

Communication

# Hetero-Trinuclear $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$ Complex with a Octadentate Bis(Salamo)-Like Ligand: Synthesis, Crystal Structure and Luminescence Properties

Yu-Hua Yang, Jing Hao, Xiao-Yan Li, Yang Zhang and Wen-Kui Dong \* 

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China; yangyuhua@mail.lzjtu.cn (Y.-H.Y.); haojingmm@126.com (J.H.); L1401569787@163.com (X.-Y.L.); zhangy8124@163.com (Y.Z.)

\* Correspondence: dongwk@126.com; Tel.: +86-931-4938-703

Received: 28 March 2018; Accepted: 16 April 2018; Published: 18 April 2018



**Abstract:** A hetero-trinuclear  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex,  $[\text{Co}_2\text{L}(\text{DMF})_2\text{Dy}(\text{NO}_3)_3]\cdot\text{C}_2\text{H}_5\text{O}_2$  was synthesized via the reaction of a multi-naphthol-based bis(Salamo)-like tetraoxime  $\text{H}_4\text{L}$  with  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  and  $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ , and fully characterized via elemental analyses, X-ray crystallography, FT-IR and UV-Vis spectra. In addition, luminescence properties of  $\text{H}_4\text{L}$  and its  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex have also been investigated.

**Keywords:** Salamo-like tetraoxime;  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex; synthesis; crystal structure; luminescence property

## 1. Introduction

In the past decades, many scientists were working on the study of Salen [1–3] and its analogues [4–9] mainly because their metal complexes can be widely used in obtaining optical [10–13] and magnetic [14] materials, biological fields [15–21], electrochemistry [15–23], ion recognition [24–32], supra-molecular buildings [33,34], catalysis activities [35–38], and so on. In the present study, some appropriate Salen-like compounds (Salamo and its analogues) were selected as a hot topic and there are many reports about the metal complexes including two or more molecules of Salen-like ligands [39–42]. Chemical modifications of substituent or functional groups in the Salen  $\text{N}_2\text{O}_2$  ligands are effective in exchanging the structures or the main functions of the complexes, such as Salamo  $\text{N}_2\text{O}_2$  ligand (1,2-Bis(salicylideneaminoxy)ethane), a Salen's analogue,  $(\text{R}-\text{CH}=\text{N}-\text{O}-(\text{CH})_n-\text{O}-\text{N}=\text{CH}-\text{R})$  one of the most versatile ligands [37,43]. Although some Salamo-like complexes have been described, there are poorly reported polynuclear hetero-bimetallic 3d–4f complexes with interesting structures and optical properties [44–48]. Moreover, a key feature of such structures is that trivalent lanthanide ions have higher coordination numbers, larger radius, more flexible coordination geometries and unusual 4f electron construction with larger spin moments and stronger spin-orbit coupling [49], therefore, the lanthanide metal complexes have shown interesting magnetic [50] and distinct luminescent properties [51–54]. In addition, 3d–4f complexes can be widely used in catalysis field [55–61].

In order to study further the hetero-bimetallic 3d–4f Salamo-like complexes and their optical properties, we have newly designed a novel hetero-trinuclear  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex by the complexation of a multi-naphthol-based symmetric bis(Salamo)-like tetraoxime  $\text{H}_4\text{L}$  with  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  and  $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ .

## 2. Experimental Section

### 2.1. Materials and Physical Measurements

2-Hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, methyl trioctyl ammonium chloride, borontribromide and pyridiniumchlorochromate were obtained from Alfa Aesar (New York, NY, USA). The other reagents and solvents were bought from Shanghai Darui Chemical Fine Chemicals Company (Tianjin, China). Solvents and all other chemicals were of analytical grade and used without further purification. Elemental analyses (C, H and N) were carried out with Elementar GmbH VarioEL V3.00 automatic elemental analysis equipment (Berlin, Germany). Elemental analyses for Co<sup>II</sup> and Dy<sup>III</sup> atoms were measured using an IRIS ER/S-WP-1 ICP atomic emission spectrometer (Berlin, Germany). Melting points were measured using an X<sub>4</sub> microscopic melting point apparatus made by Beijing Taiké Instrument Limited Company (Beijing, China) and were not corrected. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr (400–4000 cm<sup>-1</sup>). UV-Vis absorption spectra in the 200–600 nm range were measured on a Hitachi U-3900H spectrophotometer (Shimadzu, Japan) in mixed solvent (chloroform/methanol = 3:2, *v/v*). Fluorescent spectra were taken on F-7000 FL spectrophotometer (Shimadzu, Japan). <sup>1</sup>H NMR spectra were measured using a German Bruker AVANCE DRX-400 spectrometer (Bruker, AVANCE, Billerica, MA, USA). X-ray single crystal structure was determined via a Bruker Smart Apex CCD diffractometer (Bruker, AVANCE, Billerica, MA, USA).

### 2.2. Synthesis and Characterization of the Ligand H<sub>4</sub>L

H<sub>4</sub>L was synthesized according to the early reported method, the <sup>1</sup>H NMR (Figure 1), IR and UV-Vis spectra of H<sub>4</sub>L are in consistent with the data [62].

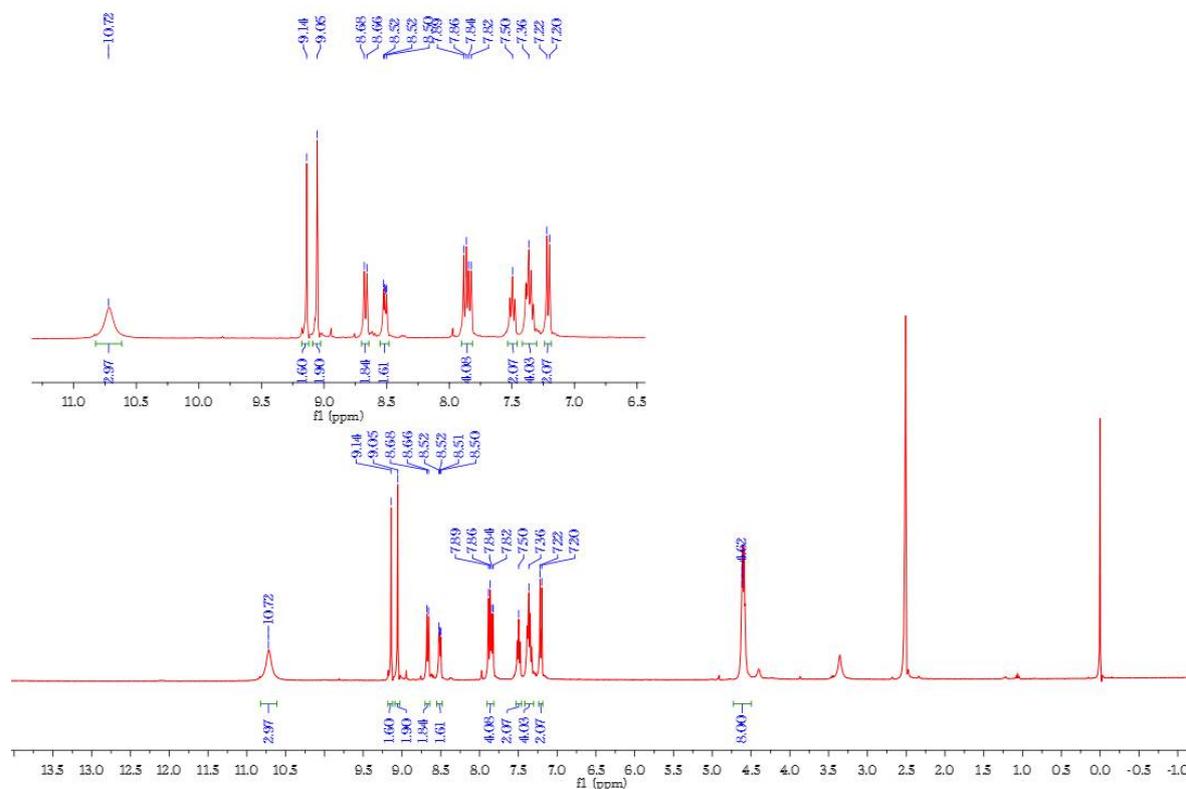
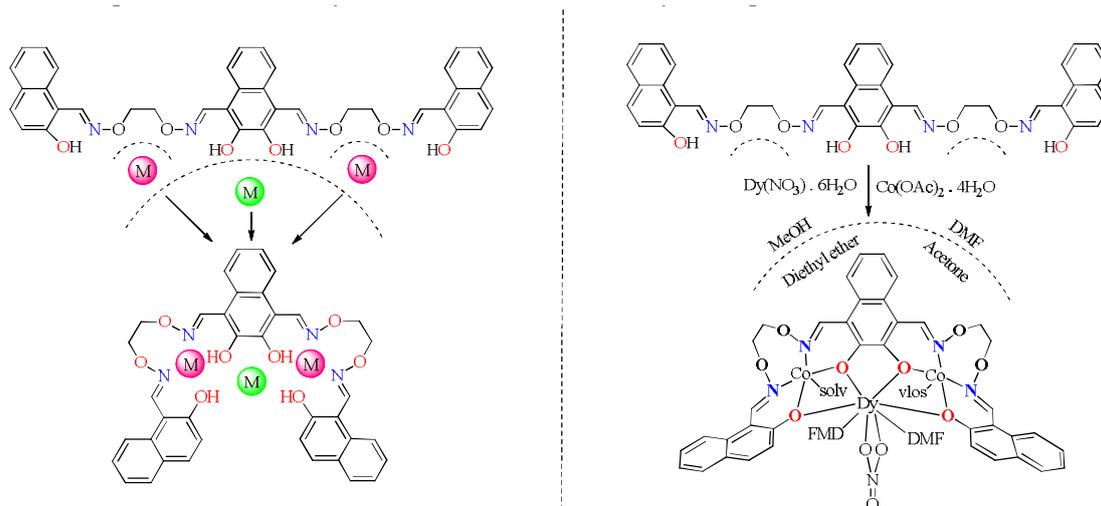


