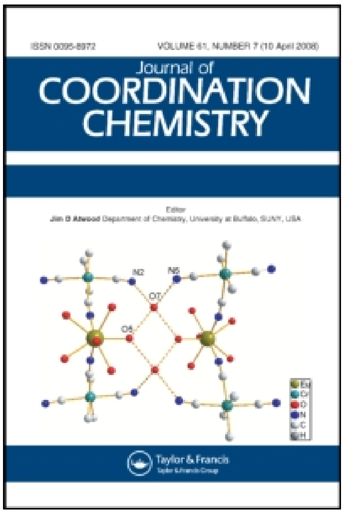

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# Synthesis, crystal structure and properties of three ternary dysprosium 2-halogenated benzoic acid complexes

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Three ternary dysprosium complexes $[Dy(2\text{-ClBA})_3\cdot phen]_2$ (**1**), $[Dy(2\text{-ClBA})_3\cdot 2,2'\text{-bipy}]_2$ (**2**), and $[Dy(2\text{-BrBA})_3\cdot phen]_2$ (**3**) (where 2-ClBAH = $2\text{-ClC}_6H_4COOH$, 2-BrBAH = $2\text{-BrC}_6H_4COOH$, phen = 1,10-phenanthroline, and 2,2′-bipy = 2,2′-bipyridine) have been synthesized and characterized by X-ray single crystal diffraction. Complex **1** consists of two independent binuclear molecules, $[Dy(2\text{-ClBA})_3\cdot phen]_2$ (a) and $[Dy(2\text{-ClBA})_3\cdot phen]_2$ (b), in which the coordination environment is similar. Each $Dy^{3+}$ is nine coordinate with two nitrogens from phen and seven oxygens from five 2-ClBA groups. 2-ClBA groups coordinate to $Dy^{3+}$ in three ways, bidentate chelating, bidentate-bridging and terdentate-bridging. Complexes **2** and **3** consist of one binuclear molecule. The crystal structure of **2** is similar to that of binuclear molecule (a) or (b) of complex **1**. In **3**, each $Dy^{3+}$ ion is eight-coordinate by two nitrogens from phen and six oxygens from five 2-BrBA groups. 2-BrBA groups coordinate to the $Dy^{3+}$ ion in two ways, bidentate chelating and bidentate-bridging. The complexes were studied by UV, DTA-TG, and fluorescence spectrometry.

*Keywords*: Dysprosium complexes; 2-Chlorobenzoic acid; 2-Bromobenzoic acid; Crystal structure; Properties

## 1. Introduction

Coordination chemistry of lanthanide carboxylates have been widely investigated, for novel structures and potential applications in biochemistry and materials science [1–4]. Samarium, europium, dysprosium, and terbium carboxylate complexes have special fluorescence properties, however, relatively less attention has been paid to the photoluminescence properties of dysprosium carboxylate complexes. When a second ligand, such as 1,10–phenanthroline (phen) or 2,2′-bipyridine (2,2′-bipy) is simultaneously bonded to the lanthanide ions complexes with higher thermal stability and strong luminescence can be obtained. A series of lanthanide complexes with benzoic acid and its derivatives has been synthesized in our laboratory. For example,

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2-fluorobenzoic acid (2-FBAH) and 2-iodobenzoic acid (2-IBAH) were used as ligands for several complexes. The complex [Tb(2-FBA)$_3 \cdot$ 2,2′-bipy]$_2$ contains three independent molecules in the asymmetric unit [5]. The terbium 2-FBAH complex with phen contains two dimers with different compositions in the asymmetric unit [5]. A praseodymium complex with 2-IBAH and 2,2′-bipy contains two binuclear molecules in the asymmetric unit [6]. In this manuscript, we choose 2-chlorobenzoic acid (2-ClBAH) and 2-bromobenzoic acid (2-BrBAH) as ligands toward lanthanide salts, in order to obtain complexes with novel structures. Our aim is to investigate the coordination chemistry of lanthanide complexes with halogen-substituted benzoate derivatives, and to investigate the effect of the substitutent on the benzoic acid and the nitrogen donor on the structure of the complexes. Three new dysprosium complexes, [Dy(2-ClBA)$_3 \cdot$ phen]$_2$ (**1**), [Dy(2-ClBA)$_3 \cdot$ 2,2′-bipy]$_2$ (**2**), and [Dy(2-BrBA)$_3 \cdot$ phen]$_2$ (**3**) were synthesized and the crystal structures and properties were investigated.

## 2. Experimental

### 2.1. *Materials and methods*

$DyCl_3 \cdot 6H_2O$ was prepared by dissolving its oxide in hydrochloric acid, and then drying out the solution. Elemental analysis was performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Bruker EQUINOX-55 using the KBr pellet technique. Thermogravimetric analysis was performed on a WCT-1A Thermal Analyzer at a heating rate of $10^\circ C\,min^{-1}$ in air. The UV spectra were measured on a TU-1810 spectrophotometer. Fluorescence spectra were measured on a F-4500 FL Spectrophotometer in the solid state at room temperature.

