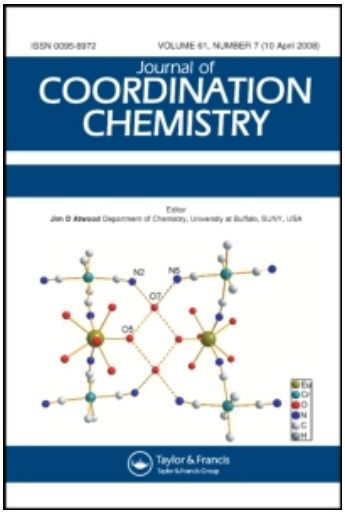

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Crystal Structure and Properties of a Terbium m -methylbenzoate Complex with 1,10-phenanthroline

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CRYSTAL STRUCTURE AND PROPERTIES OF A TERBIUM *m*-METHYLBENZOATE COMPLEX WITH 1,10-PHENANTHROLINE

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A terbium *m*-methylbenzoate complex with 1,10-phenanthroline, $[Tb(m\text{-}MBA)_3phen]\cdot H_2O$ has been obtained from ethanol solution, where *m*-MBA = *m*-methylbenzoate and phen = 1,10-phenanthroline, and its structure determined by X-ray diffraction methods. The unit cell contains binuclear molecules of the title compound. Each Tb^{3+} ion is eight-coordinated to one 1,10-phenanthroline molecule, one bidentate carboxylate group and four bridging carboxylate groups, for which the carboxylate groups are bonded to the terbium ion in two modes: chelating bidentate and bridging bidentate. Excitation and luminescence data observed at room temperature show that the complex emits very intense green fluorescence under ultraviolet light. Results of thermal analysis indicate that the complex is quite stable to heat.

Keywords: Terbium; *m*-methylbenzoic acid; 1,10-phenanthroline; Crystal structure; Luminescence; Thermal properties

INTRODUCTION

Many types of lanthanide carboxylates have been reported. These show interesting polymeric network or chain structures [1]. To our knowledge, however only a few of them fluoresce. We have synthesized and studied the crystal structures and characteristic luminescence of a number of europium complexes with aromatic acids and nitrogen-containing ligands [2–7]. These

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show intense fluorescence and are stable in air. Such characteristics are essential in order to study structures and luminescence properties of the complexes, to develop new fluorescent materials and to elaborate applications of luminescent probes [8]. The present paper reports the X-ray structure, luminescence spectroscopy and thermal analysis of the title complex.

EXPERIMENTAL

Preparation

A stoichiometric amount of $TbCl_3 \cdot 6H_2O$, *m*-methylbenzoic acid and 1,10-phenanthroline were dissolved separately in 95% C_2H_5OH. The pH of the *m*-methylbenzoic acid solution was adjusted to $6 \sim 7$ with 1 M NaOH solution. The C_2H_5OH solutions of two ligands were mixed and then this mixture was added dropwise to the ethanolic $TbCl_3$ solution, while a white precipitate formed. Crystals of $[Tb(m\text{-}MBA)_3phen] \cdot H_2O$ suitable for X-ray analysis were obtained from the mother liqour after a month. *Anal.* Calcd.(%): C, 56.70; H, 4.10; N, 3.67. Found: C, 57.24; H, 4.19; N, 4.07.

X-ray Structure Determination

Crystal Data

$Tb_2C_{72}H_{62}N_4O_{14}$, $M = 1525.15$, monoclinic, space group *Cc*, $a = 15.989(3)$, $b = 18.524(5)$ $c = 22.587(8)$Å, $\beta = 97.88(3)^\circ$, $V = 6626(3)$Å^3, $Z = 4$, $Dc = 1.53\ \mathrm{gcm}^{-3}$, $\lambda(\mathrm{MoK}_a) = 0.71069$ Å, $\mu = 21.81\ \mathrm{cm}^{-1}$, $F(000) = 3056.00$.

A colourless prismatic crystal with dimensions $0.20 \times 0.20 \times 0.30$ mm was mounted on a glass fibre. Intensity data were measured on a Rigaku AFC7R diffractometer at $20 \pm 1\,^\circ$C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. Data were corrected for Lorentz and polarization effects. Empirical absorption corrections were used. Of the 6157 reflections collected, 5922 were unique ($R_{\mathrm{int}} = 0.045$).