Figure 1. <sup>1</sup>H NMR spectrum of the ligand H<sub>4</sub>L (CDCl<sub>3</sub>, 400 MHz).

The step included in the synthetic route to the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex is shown in Scheme 1.



**Scheme 1.** Synthetic route to the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex.

### 2.3. Synthesis of the $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$ Complex

A solution of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (14.94 mg, 0.06 mmol) in methanol (2 mL) and  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (9.13 mg, 0.02 mmol) in methanol (1 mL) were added to a solution of  $\text{H}_4\text{L}$  (13.44 mg, 0.02 mmol) in acetone/DMF (1:1, 1 mL) with constant stirring. After about 30 min later, the color of the mixture turned to brown immediately, the brown mixture obtained was filtered and the filtrate was kept undisturbed at diethyl ether. One week later, clear dark brown block-like crystals suitable for X-ray diffraction were formed and carefully collected by filtration, washed with 2:1 (*v/v*) acetone:hexane, and dried at room temperature. Yield: 46%. IR (KBr;  $\text{cm}^{-1}$ ): 1594 [ $\nu(\text{C}=\text{N})$ , s], 1249 [ $\nu(\text{Ar}-\text{O})$ , s]. Anal. Calcd. for  $\text{C}_{52}\text{H}_{62}\text{Co}_2\text{DyN}_9\text{O}_{21}$  (%): C, 43.69; H, 4.37; N, 8.82; Co., 8.25; Dy, 11.37. Found: C, 43.91; H, 4.56; N, 8.56; Co., 8.03; Dy, 11.21.