### 2.2. *Synthesis of the complexes*

**2.2.1. [Dy(2-ClBA)$_3$ • phen]$_2$ (1).** 1.5 mmol 2-chlorobenzoic acid and 0.5 mmol 1,10-phenanthroline were dissolved in 25 mL ethanol. The pH of the solution was adjusted to 6~7 with $2\,mol\,L^{-1}$ NaOH solution. Then 0.5 mmol $DyCl_3 \cdot 6H_2O$ ethanol solution was added to the solution. The mixture was heated under reflux with stirring for 1.5 h and then filtered. The crystals were obtained from the mother liquor after 2 weeks. Yield: 0.25 g, 62%. $C_{66}H_{40}Cl_6Dy_2N_4O_{12}$ (1618.72). Calcd (%): C, 48.97; H, 2.49; N, 3.46. Found (%): C, 48.67; H, 2.46; N, 3.45. Selected IR (KBr pellet, $\nu/cm^{-1}$): 1617 vs, 1590 s, 1545 m, 1475 m, 1405 vs, 1051 m, 858 m, 751 s, 729 m, 649 m, 461 m, 417 w.

**2.2.2. [Dy(2-ClBA)$_3$ • 2,2′-bipy]$_2$ (2).** Preparation of **2** was similar to that of **1** except that 2,2′-bipyridine was used in place of 1,10-phenanthroline. Yield: 0.21 g, 54%. $C_{62}H_{40}Cl_6Dy_2N_4O_{12}$ (1570.68). Calcd (%): C, 47.41; H, 2.57; N, 3.57. Found (%): C, 47.49; H, 2.58; N, 3.59. Selected IR (KBr pellet, $\nu/cm^{-1}$): 1616 vs, 1591 m, 1547 m, 1477 m, 1407 vs, 1152 s, 1014 m, 859 m, 752 s, 649 m, 461 m, 416 w.

**2.2.3. [Dy(2-BrBA)$_3$ · phen]$_2$ (3).** Preparation of **3** was similar to that of complex **1** except that 2-bromobenzoic acid was used in place of 2-chlorobenzoic acid. Yield: 0.29 g, 62%. $C_{66}H_{40}Br_6Dy_2N_4O_{12}$ (1885.42). Calcd (%): C, 42.05; H, 2.14; N, 2.97. Found (%): C, 41.98; H, 2.13; N, 2.83. Selected IR (KBr pellet, $\nu$/cm$^{-1}$): 1625 vs, 1591 m, 1518 m, 1473 m, 1412 vs, 1044 s, 1024 m, 852 m, 750 s, 730 m, 693 m, 642 m, 437 m, 417 w.

### 2.3. *X-ray crystallographic study*

X-ray crystal data collection for the complexes is on a Bruker Smart 1000CCD diffractometer with monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer with the use of SHELXS-97 and SHELXL-97 programs [7, 8]. The structures were solved by direct methods and refinement on $F^2$ used the full-matrix least-squares methods. Absorption problems may result in phenyl groups with very large thermal ellipsoids and also the direction of thermal vibration in figures 2 and 3. Summary of the crystallographic data and details of the structure refinements are listed in table 1. The selected bond lengths and bond angles of **1**–**3** are listed in tables 2–4, respectively.

Table 1. Crystal data and experimental details of the complexes.

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{66}H_{40}Cl_6Dy_2N_4O_{12}$ | $C_{62}H_{40}Cl_6Dy_2N_4O_{12}$ | $C_{66}H_{40}Br_6Dy_2N_4O_{12}$ |
| Formula weight | 1618.72 | 1570.18 | 1885.42 |
| Temperature (K) | 273(2) | 273(2) | 273(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P2(1)/c$ |
| Unit cell dimensions (Å, °) | | | |
| $a$ | 13.1591(7) | 11.3325(6) | 13.1976(2) |
| $b$ | 14.1639(7) | 12.3150(7) | 21.6131(3) |
| $c$ | 17.4135(9) | 12.8010(7) | 12.1234(2) |
| $\alpha$ | 83.363(3) | 63.873(3) | 90 |
| $\beta$ | 83.969(3) | 68.769(3) | 112.7000(10) |
| $\gamma$ | 73.108(3) | 80.727(3) | 90 |
| Volume (Å$^3$) | 3076.0(3) | 1495.0914 | 3190.22(8) |
| $Z$ | 2 | 1 | 2 |
| Calculated density (mg m$^{-3}$) | 1.748 | 1.745 | 1.963 |
| Absorption coefficient (mm$^{-1}$) | 2.739 | 2.814 | 6.147 |
| $F(000)$ | 1588.0 | 770 | 1804.0 |
| Crystal size (mm$^3$) | 0.4 × 0.2 × 0.15 | 0.4 × 0.25 × 0.10 | 0.4 × 0.2 × 0.18 |
| $2\theta_{\max}$ | 56.60 | 56.62 | 45.66 |
| Reflections collected | 61070 | 29850 | 33304 |
| Independent reflections | 15179 [$R$(int) = 0.0722] | 13471 [$R$(int) = 0.0180] | 7884 [$R$(int) = 0.0509] |
| Data/restraints/parameters | 15179/0/811 | 13471/36/763 | 7884/9/406 |
| Goodness-of-fit on $F^2$ | 1.009 | 1.058 | 1.060 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0388$, $\omega R_2 = 0.0907$ | $R_1 = 0.0242$, $\omega R_2 = 0.0631$ | $R_1 = 0.0485$, $\omega R_2 = 0.1442$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.305 and −1.040 | 2.204 and −0.941 | 1.933 and −1.792 |

Table 2. Selected bond lengths (Å) and bond angles (°) of **1**.