The structure was solved by the Patterson method [9] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation. The final R and R_w values were 0.023

and 0.029, respectively. Details of X-ray data collection, structure solution and refinement, F_c and F_o tables, thermal parameters, H atom positions and full lists of bond lengths and angles are available from Ruifen Wang upon request.

Thermal Analysis

TG and DTG experiments for the title complex were performed using a Perkin-Elmer TGA7 thermogravimetric analyzer. The heating rate was $10°C\,min^{-1}$ from ambient to 710°C under a nitrogen atmosphere at a flow rate of $20\,cm^3 min^{-1}$. The sample weight was 2.116 mg.

Excitation and Luminescence Measurements

Excitation and luminescence spectra of the title complex were carried out and recorded at room temperature using an MPF-4 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Structure of $[Tb(m\text{-}MBA)_3phen]_2 \cdot 2H_2O$

The molecular structure and atom numbering of the complex are shown in Figure 1. The two Tb^{3+} ions are linked by four carboxylate groups *via* bidentate bridging modes, forming a dimeric unit with a crystallographic inversion centre. Each terbium ion is coordinated to eight atoms, of which four oxygen atoms are from bridging carboxylates, two oxygen atoms from a chelating carboxylate group and two nitrogen atoms of a phenanthroline molecule.

Final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are given in Table I, and selected bond lengths and angles in Table II. In the binuclear molecule the Tb–O bond distance formed by the bridging carboxylates is slightly longer than the bond distance formed by the chelating carboxylate groups. This is similar to the case with ternary europium complexes containing benzoic acid (or its derivatives), phen (or 2,2′-bipyridine) as ligands [2–6]. In the title complex Tb–O distances is in the range 2.294(5) ~ 2.472(5)Å; the mean bond length is 2.380 Å. The average Tb–N distance is 2.595 Å, slightly shorter than corresponding average distances of 2.389 and 2.599 Å found in the complex $[Eu(m\text{-}MBA)_3phen]\cdot H_2O$ [2]. These facts indicate that the interaction between

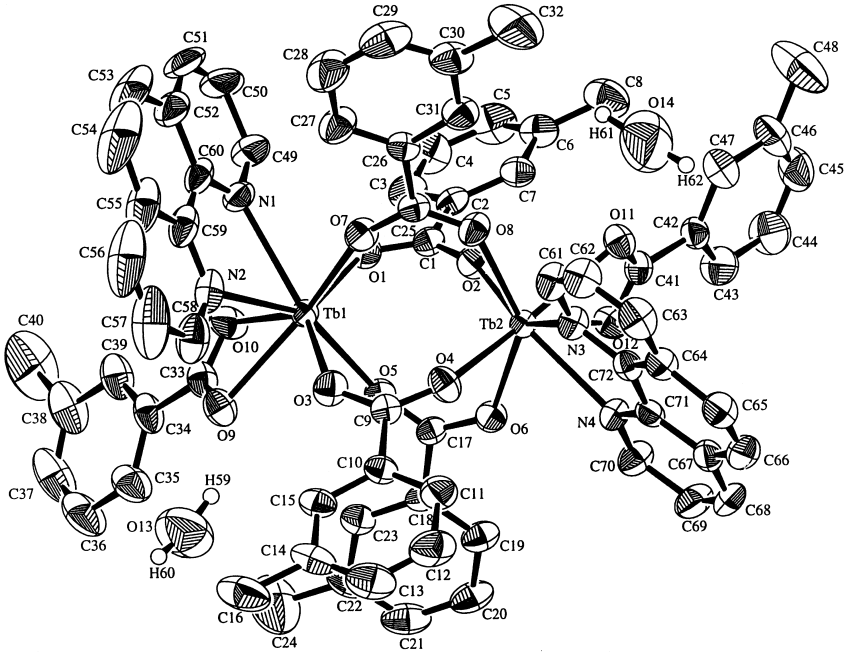

FIGURE 1 The molecular structure of the terbium complex of *m*-methylbenzoate with 1,10-phenanthroline.

