*ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 1, pp. 126–129. © Pleiades Publishing, Ltd., 2013.*

# Syntheses, Crystal Structure, and Fluorescent Properties of a Lanthanide Complex[1]

**X. H. Zhao and H. M. Peng**

*Key Laboratory of Green Packaging and Application Biological Nanotechnology of Hunan Province,*
*Hunan University of Technology, Zhuzhou, 412008 P.R. China*
**e-mail: ylcphd2011@163.com*

Received July 18, 2011

**Abstract**—A new complex $[Dy_2(Pht)_2(HPht)_2(Phen)_2(H_2O)_4]$ (**I**), where $Pht^{2-}$ = dianion of *o*-phthalic acid; $HPht^-$ = mono-anion of *o*-phthalic acid; Phen = 1,10-phenanthroline, has been synthesized and the crystal structure was determined by X-ray crystallography. The **I** crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a$ =10.1126(3) Å, $b$ =10.7029(3) Å, $c$ = 11.9360(3) Å, $\alpha$ = 90.2260(10)°, $\beta$ = 99.5340(10)°, $\gamma$ = 100.9810(10)°, $V$ = 1249.87(6) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.881 mg m$^{-3}$. The photophysical property of **I** has been studied with excitation and emission spectra.

**DOI:** 10.1134/S1070328412110085

## INTRODUCTION

Lanthanide complexes have received much attention because of their interesting photophysical properties which have potential application in the luminescence probes for chemical or biological macromolecules and the active center for luminescent materials. 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 [1]. Aromatic polycarboxylic acids such as 2,6-naphthalenedicarboxylic acid [2], 1,4-benzenedicarboxylic acid [3], and 1,3-benzenedicarboxylic acid [4, 5] were used extensively in the synthesis of coordination polymers, whereas utilization of 1,2-benzenedicarboxylic acid to construct polymeric Ln(III) complexes is much less well known, although several examples have been reported recently [6]. In this paper, $[Dy_2(Pht)_2(HPht)_2(Phen)_2(H_2O)_4]$ (**I**), where $H_2Pht$—*o*-phthalic acid, Phen—1,10-phenanthroline, has been synthesized through a hydrothermal reaction, and the crystal structure and photoluminescence properties have been investigated.

## EXPERIMENTAL

**Synthesis of I.** $Dy(NO_3)_3 \cdot 6H_2O$ (0.3 mmol), KHPhth (potassium biphthalate, 0.45 mmol), and Phen (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 white block crystals of the title complex of **I** suitable to X-ray diffraction analysis were obtained.

For $C_{28}H_{21}N_2O_{10}Dy$ (**I**)

| | | | |
|---|---|---|---|
| anal calcd., %: | C, 47.46; | H, 2.97; | N, 3.95. |
| Found, %: | C, 47.44; | H, 3.01; | N, 3.96. |

IR spectrum (KBr; ν, cm$^{-1}$): 3402 s, 3064 w, 2344 w, 1957 m, 589 m, 1538 s, 1520 m, 1449 m, 1424 m, 1386 s, 1172 s, 1040 m, 851 s, 754 s, 732 s, 590 m.

All reagents were commercially available and used without further purification. C, H, and N analysis data were obtained using an American PE 2400II CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. Excitation and emission spectra for the solid state of complex **I** were measured with an F-4500 FL mode spectrophotometer at room temperature.

Data collection for complex **I** was performed on a Bruker SMART APEXII CCD area detector equipped with a graphite monochromator (Mo$K_\alpha$ radiation, $\lambda$ = 0.71073 Å). Multi-scan absorption corrections were applied using the SADABS program [7]. The structure was solved by a direct method using the SHELXS-97 program [8]. Refinements on $F^2$ were performed using SHELXL-97 [9] by a full-matrix least-squares method with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms of the ligand were generated geometrically, while the H atoms of the coordination water molecules were located from difference Fourier synthesis and refined with restraints. A summary of crystallographic data and refinement parameters is given in Table 1. The atomic coordinates and other parameters of

---

[1] The article is published in the original.