| | | | |
|---|---|---|---|
| Dy(1)–O(1) | 2.394(3) | Dy(1)–O(2) | 2.464(3) |
| Dy(1)–O(3) | 2.412(3) | Dy(1)–O(4) | 2.763(3) |
| Dy(1)–O(5) | 2.329(3) | Dy(1)–O(4)#1 | 2.285(3) |
| Dy(1)–O(6)#1 | 2.327(3) | Dy(1)–N(1) | 2.643(3) |
| Dy(1)–N(2) | 2.549(3) | Dy(2)–O(8) | 2.310(3) |
| Dy(2)–O(9) | 2.400(3) | Dy(2)–O(10) | 2.446(3) |
| Dy(2)–O(11) | 2.315(3) | Dy(2)–O(7)#2 | 2.347(3) |
| Dy(2)–O(11)#2 | 2.811(3) | Dy(2)–O(12)#2 | 2.415(3) |
| Dy(2)–N(3) | 2.559(4) | Dy(2)–N(4) | 2.574(3) |
| O(1)–Dy(1)–O(2) | 53.59(9) | O(1)–Dy(1)–O(3) | 79.60(11) |
| O(1)–Dy(1)–O(4) | 127.48(10) | O(2)–Dy(1)–O(4) | 108.53(9) |
| O(3)–Dy(1)–O(2) | 70.96(11) | O(3)–Dy(1)–O(4) | 49.22(9) |
| O(5)–Dy(1)–O(1) | 92.08(10) | O(5)–Dy(1)–O(2) | 136.69(10) |
| O(5)–Dy(1)–O(3) | 78.06(12) | O(5)–Dy(1)–O(4) | 69.29(9) |
| O(4)#1–Dy(1)–O(1) | 150.63(10) | O(4)#1–Dy(1)–O(2) | 144.86(10) |
| O(4)#1–Dy(1)–O(3) | 124.02(10) | O(4)#1–Dy(1)–O(4) | 75.02(10) |
| O(4)#1–Dy(1)–O(5) | 78.05(10) | O(4)#1–Dy(1)–O(6)#1 | 74.07(10) |
| O(6)#1–Dy(1)–O(1) | 128.77(9) | O(6)#1–Dy(1)–O(2) | 75.29(9) |
| O(6)#1–Dy(1)–O(3) | 87.58(12) | O(6)#1–Dy(1)–O(4) | 67.94(9) |
| O(6)#1–Dy(1)–O(5) | 133.46(9) | N(2)–Dy(1)–N(1) | 63.19(11) |
| O(8)–Dy(2)–O(9) | 75.92(10) | O(8)–Dy(2)–O(10) | 128.94(9) |
| O(8)–Dy(2)–O(11) | 74.78(9) | O(8)–Dy(2)–O(7)#2 | 131.80(10) |
| O(8)–Dy(2)–O(11)#2 | 67.24(9) | O(8)–Dy(2)–O(12)#2 | 88.62(11) |
| O(9)–Dy(2)–O(10) | 53.56(10) | O(9)–Dy(2)–O(11)#2 | 111.07(10) |
| O(9)–Dy(2)–O(12)#2 | 75.24(11) | O(10)–Dy(2)–O(11)#2 | 121.04(9) |
| O(11)–Dy(2)–O(9) | 144.09(10) | O(11)–Dy(2)–O(10) | 153.73(9) |
| O(11)–Dy(2)–O(7)#2 | 77.28(10) | O(11)–Dy(2)–O(11)#2 | 75.64(9) |
| O(11)–Dy(2)–O(12)#2 | 123.98(10) | O(7)#2–Dy(2)–O(9) | 138.55(10) |
| O(7)#2–Dy(2)–O(10) | 89.97(10) | O(7)#2–Dy(2)–O(11)#2 | 68.24(9) |
| O(7)#2–Dy(2)–O(12)#2 | 75.61(10) | O(12)#2–Dy(2)–O(10) | 73.21(10) |
| O(12)#2–Dy(2)–O(11)#2 | 48.91(8) | N(3)–Dy(2)–N(4) | 63.68(12) |

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+2$, $-z+1$; #2: $-x+2$, $-y+1$, $-z+2$.

## 3. Results and discussion

### 3.1. *Structural description of complexes [Dy(2-ClBA)$_3$ • phen]$_2$ and [Dy(2-ClBA)$_3$ • 2,2′-bipy]$_2$*

The crystal structure **1** is shown in figure 1(a) and (b). Obviously, the structure consists of two centrosymmetric binuclear molecules, [Dy(2-ClBA)$_3$ · phen]$_2$ (a) (figure 1a) and [Dy(2-ClBA)$_3$ · phen]$_2$ (b) (figure 1b). In (a), the two Dy$^{3+}$ ions are bridged by four 2-ClBA groups. Two of the 2-ClBA groups are bidentate bridging and the other two are terdentate bridging. The separation of Dy1 ··· Dy1A is 4.014(3) Å. In addition, each Dy$^{3+}$ ion is also coordinated to one chelating 2-ClBA group and one phen molecule to form a nine-coordinate metal ion. The coordination environment of Dy$^{3+}$ can be described as a distorted monocapped square-antiprism arrangement. Atoms O3, O4A, O5, O6A and O1, O2, N1, N2 form the lower and upper square planes with mean deviations of 0.0948 and 0.2043 Å, respectively, and the dihedral angle between the two squares is 4.0°. The cap position is occupied by O4. Dy1–O distances are in a range 2.327(3)~2.763(3) Å with the mean distance of 2.423 Å. The average Dy1–N distance is 2.596 Å. The O–Dy1–O bond angles range from 49.22(9) to 150.6(1)°, and that of N–Dy1–N is 63.2(1)°.