TABLE I Fractional atomic coordinates and equivalent thermal parameters

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}(Å^2)$
Tb(1)	0.0233	0.10957(1)	0.0043	2.832(6)
Tb(2)	−0.16145(2)	0.18171(1)	−0.13952(2)	2.761(6)
O(1)	−0.0486(3)	0.0114(3)	−0.0406(2)	4.7(1)
O(2)	−0.1415(3)	0.0634(2)	−0.1098(2)	4.2(1)
O(3)	0.0341(3)	0.2331(3)	−0.0131(2)	4.5(1)
O(4)	−0.0677(3)	0.2597(3)	−0.0868(2)	4.4(1)
O(5)	0.0438(3)	0.1180(3)	−0.0949(2)	4.1(1)
O(6)	−0.0344(3)	0.1573(3)	−0.1775(2)	4.0(1)
O(7)	−0.1118(3)	0.1444(3)	0.0197(2)	4.3(1)
O(8)	−0.2164(3)	0.1764(3)	−0.0501(2)	4.1(1)
O(9)	0.1784(3)	0.1244(3)	0.0190(2)	4.6(1)
O(10)	0.1268(3)	0.0149(3)	0.0218(3)	4.9(1)
O(11)	−0.3058(3)	0.1449(3)	−0.1777(2)	4.1(1)
O(12)	−0.2060(3)	0.1117(2)	−0.2302(2)	4.1(l)
O(13)	0.2868(6)	0.2485(5)	0.0188(6)	12.2(4)
O(14)	−0.4437(7)	0.1890(8)	−0.1249(6)	14.0(4)
N(1)	−0.0146(4)	0.0338(3)	0.0932(3)	4.6(1)
N(2)	0.0543(4)	0.1669(4)	0.1090(3)	4.8(2)
N(3)	−0.2462(4)	0.3033(3)	−0.1331(2)	3.8(1)
N(4)	−0.1730(3)	0.2661(3)	−0.2305(2)	3.5(1)
C(1)	−0.1072(4)	0.0089(3)	−0.0835(3)	3.4(1)

TABLE I (Continued)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}(Å^2)
C(2)	−0.1394(4)	−0.0633(3)	−0.1045(3)	3.4(1)
C(3)	−0.0919(5)	−0.1252(4)	−0.0876(4)	4.7(2)
C(4)	−0.1229(7)	−0.1918(4)	−0.1051(5)	6.4(2)
C(5)	−0.2003(7)	−0.1978(5)	−0.1396(5)	6.6(3)
C(6)	−0.2503(5)	−0.1390(4)	−0.1570(3)	4.8(2)
C(7)	−0.2174(5)	−0.0706(4)	−0.1393(3)	4.0(2)
C(8)	−0.3334(7)	−0.1462(6)	−0.1918(5)	7.2(3)
C(9)	−0.0028(4)	0.2752(3)	−0.0515(3)	3.3(1)
C(10)	0.0345(4)	0.3496(4)	−0.0553(3)	3.7(1)
C(11)	−0.0059(5)	0.4004(4)	−0.0936(4)	5.3(2)
C(12)	0.0301(7)	0.4691(5)	−0.0959(5)	7.1(3)
C(13)	0.1051(7)	0.4854(5)	−0.0626(5)	6.7(3)
C(14)	0.1451(5)	0.4357(5)	−0.0251(4)	5.4(2)
C(15)	0.1102(4)	0.3670(4)	−0.0211(3)	4.2(2)
C(16)	0.2274(7)	0.4544(7)	0.0142(5)	8.2(3)
C(17)	0.0343(4)	0.1359(3)	−0.1481(3)	3.2(1)
C(18)	0.1092(4)	0.1325(3)	−0.1814(3)	3.3(1)
C(19)	0.1002(5)	0.1427(4)	−0.2433(3)	4.5(2)
C(20)	0.1693(6)	0.1389(5)	−0.2726(4)	5.7(2)
C(21)	0.2481(6)	0.1243(5)	−0.2409(5)	5.9(2)
C(22)	0.2590(5)	0.1139(4)	−0.1792(4)	5.1(2)
C(23)	0.1877(5)	0.1170(3)	−0.1507(3)	3.9(2)
C(24)	0.3455(9)	0.0969(9)	−0.1443(8)	11.4(5)
C(25)	−0.1859(4)	0.1627(4)	0.0026(3)	3.3(1)
C(26)	−0.2431(4)	0.1746(3)	0.0497(3)	3.4(1)
C(27)	−0.2124(6)	0.1704(5)	0.1094(4)	5.5(2)
C(28)	−0.2645(7)	0.1837(6)	0.1526(4)	7.2(3)
C(29)	−0.3477(7)	0.2034(6)	0.1349(5)	7.1(3)
C(30)	−0.3810(5)	0.2064(5)	0.0759(5)	5.9(2)
C(31)	−0.3277(5)	0.1927(5)	0.0325(4)	4.8(2)
C(32)	−0.4717(7)	0.2290(9)	0.0535(7)	11.1(5)
C(33)	0.1884(4)	0.0576(4)	0.0241(3)	4.2(2)
C(34)	0.2761(4)	0.0235(5)	0.0323(3)	4.8(2)
C(35)	0.3445(5)	0.0655(6)	0.0198(4)	5.9(2)
C(36)	0.4239(6)	0.0326(7)	0.0257(5)	7.6(3)
C(37)	0.4329(6)	−0.0364(7)	0.0444(6)	7.9(3)
C(38)	0.3682(6)	−0.0770(6)	0.0583(5)	7.0(3)
C(39)	0.2885(5)	−0.0455(5)	0.0516(4)	5.6(2)
C(40)	0.3819(9)	−0.1534(8)	0.0818(9)	12.6(5)
C(41)	−0.2812(4)	0.1086(3)	−0.2203(3)	3.5(1)
C(42)	−0.3425(4)	0.0620(4)	−0.2593(3)	3.7(1)
C(43)	−0.3164(6)	0.0289(5)	−0.3080(4)	5.6(2)
C(44)	−0.3714(7)	−0.0167(6)	−0.3429(4)	7.0(3)
C(45)	−0.4514(7)	−0.0278(5)	−0.3302(4)	6.7(2)
C(46)	−0.4787(5)	0.0042(5)	−0.2820(5)	6.3(2)
C(47)	−0.4229(5)	0.0500(5)	−0.2464(4)	5.3(2)
C(48)	−0.5643(8)	−0.0100(9)	−0.2681(7)	10.9(4)
C(49)	−0.0448(6)	−0.0329(5)	0.0865(4)	6.3(2)
C(50)	−0.0780(7)	−0.0690(8)	0.1336(7)	10.0(4)
C(51)	−0.0821(7)	−0.036(1)	0.1850(6)	9.9(4)
C(52)	−0.0513(6)	0.0346(8)	0.1933(4)	7.8(3)
C(53)	−0.053(1)	0.076(1)	0.2481(6)	11.7(6)
C(54)	−0.022(1)	0.141(l)	0.2539(6)	13.4(7)
C(55)	0.0172(7)	0.1733(8)	0.2091(4)	7.8(3)

