ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 11, pp. 864–867. © Pleiades Publishing, Ltd., 2009.

Bis(μ_2-1-Carboxybenzene-2-Carboxylato)diaqua(monohydrogen Phthalato)-(1,10-Phenanthroline)samarium(III): Hydrothermal Synthesis and Crystal Structure[1]

L. C. Yu*, L. Lai, S. L. Liu, and Y. Xia

College of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangta 411201, P.R. China

**E-mail: ylcphd@163.com*

Received December 8, 2008

Abstract—A new lanthanide complex $[\{Sm(HPht)(Phen)(H_2O)_2\}_2(\mu\text{-}Pht)_2]$ (I), where Pht^{2-} is dianion of *o*-phthalic acid; $HPht^-$ is monoanion of *o*-phthalic acid; Phen is 1,10-phenanthroline, has been synthesized, and its crystal structure was determined by X-ray crystallography. Complex I crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 10.1126(3)$, $b = 10.7029(3)$, $c = 11.9360(3)$ Å, $\alpha = 90.2260(10)°$, $\beta = 99.526(2)°$, $\gamma = 100.9810(10)°$, $V = 1249.87(6)$ Å^3, $Z = 2$, $\rho_c = 1.849$ mg/m^3, final R indices $I > 2\sigma(I)$: $R_1 = 0.0202$, $wR_2 = 0.0493$; R indices (all data): $R_1 = 0.0220$, $wR_2 = 0.0504$.

DOI: 10.1134/S1070328409110128

INTRODUCTION

Lanthanide ions are known for their luminescence properties, which make them interesting candidates for luminescence applications, such as bioactive probes for magnetic resonance and luminescence [1–7]. Since the emission mechanism is based on *f–f* transitions with consequent narrow bandwidth and no theoretical cap on the quantum efficiency, they are especially interesting candidates for LED (liquid electronic display) applications. The *f–f* transitions are spin and parity forbidden, and to exploit the luminescent properties, ligands that function as sensitizers are used. Benzoic acid and its derivatives have been described as efficient sensitizers for lanthanide emission [8–11]. Of the numerous lanthanide complexes with carboxylate ligands widely studied, most possess a variety of dimeric or infinite chain structures in which the carboxylate groups act as bridges between metal atoms, and the number of bridging carboxylate groups varies in different complexes [12]. Aromatic polycarboxylic acids, such as 2,6-naphthalenedicarboxylic acid [13], 1,4-benzenedicarboxylic acid [14], and 1,3-benzenedicarboxylic acid [15, 16] were used extensively in the synthesis of coordination polymers, whereas the utilization of 1,2-benzenedicarboxylic acid, monobenzoate and derivatives to construct polymeric Ln(III) complexes is much less well known, although several examples have been reported recently [17, 18].

In this paper, a dimeric complex $[\{Sm(HPht)(Phen)(H_2O)_2\}_2(\mu\text{-}Pht)_2]$ (**I**), where Pht^{2-} is dianion of *o*-phthalic acid; $HPht^-$ is monoanion of *o*-phthalic acid; Phen is 1,10-phenanthroline has been synthesized through the hydrothermal reaction, and its crystal structure has been investigated.

EXPERIMENTAL

Synthesis of I. $Sm(NO_3)_3 \cdot 6H_2O$ (0.1370 g, 0.3 mmol), KHPhth (potassium biphthalate, 0.0920 g, 0.45 mmol), and Phen (0.0590 g, 0.3 mmol) were mixed in 10 ml of deionized water. After being stirred half an hour, the mixture was placed in a 25-ml teflon-lined reactor, heated at 160°C in an oven for 3 days, and cooled slowly to room temperature, and the pink block crystals of complex **I** suitable to X-ray diffraction analysis were obtained. IR spectrum exhibits a complicated pattern of bands in the range 4000–400 cm^{-1}: 1417 cm^{-1} ($\nu_s COO^-$), 1545 cm^{-1} ($\nu_{as} COO^-$).

The X-ray single crystal data collections for complex **I** was performed on a Bruker Smart CCD diffractometer equipped with a graphite monochromator MoK_α radiation ($\lambda = 0.71073$ Å). Multiscan absorption correction was applied using the SADABS program [19]. The structure was solved by a direct method using the SHELXS-97 program [20]. Refinement on F^2 was performed using SHELXL-97 [21] by a full-matrix least-squares method with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms of the ligands were generated geometrically, while the H

---

[1] The article is published in the original.