**Table 1.** Crystal data and structure refinement parametes for **I**

| Parameter | Value |
|---|---|
| Formula weight | 707.97 |
| Crystal system | Triclinic |
| Space group | $P\overline{1}$ |
| Crystal size, mm | 0.30 × 0.27 × 0.25 |
| $a$, Å | 10.1126(3) |
| $b$, Å | 10.7029(3) |
| $c$, Å | 11.9360(3) |
| α, deg | 90.2260(10) |
| β, deg | 99.5340(10) |
| γ, deg | 100.9810(10) |
| $V$, Å$^3$ | 1249.87(6) |
| $Z$ | 2 |
| $\rho_{calcd}$, mg/m$^3$ | 1.881 |
| $F$(000) | 698 |
| Temperature, K | 296(2) |
| Limiting indices $h, k, l$ | $-12 \le h \le 7, -8 \le k \le 12,$<br>$-14 \le l \le 14$ |
| Reflection collected | 9894 |
| Independent reflections ($R_{int}$) | 0.0139 |
| Reflections with $I > 2\sigma(I)$ | 5670 |
| Parameters | 390 |
| Completeness, % | 97.8 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0146$, $wR_2 = 0.0344$ |
| $R$ indices (all data) | $R_1 = 0.0156$, $wR_2 = 0.0350$ |
| Goodness-of-fit on $F^2$ | 1.021 |
| $\Delta\rho_{min}/\Delta\rho_{max}$, $e$ Å$^{-3}$ | −0.561 and 0.519 |

structure **I** have been deposited with the Cambridge Crystallographic Center (no. 707667; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

Selected bond distances (Å) and bond angles (deg) for complex **I** are listed in Table 2. The ORTEP drawing of **I** is shown in Fig. 1. Central $Dy^{3+}$ ion is nine-coordinated, whose coordination geometry can be described as a distorted square monoantiprism. Among the nine coordination, four oxygen atoms are from the two bridging $Pht^{2-}$ groups (for Dy(1) ion, O(5), O(6) from one bridging $Pht^{2-}$ and O(7*A*), O(8*A*) from the other bridging $Pht^{2-}$ with the bond distances of 2.3818(14)–2.4898(15) Å between the $Dy^{3+}$ ion and the oxygen atoms), and one oxygen atom is from the chelating $HPht^{-}$ group (O(1) for Dy(1)), whose bond distance is shorter (2.3334(16) Å). Besides this, there are another two coordinated oxygen atoms from the two water molecules (O(9) and O(10)) with bond distances of 2.4082(16) Å for Dy(1)–O(9) and 2.3100(15) Å for Dy(1)–O(10). One terminal Phen provides two nitrogen atoms chelated to $Dy^{3+}$ ion whose bond distances are 2.5639(18) and 2.5260(18) Å, respectively. The bond angles consisting of Dy(III) and the oxygen atoms from the bridging $Pht^{2-}$ molecules range in 53.36(5)°–53.78(5)°; the bond angle consisting of Dy(III) and the two nitrogen atoms is 64.66(6)°. The distance of Dy(1)–Dy(1*A*) in the dimeric unit was determined to be 5.856 Å. Two types of coordination modes of $Pht^{2-}$

**Table 2.** Selected bond distances (Å) and bond angles (deg) for complex **I**

| Bond | $d$, Å | Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|---|---|
| Dy(1)–N(1) | 2.5639(18) | Dy (1)–N(2) | 2.5260(18) | Dy(1)–O(1) | 2.3334(16) |
| Dy (1)–O(5) | 2.3818(14) | Dy (1)–O(6) | 2.4898(15) | Dy (1)–O(7*A*) | 2.4015(15) |
| Dy (1)–O(8*A*) | 2.4465(18) | Dy (1)–O(9) | 2.4082(16) | Dy (1)–O(10) | 2.3100(15) |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| N(2)Dy(1)N(1) | 64.66(6) | O(6)Dy(1)O(5) | 53.36(5) | O(7*A*)Dy(1)O(8*A*) | 53.78(5) |
| O(10)Dy(1)O(1) | 83.79(6) | O(1)Dy(1)O(5) | 87.31(6) | O(1)Dy(1)O(7*A*) | 143.41(5) |
| O(10)Dy(1)O(9) | 74.91(6) | O(5)Dy(1)O(9) | 79.72(6) | O(10)Dy(1)O(8*A*) | 84.04(6) |
| O(10)Dy(1)O(6) | 77.97(6) | O(1)Dy(1)O(6) | 68.96(5) | O(9)Dy(1)N(1) | 135.73(6) |
| O(6)Dy(1)N(1) | 135.03(5) | O(10)Dy(1)N(2) | 140.04(6) | O(1)Dy(1)N(2) | 72.15(6) |
| O(8*A*)Dy(1)N(1) | 69.93(6) | O(9)Dy(1)N(2) | 142.86(6) | O(5)Dy(1)N(2) | 80.91(5) |