TABLE I (Continued)

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}(Å^2)$
C(56)	0.058(1)	0.242(1)	0.2158(5)	11.4(5)
C(57)	0.093(1)	0.2694(7)	0.1714(6)	10.3(4)
C(58)	0.0912(7)	0.2302(4)	0.1170(4)	6.3(2)
C(59)	0.0193(5)	0.1381(6)	0.1548(3)	5.4(2)
C(60)	−0.0167(5)	0.0673(6)	0.1464(3)	5.4(2)
C(61)	−0.2794(5)	0.3239(4)	−0.0861(3)	4.5(2)
C(62)	−0.3289(5)	0.3866(4)	−0.0837(4)	4.9(2)
C(63)	−0.3462(5)	0.4269(4)	−0.1341(4)	5.2(2)
C(64)	−0.3124(4)	0.4075(3)	−0.1851(3)	4.0(2)
C(65)	−0.3259(5)	0.4480(4)	−0.2407(4)	4.9(2)
C(66)	−0.2941(5)	0.4281(4)	−0.2895(4)	5.0(2)
C(67)	−0.2405(4)	0.3650(4)	−0.2881(3)	4.1(2)
C(68)	−0.2045(6)	0.3422(5)	−0.3374(3)	5.0(2)
C(69)	−0.1534(6)	0.2834(5)	−0.3329(4)	5.4(2)
C(70)	−0.1385(5)	0.2471(4)	−0.2783(3)	4.5(2)
C(71)	−0.2238(4)	0.3248(3)	−0.2350(3)	3.4(1)
C(72)	−0.2617(4)	0.3456(3)	−0.1835(3)	3.3(1)