Table 1. Selected bond distances and bond angles for compound **I***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Sm(1)–N(1)	2.563(2)	Sm(1)–N(2)	2.527(2)	Sm(1)–O(1)	2.332(2)
Sm(1)–O(5)	2.3819(18)	Sm(1)–O(6)	2.4886(19)	Sm(1)–O(7*A*)	2.4043(19)
Sm(1)–O(8*A*)	2.448(2)	Sm(1)–O(9)	2.409(2)	Sm(1)–O(10)	2.3098(18)
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
N(2)Sm(1)N(1)	64.66(7)	O(5)Sm(1)O(6)	53.42(6)	O(7A)Sm(1)O(8*A*)	53.81(7)
O(10)Sm(1)O(1)	83.78(8)	O(10)Sm(1)O(5)	130.33(7)	O(1)Sm(1)O(5)	87.36(7)
O(10)Sm(1)O(7*A*)	131.71(7)	O(1)Sm(1)O(7*A*)	143.44(7)	O(5)Sm(1)O(7*A*)	75.61(7)
O(10)Sm(1)O(9)	74.97(7)	O(1)Sm(1)O(9)	137.67(8)	O(5)Sm(1)O(9)	79.67(7)
O(7*A*)Sm(1)O(9)	71.28(7)	O(10)Sm(1)O(8*A*)	84.05(8)	O(1)Sm(1)O(8*A*)	140.91(7)
O(5)Sm(1)O(8*A*)	127.79(7)	O(9)Sm(1)O(8*A*)	73.20(8)	O(10)Sm(1)O(6)	77.99(7)
O(1)Sm(1)O(6)	68.88(7)	O(7*A*)Sm(1)O(6)	120.37(6)	O(9)Sm(1)O(6)	71.09(7)
O(8*A*)Sm(1)O(6)	143.07(8)	O(10)Sm(1)N(2)	140.02(7)	O(1)Sm(1)N(2)	72.16(7)
O(5)Sm(1)N(2)	80.92(7)	O(7*A*)Sm(1)N(2)	73.33(7)	O(9)Sm(1)N(2)	142.82(7)
O(8*A*)Sm(1)N(2)	94.77(8)	O(6)Sm(1)N(2)	119.58(7)	O(10)Sm(1)N(1)	77.70(8)
O(1)Sm(1)N(1)	71.26(7)	O(5)Sm(1)N(1)	143.46(7)	O(8A)Sm(1)N(1)	69.88(7)

* Coordinates of atoms A: $-x + 1$, $-y$, $-z + 1$.

atoms of the coordination water molecules were located from Fourier difference synthesis and refined with restraints.

Selected bond distances and bond angles for compounds **I** are listed in Table 1. The ORTEP drawing of **I** is shown in Fig. 1. Crystallographic data for com-

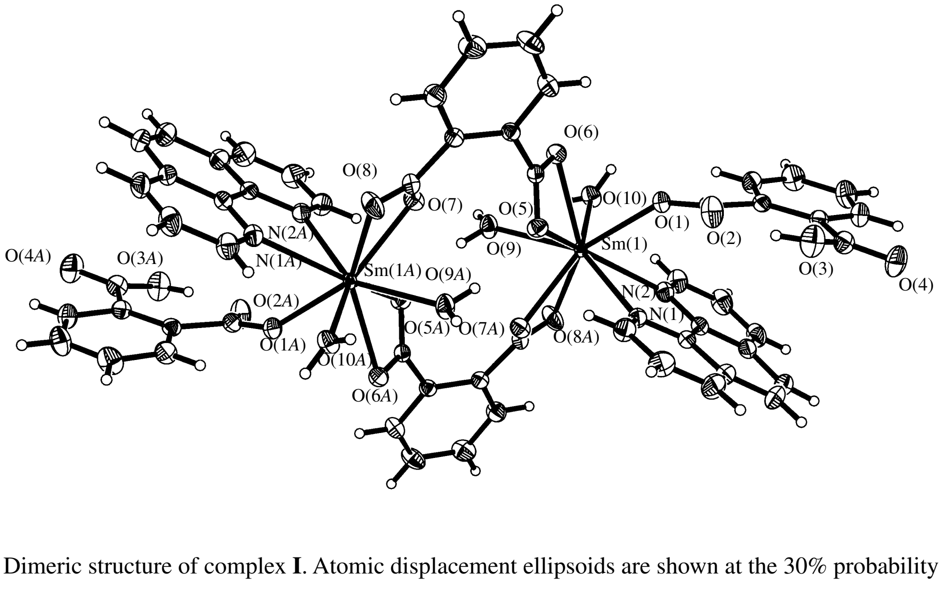

Fig. 1. Dimeric structure of complex **I**. Atomic displacement ellipsoids are shown at the 30% probability level.