Table 3. Selected bond lengths (Å) and bond angles (°) of **2**.

| | | | |
|---|---|---|---|
| Dy(1)–O(1) | 2.618(7) | Dy(1)–O(2) | 2.459(8) |
| Dy(1)–O(6) | 2.325(7) | Dy(1)–O(7) | 2.327(6) |
| Dy(1)–O(9) | 2.375(8) | Dy(1)–O(11) | 2.415(10) |
| Dy(1)–O(12) | 2.410(7) | Dy(1)–N(1) | 2.545(9) |
| Dy(1)–N(2) | 2.572(9) | Dy(2)–O(1) | 2.346(7) |
| Dy(2)–O(3) | 2.420(9) | Dy(2)–O(4) | 2.430(8) |
| Dy(2)–O(5) | 2.324(8) | Dy(2)–O(7) | 2.616(7) |
| Dy(2)–O(8) | 2.446(9) | Dy(2)–O(10) | 2.337(7) |
| Dy(2)–N(3) | 2.551(8) | Dy(2)–N(4) | 2.630(9) |
| O(2)–Dy(1)–O(1) | 50.2(2) | O(6)–Dy(1)–O(1) | 66.9(3) |
| O(6)–Dy(1)–O(2) | 84.4(3) | O(6)–Dy(1)–O(9) | 134.5(3) |
| O(6)–Dy(1)–O(11) | 81.1(3) | O(6)–Dy(1)–O(12) | 131.7(3) |
| O(7)–Dy(1)–O(1) | 73.2(2) | O(7)–Dy(1)–O(2) | 123.4(3) |
| O(7)–Dy(1)–O(6) | 75.0(3) | O(7)–Dy(1)–O(9) | 75.5(3) |
| O(7)–Dy(1)–O(11) | 82.2(3) | O(7)–Dy(1)–O(12) | 81.5(3) |
| O(9)–Dy(1)–O(1) | 71.9(3) | O(9)–Dy(1)–O(2) | 83.8(3) |
| O(9)–Dy(1)–O(11) | 127.6(3) | O(9)–Dy(1)–O(12) | 76.0(3) |
| O(11)–Dy(1)–O(1) | 143.6(3) | O(11)–Dy(1)–O(2) | 145.9(3) |
| O(12)–Dy(1)–O(1) | 143.0(3) | O(12)–Dy(1)–O(2) | 142.8(2) |
| O(12)–Dy(1)–O(11) | 53.9(3) | N(1)–Dy(1)–N(2) | 63.1(3) |
| O(1)–Dy(2)–O(3) | 81.3(3) | O(1)–Dy(2)–O(4) | 80.8(2) |
| O(1)–Dy(2)–O(7) | 72.98(18) | O(1)–Dy(2)–O(8) | 124.7(2) |
| O(3)–Dy(2)–O(4) | 53.7(3) | O(3)–Dy(2)–O(7) | 142.7(3) |
| O(3)–Dy(2)–O(8) | 146.3(3) | O(4)–Dy(2)–O(7) | 142.4(2) |
| O(4)–Dy(2)–O(8) | 141.9(3) | O(5)–Dy(2)–O(1) | 75.9(3) |
| O(5)–Dy(2)–O(3) | 128.5(3) | O(5)–Dy(2)–O(4) | 77.2(3) |
| O(5)–Dy(2)–O(7) | 70.7(3) | O(5)–Dy(2)–O(8) | 82.3(3) |
| O(5)–Dy(2)–O(10) | 135.3(3) | O(8)–Dy(2)–O(7) | 51.8(2) |
| O(10)–Dy(2)–O(1) | 75.6(3) | O(10)–Dy(2)–O(3) | 79.6(3) |
| O(10)–Dy(2)–O(4) | 130.3(3) | O(10)–Dy(2)–O(7) | 68.3(3) |
| O(10)–Dy(2)–O(8) | 86.3(3) | N(3)–Dy(2)–N(4) | 62.7(3) |

Table 4. Selected bond lengths (Å) and bond angles (°) of **3**.

| | | | |
|---|---|---|---|
| Dy(1)–O(1) | 2.428(5) | Dy(1)–O(2) | 2.461(4) |
| Dy(1)–O(3) | 2.271(5) | Dy(1)–O(4) | 2.305(4) |
| Dy(1)–O(5) | 2.308(5) | Dy(1)–O(6) | 2.326(5) |
| Dy(1)–N(1) | 2.550(6) | Dy(1)–N(2) | 2.542(5) |
| O(1)–Dy(1)–O(2) | 52.99(15) | O(3)–Dy(1)–O(1) | 82.3(2) |
| O(3)–Dy(1)–O(2) | 80.94(19) | O(3)–Dy(1)–O(4) | 76.7(2) |
| O(3)–Dy(1)–O(5) | 77.1(2) | O(3)–Dy(1)–O(6) | 124.2(2) |
| O(4)–Dy(1)–O(1) | 89.30(19) | O(4)–Dy(1)–O(2) | 138.41(19) |
| O(4)–Dy(1)–O(5) | 125.97(19) | O(4)–Dy(1)–O(6) | 77.0(2) |
| O(5)–Dy(1)–O(1) | 132.13(17) | O(5)–Dy(1)–O(2) | 81.17(17) |
| O(5)–Dy(1)–O(6) | 80.3(2) | O(6)–Dy(1)–O(1) | 144.8(2) |
| O(6)–Dy(1)–O(2) | 143.71(16) | N(2)–Dy(1)–N(1) | 64.39(17) |

The structure of (b) is similar to that of (a). In (b), $Dy^{3+}$ is nine-coordinate with a monocapped square antiprism as the coordination polyhedron. Atoms O7A, O8, O11, O12A and O9, O10, N3, N4 form the two square planes with mean deviations of 0.0804 and 0.1246 Å, respectively; the dihedral angle between the two squares is 4.2°. The cap position is occupied by O11A. The Dy2 $\cdots$ Dy2A distance is 4.061(3) Å. Dy2–O distances are 2.310(3)~2.811(3) Å with the mean distance of 2.434 Å. The average Dy2–N distance is 2.566 Å. The O–Dy2–O bond angles range from 48.91(8) to 153.73(9)°,