TABLE II Selected bondlengths (Å) and angles (°) for the complex

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Tb(1)	O(1)	2.309(5)	Tb(1)	O(3)	2.333(5)
Tb(1)	O(5)	2.313(5)	Tb(1)	O(7)	2.326(4)
Tb(1)	O(9)	2.472(5)	Tb(1)	O(10)	2.407(5)
Tb(1)	N(1)	2.590(6)	Tb(1)	N(2)	2.578(6)
Tb(2)	O(2)	2.302(5)	Tb(2)	O(4)	2.294(5)
Tb(2)	O(6)	2.355(4)	Tb(2)	O(8)	2.312(5)
Tb(2)	O(11)	2.448(5)	Tb(2)	O(12)	2.446(5)
Tb(2)	N(3)	2.643(6)	Tb(2)	N(4)	2.567(5)
O(1)	C(1)	1.253(8)	O(2)	C(1)	1.258(8)
O(3)	C(9)	1.252(8)	O(4)	C(9)	1.252(8)
O(5)	C(17)	1.236(8)	O(6)	C(17)	1.265(8)
O(7)	C(25)	1.243(8)	O(8)	C(25)	1.248(8)
O(9)	C(33)	1.251(9)	O(10)	C(33)	1.260(9)
O(11)	C(41)	1.278(8)	O(12)	C(41)	1.254(8)

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(1)	Tb(1)	O(3)	138.0(2)	O(1)	Tb(1)	O(5)	75.9(2)
O(1)	Tb(1)	O(7)	82.4(2)	O(1)	Tb(1)	O(9)	125.2(2)
O(1)	Tb(1)	O(10)	77.8(2)	O(1)	Tb(1)	N(1)	76.0(2)
O(1)	Tb(1)	N(2)	138.4(2)	O(3)	Tb(1)	O(5)	75.4(2)
O(3)	Tb(1)	O(7)	81.1(2)	O(3)	Tb(1)	O(9)	79.5(2)
O(3)	Tb(1)	O(10)	132.7(2)	O(3)	Tb(1)	N(1)	133.8(2)
O(3)	Tb(1)	N(2)	75.0(2)	O(5)	Tb(1)	O(7)	112.6(2)
O(5)	Tb(1)	O(9)	81.4(2)	O(5)	Tb(1)	O(10)	91.3(2)
O(5)	Tb(1)	N(1)	150.1(2)	O(5)	Tb(1)	N(2)	145.7(2)
O(7)	Tb(1)	O(9)	152.2(2)	O(7)	Tb(1)	O(10)	144.0(2)
O(7)	Tb(1)	N(1)	73.3(2)	O(7)	Tb(1)	N(2)	79.3(2)
O(9)	Tb(1)	O(10)	53.4(2)	O(9)	Tb(1)	N(1)	107.0(2)

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(9)	Tb(1)	N(2)	76.6(2)	O(10)	Tb(1)	N(1)	72.9(2)
O(10)	Tb(1)	N(2)	96.2(2)	N(1)	Tb(1)	N(2)	63.1(2)
O(2)	Tb(2)	O(4)	113.2(2)	O(2)	Tb(2)	O(6)	80.3(2)
O(2)	Tb(2)	O(8)	76.0(2)	O(2)	Tb(2)	O(11)	85.6(2)
O(2)	Tb(2)	O(12)	75.7(2)	O(2)	Tb(2)	N(3)	147.9(2)
O(2)	Tb(2)	N(4)	143.6(2)	O(4)	Tb(2)	O(6)	77.0(2)
O(4)	Tb(2)	O(8)	82.7(2)	O(4)	Tb(2)	O(11)	151.2(2)
O(4)	Tb(2)	O(12)	149.7(2)	O(4)	Tb(2)	N(3)	74.8(2)
O(4)	Tb(2)	N(4)	90.1(2)	O(6)	Tb(2)	O(8)	139.4(2)
O(6)	Tb(2)	O(11)	129.6(2)	O(6)	Tb(2)	O(12)	76.1(2)
O(6)	Tb(2)	N(3)	131.2(2)	O(6)	Tb(2)	N(4)	78.3(2)
O(8)	Tb(2)	O(11)	81.0(2)	O(8)	Tb(2)	O(12)	127.3(2)
O(8)	Tb(2)	N(3)	74.3(2)	O(8)	Tb(2)	N(4)	136.9(2)
O(11)	Tb(2)	O(12)	53.5(2)	O(11)	Tb(2)	N(3)	78.0(2)
O(11)	Tb(2)	N(4)	85.8(2)	O(12)	Tb(2)	N(3)	113.9(2)
O(12)	Tb(2)	N(4)	70.9(2)	N(3)	Tb(2)	N(4)	62.9(2)

europium ion and oxygen and nitrogen atoms in $[Eu(m\text{-}MBA)_3phen]\cdot H_2O$ is weaker than that in $[Tb(m\text{-}MBA)_3phen]\cdot H_2O$. This is possibly related to $r(Tb^{3+})$ being less than $r(Eu^{3+})$. Compared with the binuclear molecule $Eu(p\text{-}MBA)_3phen$ [3], the title complex has a similar bridging structure, as the Eu–O and the Tb–O average distances both are 2.380 Å. Average Eu–N is 2.626 Å, longer than average Tb–N, 2.595 Å. This is possibly caused by electronic effects of the methyl substituent on the benzene ring and steric effects.

