)	49.51(7)	O(9)—Sm(2)—O(10)	49.30(7)
O(2)—Sm(1)—O(4)	121.51(7)	O(7)—Sm(2)—O(10)	110.53(7)
N(2)—Sm(1)—O(4)	140.62(8)	N(4)—Sm(2)—O(10)	141.69(8)
N(1)—Sm(1)—O(4)	139.17(8)	N(3)—Sm(2)—O(10)	138.42(7)

#1 $-x+1, -y+1, -z+2$; #2 $-x, -y, -z+1$.

Table 5
Thermal decomposition data for [Sm(*o*-MBA)$_3$phen]$_2$ ($\beta = 5\,^{\circ}\mathrm{C\,min^{-1}}$)

Stage	Temperature range (°C)	DTG peak temperature (°C)	Mass loss rate (%)		Probable composition of removed groups	Intermediate
			TG	Theory		
I	256.26–484.63	316.96	28.01	28.56	–2phen, –4CH$_3$	[Sm(*o*-MBA)(C$_6$H$_4$COO)$_2$]$_2$
II	484.63–704.33	565.57	48.24 76.25[a]	47.68 76.24[a]	–C$_{44}$H$_{30}$O$_9$	Sm$_2$O$_3$

[a] Total loss of mass (%).



(a)

(b)

Fig. 1. (a) Molecular structure of [Sm(o-MBA)$_3$ phen]$_2$. (b) Molecular structure of [Sm(o-MBA)$_3$ phen]$_2$.

complex of [Sm(o-MBA)$_3$phen]$_2$ was completely degraded into Sm$_2$O$_3$, with a total loss of 76.25%. The experimental data of the mass loss coincide quite well with theoretical calculations (see Table 5). Based on the thermal analysis above, the thermal decomposition process may be expressed in the following way.

$$[\mathrm{Sm}(o-\mathrm{MBA})_3\mathrm{phen}]_2$$
$$\rightarrow [\mathrm{Sm}(o-\mathrm{MBA})\,(\mathrm{C_6H_4COO})_2]_2 \rightarrow \mathrm{Sm_2O_3}$$

3.5. Thermal decomposition kinetics

The values of E corresponding to the values of α for the first-stage decomposition reaction obtained by Ozawa-iterative procedure [13] are shown in Fig. 3. It is clear that the values of E don't seem to keep constant in the decomposition process, but varied with the extent of conversion. This fact indicates that the first-stage decomposition process is a multiple-step reaction [14–16]. Therefore, it is difficult to properly interpret the E-dependences on α by means of kinetic mechanism [16].

3.6. Lifetime

The general lifetime formula of materials is [17]

$$\ln \tau = \frac{a+b}{T} \qquad (1)$$

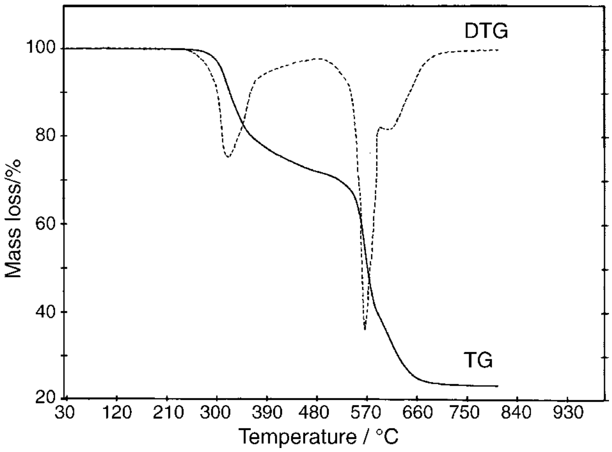


Fig. 2. TG-DTG curves of [Sm(o-MBA)$_3$ phen]$_2$ ($\beta = 5\,°\mathrm{C\,min}^{-1}$).

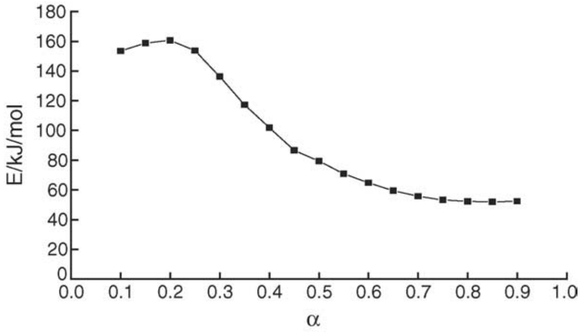


Fig. 3. The relation between E and α for the first-stage decomposition reaction of [Sm(o-MBA)$_3$phen]$_2$.

Table 6
The lifetime of the [Sm$_2$(o-MBA)$_6$(phen)$_2$] by isothermal temperature TG

T (K)	$\tau_{10\%}$ (min)	T (K)	$\tau_{10\%}$ (min)
528.15	236.99	548.15	54.11
538.15	110.62	558.15	37.10

where τ is the lifetime at temperature T(K), a and b are constant. In this paper, the mass-loss of 10% lifetime was measured by isothermal temperature TG at 528.15, 538.15, 548.15 and 558.15 K and listed in Table 6. On substitution the values in Table 6 into Eq. (1), the constant a, b and linear correlation coefficients r were obtained by the linear least squares method. The lifetime equation is $\ln \tau = -25.5547 + 18511.68/T$. Linear correlation coefficients r is 0.9924.

4. Conclusion

In summary, the title complex has been successfully synthesized. Its crystal structure was determined by single crystal X-ray diffraction. In the complex each Sm^{3+} ion is nine-coordinated. The thermal decomposition mechanism of [Sm(o-MBA)$_3$phen]$_2$ could be expressed by the scheme shown in the text. Meanwhile, the E values varied with reaction progress, indicating the complexity of the decomposition process. The lifetime equation at mass-loss of 10% was deduced as $\ln \tau = -25.5547 + 18511.68/T$ by isothermal thermogravimetric analysis.

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