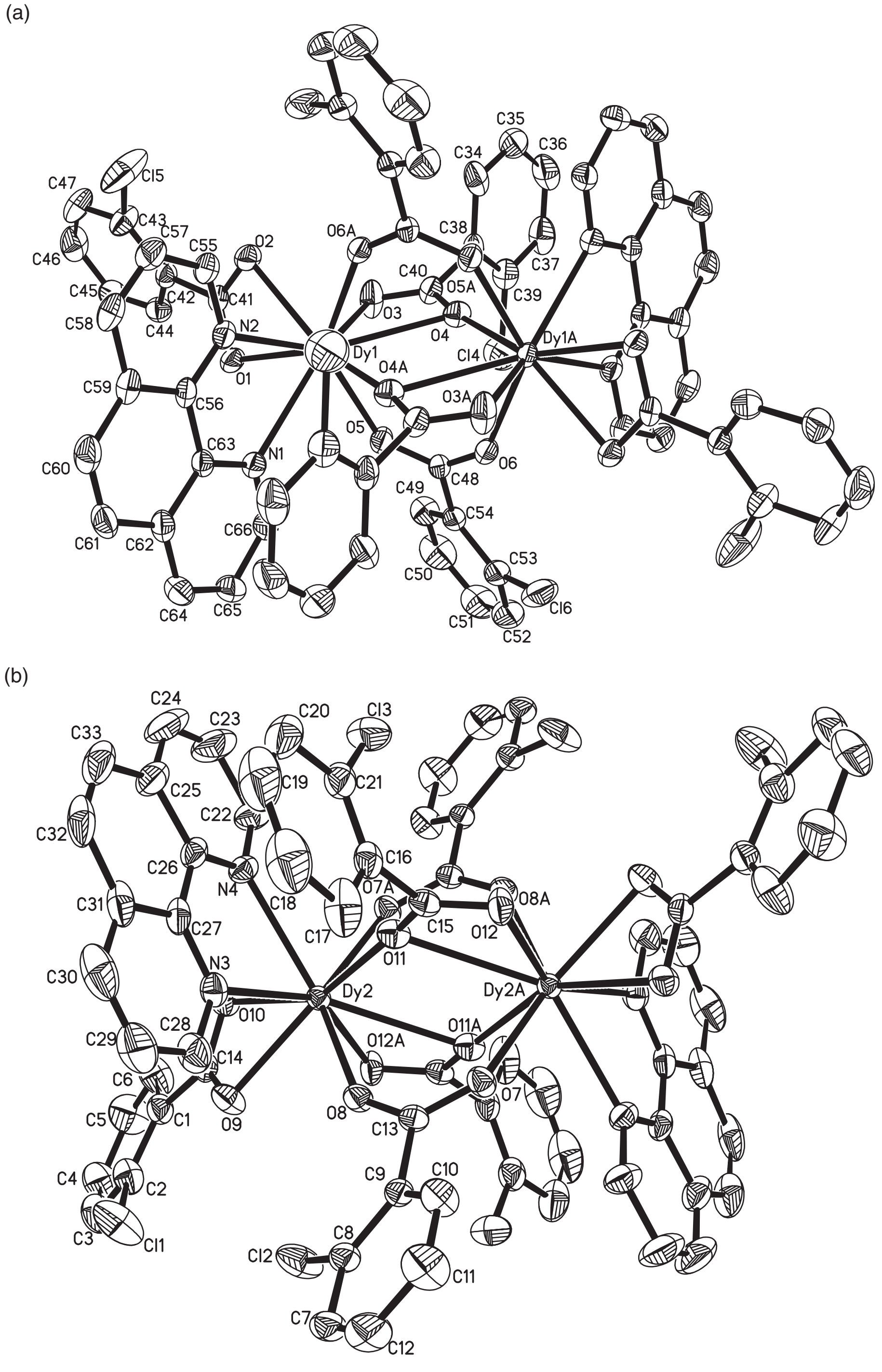

Figure 1. (a) and (b) show two molecules of **1** in the asymmetric unit. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

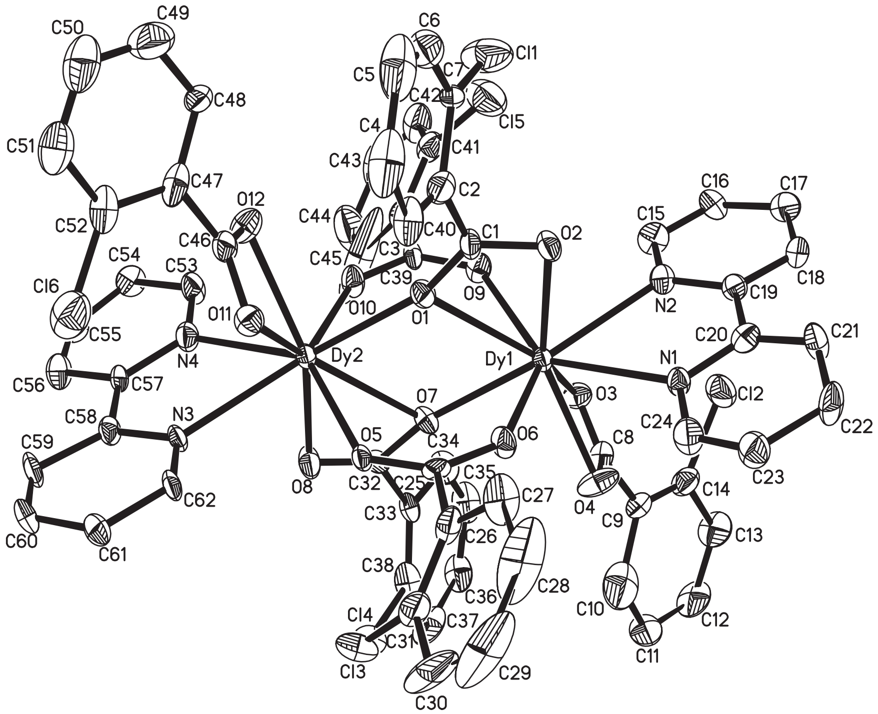

Figure 2. Molecular structure of **2**. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