In the carboxylate groups, C–O distances differ significantly; coordination causes lengthening of C–O [1.251(9)–1.278(8)Å] for the bidentate-chelating carboxylate groups in comparison to the bidentate-bridging carboxylate groups [1.236(8)–1.265(8)Å]. This is the same as in the ternary complex $[Eu(BA)_3dmbpy]_2$ (BA = benzoate, dmbpy = 4,4′-dimethyl-2,2′-bipyridine) [5]. The O(9)–C(33)–O(10) [O(11)–C(41)–O(12)] angle in the bidentate-chelating carboxylate group is 121.9(6)° [120.7(6)°]. The O(3)–C(9)–O(4) [O(5)–C(l7)–O(6), O(1)–C(l)–O(2), O(7)–C(25)–O(8)] angle in the bidentate bridging carboxylate group is 124.6(6)° [125.1(6), 124.5(6), 125.7(6)°]. This is characteristic of chelating carboxylate groups and bridging carboxylate groups. The five atoms of the chelate ring containing the two chelated nitrogen atoms and the terbium ion are coplanar in the dimer since the 1,10-phenanthroline molecule is rigid.

Thermal Decomposition

Thermoanalytical data for the complex are given in Table III. The Tb(III) complex decomposes *via* intermediates to give terbium oxide as end product.

TABLE III Thermal decomposition data for $[Tb(m\text{-}MBA)_3phen]_2 \cdot 2H_2O$ under nitrogen

	Temperature	*DTG peak*	*Loss of mass/wt%*		*Probable composition*	
Stage	*range/°C*	*temperature/°C*	*TG*	*Theory*	*of expelled groups*	*Intermediate*
I	197 ~ 410	269	26.26	25.99	$2H_2O$, $2C_{12}H_8N_2$	$[Tb(m\text{-}MBA)_3]_2$
II	410 ~ 630	506, 538	48.45	49.50	6(*m*-MBA)-3.5O	$(1/2)Tb_4O_7$
			74.71*	75.49*		

* Totol mass loss.

The results indicate that the complex begins to decompose at 197°C and decomposition ends at 630°C. The TG reveals two decomposition stages, as predicted by the DTG curve and there are weight losses with maximum rate at 269, 506 and 538°C in the DTG curve. The first, from 197 to 410°C with a mass loss 26.26 wt%, corresponds to the loss of 2 mol of $C_{12}H_8N_2$ and 2 mol of H_2O (theoretical loss is 25.99 wt%). In the structure (Tab. II). Tb – N distance is longer than any other bond distance and this bond seems thus to be less stable. The second degradation occurs in the range 410 ~ 630°C with a mass loss of 48.45 wt%, in which $6CH_3C_6H_4COO$-3.5O is removed with theoretical loss of 49.50 wt%. 1,10-Phenanthroline-*tris*(*m*-methylbenzoate) terbium(III) is completely degraded into Tb_4O_7 with a total loss of 74.71 wt% (theoretical loss 75.49 wt%).

Luminescence Properties

Excitation and luminescence spectra of the title complex were recorded at room temperature. Excitation of $[Tb(m\text{-}MBA)_3phen]_2 \cdot 2H_2O$ was effected in a range 240 ~ 400 nm. Fluorescence was observed in a range of 400 ~ 700 nm by selective excitation at 320 nm. There are four emission peaks in the luminescence spectra, centred at 492, 549, 590 and 624 nm. The bands originate from the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transition of the Tb^{3+} ion, respectively. The intensity of the luminescence band arising from the $^5D_4 \rightarrow {}^7F_5$ transition is most intense. Luminescence properties of $[Tb(m\text{-}MBA)_3phen]_2 \cdot 2H_2O$ are very similar to $Tb(N\text{-}PA)_3phen \cdot 2H_2O$ (*N*-PA: *N*-phenylanthranilic acid anion) [10].

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