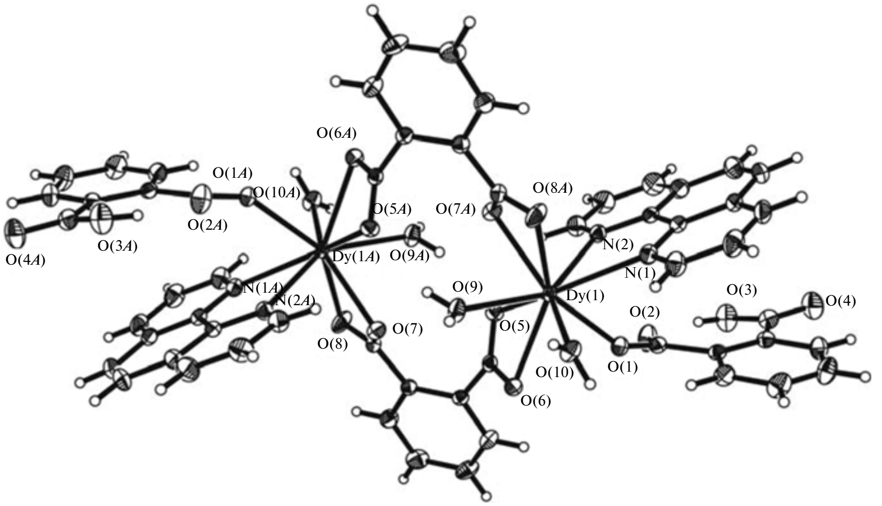

**Fig. 1.** Crystallographically independent structure fragment in complex **I**. Atomic displacement ellipsoids are shown at the 30% probability level.

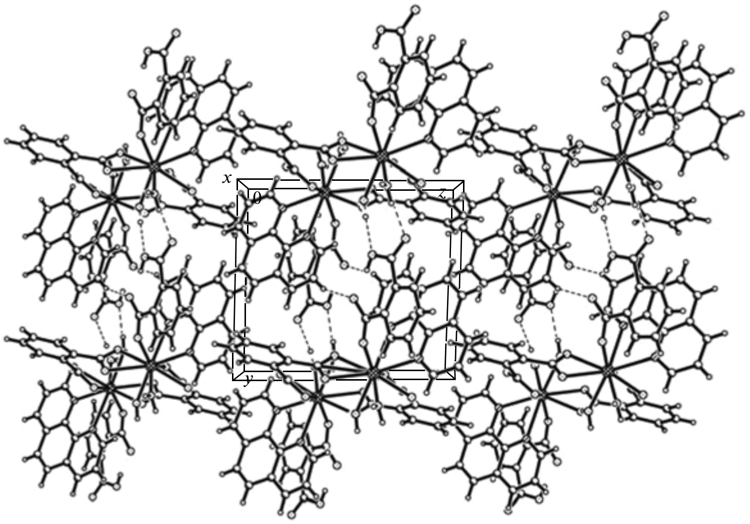

**Fig. 2.** Crystal packing perspective view of **I** along *x* axis showing supramolecular weak aromatic π–π stacking interactions and hydrogen-bonding.

and $HPht^-$ ligands exist in the molecular structure of the dinuclear complex: (1) bidentate bridging, the $Pht^{2-}$ anions are completely deprotonated and all the oxygen atoms take part in the coordination to the two central metal ions and the $Dy^{3+}$ 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 $Dy^{3+}$ ion. There are rich intra-molecular hydrogen bonds, such as O(3)–H(3*A*)···O(2) 2.389(3), C(1)–H(1)···O(10) 3.068(3), C(12)–H(12)···O(5) 3.117(3), C(15)–H(15)···O(1) 2.689(3), and C(18)–H(18)···O(4) 2.664(3) Å. 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)$^{\#1}$ 2.910(2) Å and O(10)–H(10*B*)···O(6)$^{\#1}$ 2.807(2) Å. The second type is formed between the oxygen atom of coordinated water molecule and the oxygen atom of $HPht^-$ group from an adjacent molecule, such as O(9)–H(9*B*)···O(3)$^{\#2}$ 2.881(2) Å and O(10)–H(10*A*)···O(4)$^{\#2}$ 2.660(2) Å. The third one is formed between the O atom of $Pht^{2-}$ group and C atom of $HPht^-$ C(15)–H(15)···O(6)$^{\#4}$ 3.341(3) Å, $Pht^{2-}$ from adjacent molecular units. The forth one is