and that of N–Dy2–N is 62.7(3)°. It can be seen that the distances (Dy2–O and Dy2–N) and angles (O–Dy2–O and N–Dy2–N) in molecule (b) are in good agreement with corresponding ones in (a). The distance between neighboring $Dy^{3+}$ in (a) and (b) is 9.906 Å.

Complex **1** is different from $[Dy(4\text{-}CH_3C_6H_4COO)_3 \cdot (phen)]_2$ [9], in that the latter contains two different kinds of molecules in the unit cell with different coordination modes of carboxylate. In one molecule, two $Dy^{3+}$ ions are held together by four bidentate bridging and chelating-bridging $4\text{-}CH_3C_6H_4COO^-$ groups, in the other, two $Dy^{3+}$ ions are linked together by four bidentate bridging $4\text{-}CH_3C_6H_4COO^-$ groups. The europium 3-chlorobenzoate (3-ClBA) complex, $[Eu(3\text{-}ClBA)_3 \cdot phen]_2$, consists of only one binuclear molecule in the unit cell, in which each $Eu^{3+}$ ion is nine-coordinate, and the $Eu^{3+}$ ions are linked by bidentate bridging and chelating-bridging 3-ClBA groups [10]. The reported europium 4-chlorobenzoate (4-ClBA) complex $[Eu(4\text{-}ClBA)_3 \cdot phen]_2$ has only one binuclear molecule in the unit cell, with each $Eu^{3+}$ eight-coordinate, and $Eu^{3+}$ ions linked by four bidentate bridging 4-ClBA groups [11].

The same crystallization system and space group for complexes **2** and **1** (see table 1) indicate that complexes **2** and **1** are isostructural. The crystal structure of **2** is shown in figure 2. Both $Dy^{3+}$ ions in the dimeric unit are linked by four bidentate bridging and chelating-bridging 2-ClBA groups and one 2-ClBA group and 2,2′-bpy molecule chelate $Dy^{3+}$. The structure of **2** is similar to (a) or (b) in **1**; the geometry of $Dy^{3+}$ can also be described as distorted monocapped square-antiprism. The Dy1 ⋯ Dy1A separation is 3.9827(2) Å. Dy1–O distances range from 2.325(7)–2.618(7) Å with the mean distance

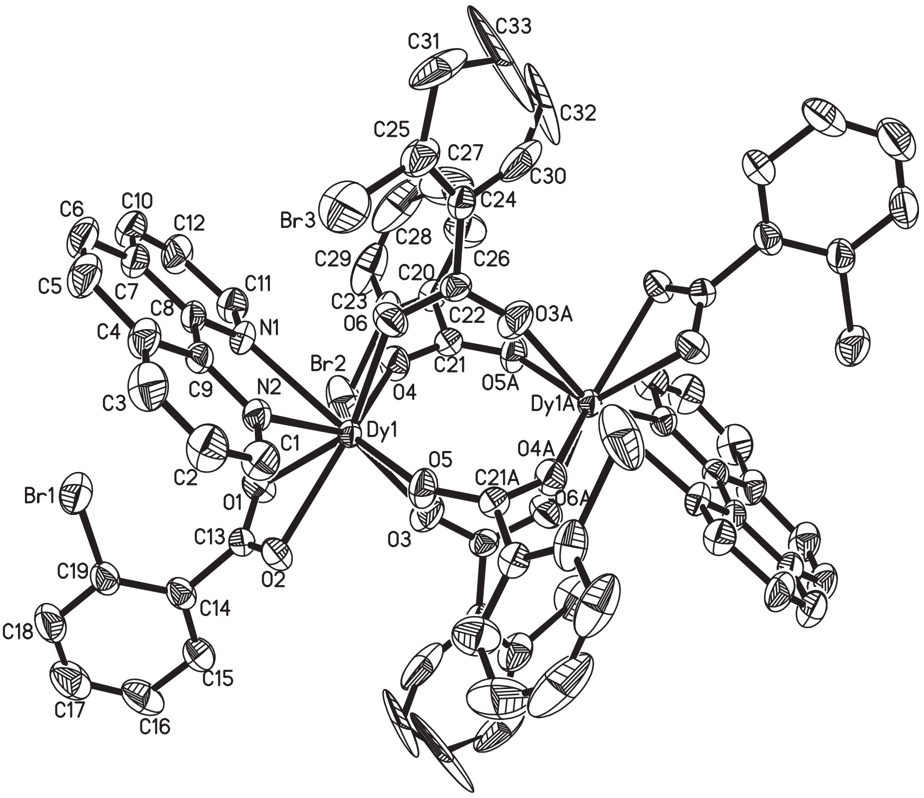

Figure 3. Molecular structure of **3**. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

of 2.418 Å. The average Dy1–N distance is 2.559 Å. The O–Dy1–O bond angles range from 50.2(2) to 145.9(3)°, and N–Dy1–N is 63.1(3)°.