### 2.4. X-ray Structure Determination of the $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$ Complex

The single crystal of the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex with approximate dimensions of  $0.26 \times 0.24 \times 0.23$  mm, was placed on Bruker Smart 1000 CCD area detector. The crystal diffraction data were collected using a graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm) at 293(2) K. The structure was solved the using the program SHELXS-2015 and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$  using SHELXL-2015 [63]. Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Details of the data collection and refinements are presented in Table 1.

**Table 1.** Crystal data and structure refinements for the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex.

$[\text{Co}_2\text{L}(\text{DMF})_2\text{Dy}(\text{NO}_3)_3] \cdot \text{C}_2\text{H}_5\text{O}_2$	
Formula	$\text{C}_{52}\text{H}_{62}\text{Co}_2\text{DyN}_9\text{O}_{21}$
Formula weight	1429.46
Temperature (K)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	monoclinic
Space group	$P12_1/m_1$
<i>a</i> ( $\text{\AA}$ )	9.2838(4)
<i>b</i> ( $\text{\AA}$ )	24.9653(11)
<i>c</i> ( $\text{\AA}$ )	12.7982(6)
$\beta$ ( $^\circ$ )	97.059(4) $^\circ$
<i>V</i> ( $\text{\AA}^3$ )	2943.8(2)
<i>Z</i>	2
$D_{\text{calc}}$ ( $\text{g}\cdot\text{cm}^{-3}$ )	1.613

Table 1. Cont.

[Co <sub>2</sub> L(DMF) <sub>2</sub> Dy(NO <sub>3</sub> ) <sub>3</sub> ]·C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	
$\mu$ (mm <sup>-1</sup> )	1.897
Formula	C <sub>52</sub> H <sub>62</sub> Co <sub>2</sub> DyN <sub>9</sub> O <sub>21</sub>
<i>F</i> (000)	1450
Crystal size (mm)	0.26 × 0.24 × 0.23
$\theta$ Range (°)	3.310–26.017
Index ranges	–11 ≤ <i>h</i> ≤ 10 –30 ≤ <i>k</i> ≤ 25 –15 ≤ <i>l</i> ≤ 11
Reflections collected	11,948
Independent reflections	5933
<i>R</i> <sub>int</sub>	0.0456
Completeness to $\theta$	99.7% ( $\theta = 26.32$ )
Data/restraints/parameters	5933/3/422
GOF	1.028
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0426/0.0758
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices (all data)	0.0590/0.0854
Largest differences peak and hole (e Å <sup>-3</sup> )	0.840/–1.044

Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (1817410) and can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

### 3. Results and Discussion

#### 3.1. IR Spectra of H<sub>4</sub>L and Its Corresponding Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> Complex

The FT-IR spectra of H<sub>4</sub>L and its corresponding Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex exhibited various bands in the range of 400–4000 cm<sup>-1</sup>. As depicted in Figure 2, H<sub>4</sub>L showed a typical C=N stretching band at ca. 1613 cm<sup>-1</sup> [64,65], while the C=N stretching band of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex was observed at ca. 1594 cm<sup>-1</sup>. The shift to lower frequency by ca. 19 cm<sup>-1</sup> upon complexation shows a decrease in the C=N bond order due to the coordinative bonds of the metal atom with the oxime nitrogen lone pair [66]. The Ar–O typical stretching band of H<sub>4</sub>L appeared as a strong band at ca. 1258 cm<sup>-1</sup>, but was observed at ca. 1249 cm<sup>-1</sup> for the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex and shift to lower frequency by ca. 9 cm<sup>-1</sup> in the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex, exhibiting that the Co–O<sub>Ar</sub> and Dy–O<sub>Ar</sub> bonds were formed between phenolic oxygen atoms and the metal atoms [67–69]. Besides, the coordinated nitrate groups appeared at ca. 1300 cm<sup>-1</sup> for the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex [23]. Furthermore, the O–H stretching bands appeared at ca. 3419 cm<sup>-1</sup> in H<sub>4</sub>L [70], and disappeared in the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex.