Table 2. Intra- and intermolecular hydrogen bond geometry for structure **I***

Contect D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(3)–H(3*A*)···O(2)	0.82(5)	1.58(5)	2.388(3)	169(7)
O(9)–H(9*A*)···O(5)$^{\#1}$	0.86(2)	2.07(2)	2.904(3)	164(5)
O(9)–H(9*B*)···O(3)$^{\#2}$	0.86(2)	2.02(3)	2.881(3)	176(5)
O(10)–H(10*A*)···O(4)$^{\#2}$	0.87(2)	1.80(3)	2.661(3)	169(5)
O(10)–H(10*B*)···O(6)$^{\#1}$	0.86(4)	1.95(3)	2.806(3)	175(5)
C(1)–H(1)···O(10)	0.93	2.46	3.065(4)	123
C(11)–H(11)···O(2)$^{\#3}$	0.93	2.47	3.354(4)	158
C(12)–H(12)···O(5)	0.93	2.48	3.116(4)	125
C(15)–H(15)···O(1)	0.93	2.33	2.687(4)	102
C(15)–H(15)···O(6)$^{\#4}$	0.93	2.53	3.342(4)	147
C(18)–H(18)···O(4)	0.93	2.29	2.663(4)	103

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $1 - x, -y, 1 - z$; $^{\#2}$ $-x, -y, 1 - z$; $^{\#3}$ $1 - x, 1 - y, 1 - z$; $^{\#4}$ $x, -1 + y, z$.

pound **I** was deposited with the Cambridge Crystallographic Data Center (no. 707666; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The title complex **I** crystallizes in the triclinic system, with space group $P\bar{1}$. The two Sm^{3+} ions are both equivalent in the same coordination environment and so there is only one type of metal configuration. Each central Sm^{3+} ion is nine-coordinated, whose coordination geometry can be described as a distorted square monoantiprism. Among the nine coordinations, four oxygen atoms are from the two bridging Pht^{2-} groups (for Sm(1) ion, O(5), O(6) from one chelate-bridging Pht^{2-} and O(7*A*), O(8*A*) from the symmetric Pht^{2-} with the bond distances of 2.3819(18)–2.4886(19) Å for Sm(1)–O, and one oxygen atom is from the $HPht^{-}$ group (O(1) for Sm(1)), whose bond distance is shorter (2.332(2) Å). Besides this, there are other two coordinated oxygen atoms from the two water molecules (O(9) and O(10)) with bond distances of 2.409(2) Å for Sm(1)–O(9) and 2.3098(18) Å for Sm(1)–O(10). One bidentate Phen provides two nitrogen atoms chelated to the Sm^{3+} ion, whose bond distances are 2.563(2) and 2.527(2) Å. The bond angles consisting of Sm(III) and the oxygen atoms from the Pht^{2-} ions range from 53.42(6)° to 53.81(7)°; the bond angle consisting of Sm(III) and the two nitrogen atoms is 64.66(7)°. The distance of Sm(1)–Sm(1*A*) in the dimeric unit was determined to be 5.855 Å.

Two types of coordination modes of the Pht^{2-} and $HPht^{-}$ ligands exist in the molecular structure of the binuclear complex: (1) tetradentate *bis*(chelating) bridging, the Pht^{2-} anions are completely deprotonated and all four oxygen atoms take part in the coordination to the two central metal ions and the Sm^{3+} ions are connected into dinuclear structure by this coordination mode, and (2) monodentate coordination, the $HPht^{-}$ anions merely lose one proton and the deprotonated carboxylic acid group provides one carbonyl oxygen atom coordinated with the Sm^{3+} ion. There are rich intramolecular hydrogen bonds (Table 2). The unit cell (Fig. 2) diagram indicates that there are four types of intermolecular hydrogen bonds. The first type is formed between the oxygen atom of the bridging Pht^{2-} ligand and the oxygen atom of the coordinated water molecules in the adjacent molecular unit, such as O(9)–H(9*A*)···O(5)$^{\#1}$ and O(10)–H(10*B*)···O(6)$^{\#1}$. The second