**Table 3.** Geometric parameters of hydrogen bonds for **I***

| Contact D–H···A | Distance, Å | | | Angle DHA, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| O(3)–H(3*A*)···O(2) | 0.83(3) | 1.56(2) | 2.389(3) | 170(4) |
| O(9)–H(9*A*)···O(5)$^{\#1}$ | 0.854(17) | 2.083(15) | 2.910(2) | 163(3) |
| O(9)–H(9*B*)···O(3)$^{\#2}$ | 0.856(18) | 2.027(18) | 2.881(2) | 176.9(11) |
| O(10)–H(10*A*)···O(4)$^{\#2}$ | 0.856(17) | 1.808(17) | 2.660(2) | 173(3) |
| O(10)–H(10*B*)···O(6)$^{\#1}$ | 0.87(2) | 1.95(2) | 2.807(2) | 172(3) |
| C(1)–H(1)···O(10) | 0.93 | 2.47 | 3.068(3) | 123 |
| C(11)–H(11)···O(2)$^{\#3}$ | 0.93 | 2.48 | 3.364(4) | 158 |
| C(12)–H(12)···O(5) | 0.93 | 2.49 | 3.117(3) | 125 |
| C(15)–H(15)···O(1) | 0.93 | 2.33 | 2.689(3) | 102 |
| C(15)–H(15)···O(6)$^{\#4}$ | 0.93 | 2.52 | 3.341(3) | 147 |
| C(18)–H(18)···O(4) | 0.93 | 2.29 | 2.664(3) | 103 |

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

formed between the O atom of $HPht^-$ and the C atom of Phen molecule C(11)–H(11)···O(2)$^{\#3}$ from adjacent molecular units (Table 3). The intermolecular hydrogen bonds link up the complex to form a 3D network.

We measured the emission spectra by excitation with the wavelength of 330 nm. Fig. 3 gives the emission spectra of **I**, which shows two emission bands at 478 and 570 nm, respectively, corresponding to the characteristic emission originating from the $^4F_{9/2} \to {}^6H_{15/2}$ and $^4F_{9/2} \to {}^6H_{13/2}$ transitions of $Dy^{3+}$ ion. The $^4F_{9/2} \to {}^6H_{15/2}$ transition exhibits blue emission and $^4F_{9/2} \to {}^6H_{13/2}$ transition shows yellow emission also. The relative intensity of $^4F_{9/2} \to {}^6H_{13/2}$ is 2.25 times as that of $^4F_{9/2} \to {}^6H_{15/2}$ in **I**.

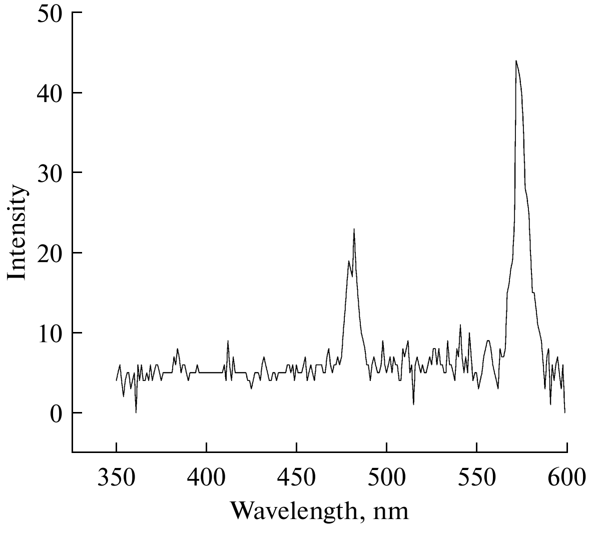

**Fig. 3.** Emission spectrum of **I**.

## ACKNOWLEDGMENTS

The author acknowledges the financial supports from National Natural Scientific Foundation of China (no. 50874041) and from Natural Science Foundation of Hunan (no. 08JJ5036).

## REFERENCE

1. Wei, P.R., Wu, D.D., Zhou, Z.Y., et al., *Polyhedron*, 1997, no. 16, p. 749.
2. Rosi, N.L., Eddaoudi, M., and Kim, J., *Angew. Chem. Int. Ed.*, 2002, no. 41, p. 284.
3. Bourne, S.A., Lu, J.J., and Mondal, A.B., *Angew. Chem., Int. Ed.*, 2001, no. 40, p. 2111.
4. Zheng, C.G., Zhang, J., Chen, Z.F., et al., *J. Coord. Chem.*, 2002, no. 55, p. 835.
5. Zhang, L.P., Wan, Y.H., and Jin, L.P., *Polyhedron*, 2003, no. 22, p. 981.
6. Roh, S.G., Nah, M.K., Oh, J.B., et al., *Polyhedron*, 2005, no. 24, p. 137.
7. Sheldrick, G.M., *SADABS*, *Program for Empirical Absorption Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1996.
8. Sheldrick, G.M., *SHELXS-97*, *Program for Crystal Structure Solution*, Göttingen (Germany): Univ. of Göttingen, 1997.
9. Sheldrick, G.M., *SHELXL-97*, *Program for Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.