Binary lanthanide 2-ClBA complexes $Ln(2\text{-}ClBA)_3 \cdot 2H_2O$ are infinite one-dimensional polymeric structures through bidentate bridging and tetradentate bridging 2-ClBA groups [12]. Many binary lanthanide mono-carboxylate complexes are polymeric [13–16]. A second ligand, 2,2′-bipy or phen, forming mixed-ligand complexes, changes the structure to dimeric [14–21].

### 3.2. *Structural description of complex of [Dy(2-BrBA)$_3$ • phen]$_2$ (3)*

Unlike $[Dy(2\text{-}ClBA)_3 \cdot phen]_2$ (**1**), $[Dy(2\text{-}BrBA)_3 \cdot phen]_2$ (**3**) crystallizes in the monoclinic system with space group $P2(1)/c$ (**1** belongs to triclinic system with space group $P\bar{1}$). As shown in figure 3, the structure of **3** is different from **1**. Both $Dy^{3+}$ ions in the dimeric unit are linked by four bidentate bridging 2-BrBA groups. Each $Dy^{3+}$ is further coordinated to one chelating 2-BrBA group and a phen to complete the $DyO_6N_2$ unit, in a distorted square-antiprism. Atoms O3, O4, O5, O6 and O1, O2, N1, N2 form the two square planes with mean deviations of 0.0134 and 0.0275 Å, respectively, and the dihedral angle between the two square is 5.4°. In **1**, carboxylate groups adopt three different coordination modes, bidentate chelating, bidentate-bridging and terdentate-bridging, resulting in nine-coordinate metal ion. The Dy ··· Dy distance is longer and Dy ··· O is shorter in **1** than corresponding distances in **3**. For example, in **3**, the separation of Dy1 ··· Dy1A is 4.304(6) Å. Dy1–O distances are 2.271(5)–2.461(4) Å with the mean distance of 2.350 Å. In addition, these differences and the smaller coordination number of the metal can be attributed to the larger radius of Br. In **3**, the average Dy1 ··· N distance is 2.546 Å. The O–Dy1–O bond angles range from 53.0(1) to 144.8(2)°, and N–Dy1–N is 64.4(1)°.

Many lanthanide mono-carboxylate complexes with phen or 2,2′-bipy contain only one binuclear molecule in the asymmetric unit, such as $[Eu(m\text{-MOBA})_3 \cdot 2,2'\text{-bipy}]_2$ ($m$-MOBA = $m$-methoxybenzoate) [17], $[Eu(FA)_2 \cdot NO_3 \cdot 2,2'\text{-bipy}]_2$ (FA = $\alpha$-furancarboxylate) [18], $[Ln_2(MeCH{=}CHCO_2)_6 \cdot (phen)_2] \cdot 2H_2O$, (Ln = Eu, Tb) [19] and $[Ln_2(CH_3CO_2)_6 \cdot (phen)_2]$, (Ln = Ce, Gd) [20]. $[Dy(2\text{-ClBA})_3 \cdot phen]_2$ (**1**) contains two binuclear molecules in the asymmetric unit, and $[Dy(2\text{-ClBA})_3 \cdot 2,2'\text{-bipy}]_2$ (**2**) and $[Dy(2\text{-BrBA})_3 \cdot phen]_2$ (**3**) contain only one binuclear molecule in the asymmetric unit. The coordination modes of carboxylate groups and coordination number of the metal are the same in **1** and **2**. However the coordination carboxylate and coordination number of the metal are different in **1** and **3**. The crystal structures of dysprosium complexes with 2-chlorobenzoic acid (2-ClBAH) and 2-bromobenzoic acid (2-BrBAH) containing 2,2′-bipy and phen in this article are different from reported corresponding terbium complexes with 2-fluorobenzoic acid (2-FBAH) [5] and praseodymium complexes with 2-iodobenzoic acid (2-IBAH) [6]. $[Tb(2\text{-FBA})_3 \cdot 2,2'\text{-bipy}]_2$ contains three independent molecules in the asymmetric unit [5]. In two of the molecules, two $Tb^{3+}$ ions are held together by four bidentate bridging and chelating-bridging 2-FBA groups; in the other one, two $Tb^{3+}$ ions are linked together by four bidentate bridging 2-FBA groups. The terbium complex with 2-FBAH and phen contains two dimers with different compositions and structures in the asymmetric unit, $[Tb(2\text{-FBA})_3 \cdot phen \cdot CH_3CH_2OH]_2$ and $[Tb(2\text{-FBA})_3 \cdot phen]_2$ [5]. The praseodymium complex with 2-IBAH and 2,2′-bipy contains two binuclear molecules in the asymmetric unit, $[Pr(2\text{-IBA})_3 \cdot 2,2'\text{-bipy}]_2$ (a) and $[Pr(2\text{-IBA})_3 \cdot 2,2'\text{-bipy}]_2$ (b) [6], in which the coordination environment of $Pr1^{3+}$ in (a) and $Pr2^{3+}$ in (b) is the same. The complex $[Pr(2\text{-IBA})_3 \cdot phen]_2$ contains only one binuclear molecule in the asymmetric unit [6]. However, the structures of lanthanide complexes with 2-fluorobenzoate, 2-chlorobenzoate, 2-bromobenzoate, and 2-iodobenzoate containing 2,2′-bipy or phen are different, due to the steric effect of halogen. Different substituents on benzoic acid result in different structures. Many ternary lanthanide complexes with 2-halogenated benzoate derivatives contain several independent molecules in the asymmetric unit. The crystal structure of the complexes depends not only on the carboxylic acid, but also on the second ligand. When an aromatic diimine such as phen or 2,2′-bipy is bonded to lanthanide, complexes with different structures can be obtained. However, lanthanide complexes containing several different independent molecules in the asymmetric unit like **1** are less reported.