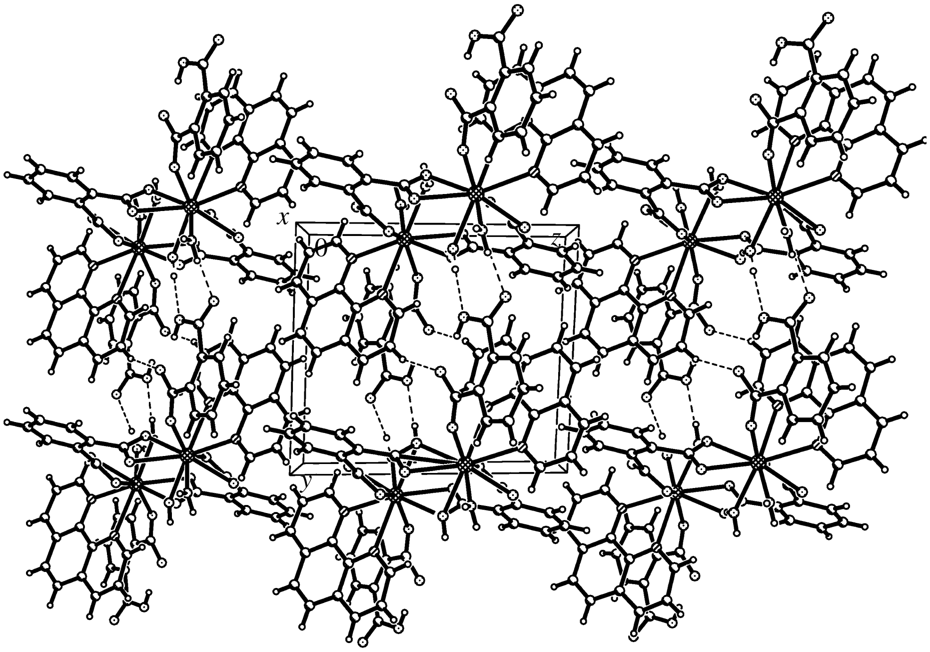

Fig. 2. Crystal packing perspective view of **I** showing supramolecular weak interaction of hydrogen bonds.

type is formed between the oxygen atom of the coordinated water molecule and the oxygen atom of the $HPht^-$ group from an adjacent molecule, such as O(9)–H(9*B*)···O(3)$^{\#2}$ and O(10)–H(10*A*)···O(4)$^{\#2}$. The third one is formed between the O atom of the Pht^{2-} group and the C atom of $HPht^-$ C(15)–H(15)···O(6)$^{\#4}$ from adjacent molecular units. The forth one is formed between the O atom of $HPht^-$ and the C atom of the Phen molecule C(11)–H(11)···O(2)$^{\#3}$ from an adjacent molecule (Table 2). The intermolecular hydrogen bonds link up the complex to form a 3D network.

ACKNOWLEDGMENTS

This work was supported by the Scientific Research Fund of the Hunan Provincial Education Department (08c340) and the Foundation of the Hunan University of Science and Technology (E55106).

REFERENCES

1. Parker, D., *Chem. Soc. Rev.*, 2004, vol. 33, p. 156.
2. Aspinall, H.C., *Chem. Rev.*, 2002, vol. 102, p. 1807.
3. Yan, B., Zhang, H.J., Wang, S.B., and Ni, J.Z., *Mater. Res. Bull.*, 1998, vol. 33, p. 1517.
4. Lis, S., Hnatejko, Z., Barczynski, P., and Elbanowski, M.J., *Alloys. Compd.*, 2002, vol. 344, p. 70.
5. Scott, L.K. and Horrock, W.D., *J. Inorg. Biochem.*, 1992, vol. 46, p. 193.
6. Wang, Z.M., van de Burget, L.J., and Choppin, G.R., *Inorg. Chim. Acta*, 1996, vol. 293, p. 167.
7. Dickins, R.S., Aime, S., Batsanov, A.S., et al., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 12697.
8. Barja, B., Baggio, R., Garland, M.T., et al., *Inorg. Chim. Acta*, 2003, vol. 346, p. 187.
9. Wang, Z., Strobele, M., Zhang, K.L., et al., *Inorg. Chem. Commun.*, 2002, vol. 5, p. 230.
10. Wan, Y., Zhang, L., Jin, L., et al., *Inorg. Chem.*, 2003, vol. 42, p. 4985.
11. Wan, Y., Jin, L., Wang, K., et al., *New J. Chem.*, 2002, vol. 26, p. 1590.
12. Serre, C., Millange, F., Thouvenot, C., et al., *J. Mater. Chem.*, 2004, vol. 14, p. 1540.
13. Wei, P.R., Wu, D.D., Zhou, Z.Y., et al., *Polyhedron.*, 1997, vol. 16, p. 749.
14. Rosi, N.L., Eddaoudi, M., Kim, J., et al., *Angew. Chem. Int. Ed.*, 2002, vol. 41, p. 284.
15. Bourne, S.A., Lu, J.J., Mondal, A., et al., *Angew. Chem. Int. Ed.*, 2001, vol. 40, p. 2111.
16. Zheng, C.G., Zhang, J., Chen, Z.F., et al., *J. Coord. Chem.*, 2002, vol. 55, p. 835.
17. Zhang, L.P., Wan, Y.H., and Jin, L.P., *Polyhedron.*, 2003, vol. 22, p, 981.
18. Roh, S.G., Nah, M.K., Oh, J.B., et al., *Polyhedron.*, 2005, vol. 24, p. 137.
19. Sheldrick, G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector Data,* Göttingen (Germany): Univ. of Göttingen, 1996.
20. Sheldrick, G.M., *SHELXS-97*, *Program for Crystal Structure Solution*, Göttingen (Germany): Univ. of Göttingen, 1997.
21. Sheldrick, G.M., *SHELXL-97*, *Program for Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.