### 3.3. *Thermogravimetric analysis*

Thermal behaviour of the complexes was studied from 25 to 1000°C. The DTA-TG diagram of **1** shows decomposition begins at 305.0°C and ends at 562.0°C with two uninterrupted steps of weight loss, 45.21 and 29.04%. The total mass loss of 74.25% indicates the complex is completely degraded to $Dy_2O_3$ (Calcd 76.96%). For **3**, an endothermic peak, a strong exothermic peak, and a weak exothermic peak on the DTA curve at 326, 554.0 and 721.0°C, correspond to three decomposition steps on the TG curve, 40.22, 20.79, and 19.08%, respectively. The total mass loss of 80.09% indicates the final decomposition product is $Dy_2O_3$ (Calcd 80.22%).

The TG-DTA of **2** indicates the complex decomposes in two steps. At the endothermic peak of 250°C, one 2,2′-bipy molecule decomposes (observed, 19.22%;

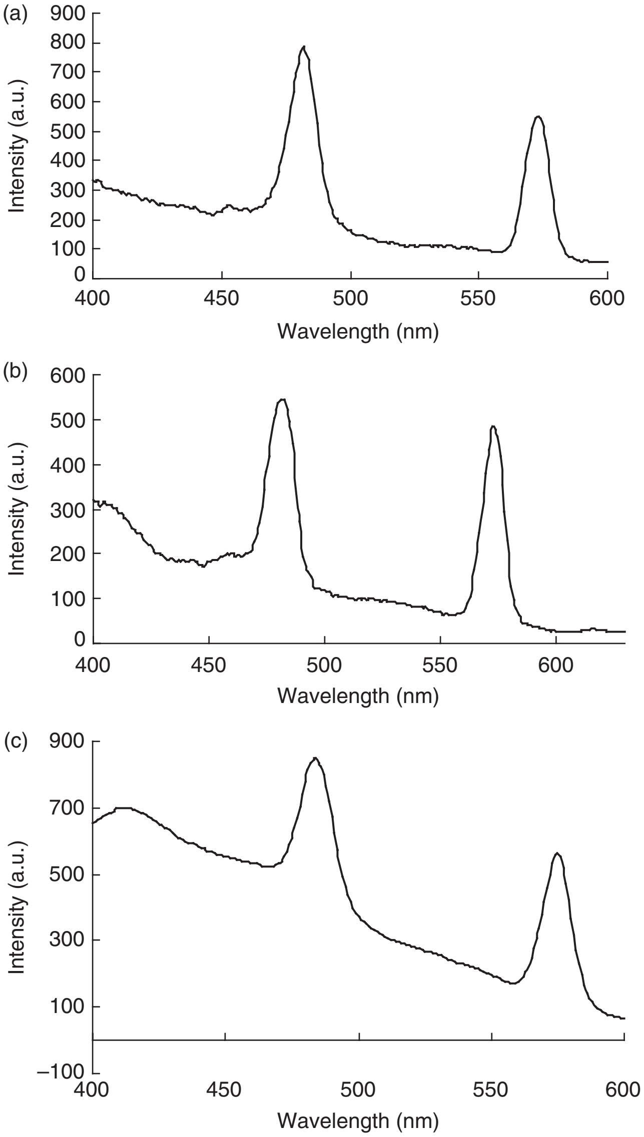

Figure 4. The fluorescence spectra of complexes. (a) **1** ($\lambda_{exc} = 310$ nm), (b) **2** ($\lambda_{exc} = 330$ nm), and (c) **3** ($\lambda_{exc} = 346$ nm).

Calcd 19.86%) and then at the exothermic peak of 525.0°C, the 2-BrBA ligands decomposed. The total mass loss of 75.01% indicates $Dy_2O_3$ remains (Calcd 76.24%).

The three complexes show high thermal stability. Comparing decomposition temperature of **2** with those of **1** and **3**, the high stability of **1** and **3** may be due to the phen.

### 3.4. *Photophysical properties*

The UV absorption spectra of the three complexes were measured from 200 to 400 nm in DMF solution with $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$. Broad absorption bands were at 280.0 nm ($\varepsilon = 1.76 \times 10^4$) for **1**, 286.0 nm ($\varepsilon = 1.89 \times 10^4$) for **2**, and 282 nm ($\varepsilon = 2.98 \times 10^4$) for **3**, which imply UV-spectra of complexes arose from the $\pi$–$\pi^*$ transition of the ligand. The emission spectra of the three solid complexes, recorded at room temperature in the range from 400 to 600 nm under selective excitation wavelength of 310 nm for **1**, 330 nm for **2**, and 346 nm for **3**, indicates that ligand-to-$Dy^{3+}$ energy transfer occurs. The emission spectra of the three complexes are shown in figure 4(a–c). The photoluminescence spectra of the complexes are similar with two emission bands at 483 and 574 nm, ascribed to the characteristic emissions $^4F_{5/2} \rightarrow {}^6H_{15/2}$ and $^4F_{5/2} \rightarrow {}^6H_{13/2}$ of $Dy^{3+}$. Coordination of the 2,2′-bipy or phen would increase conjugation of the complex, enhancing the luminescence intensity.

## Supplementary data

CCDC-612858, 612859, and 623758 for complexes **1**, **2** and **3**, respectively, contain the supplementary crystallographic data for this article. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk.

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