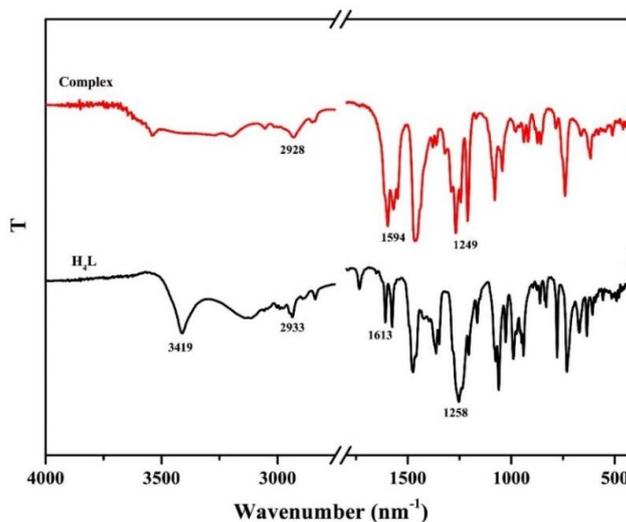
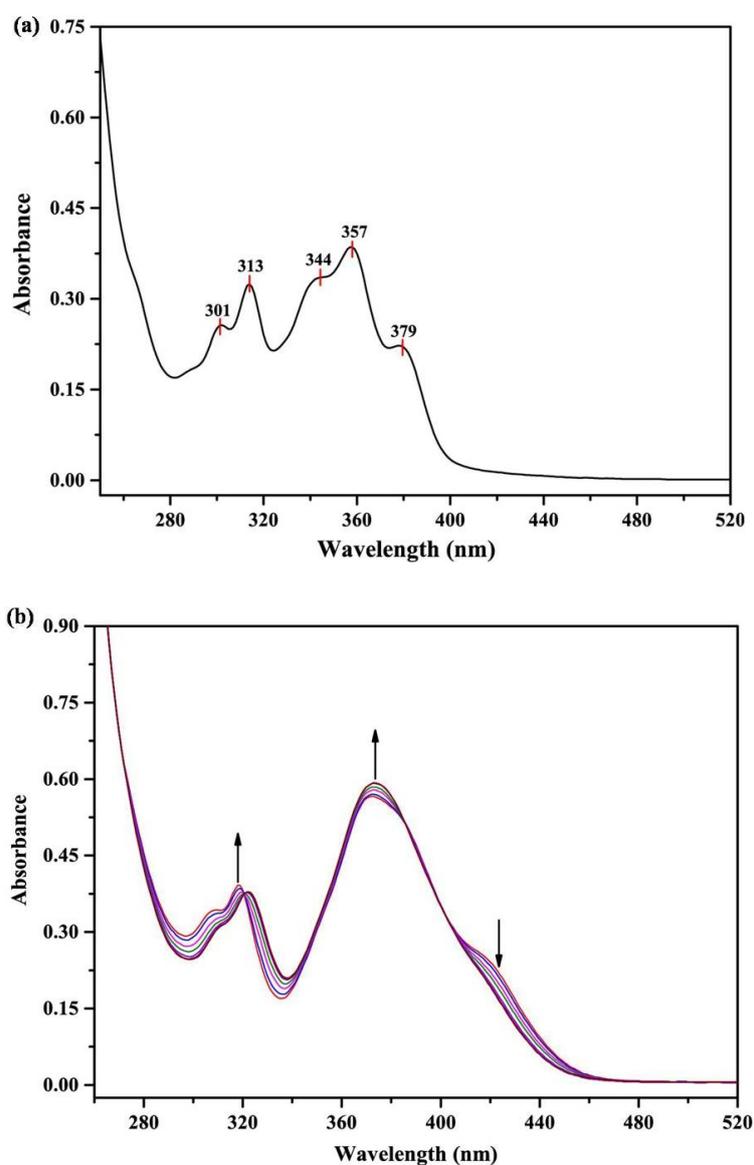


Figure 2. IR spectra of H<sub>4</sub>L and its corresponding Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex.

### 3.2. UV-Vis Absorption Spectra of $H_4L$ and Its Corresponding $Co^{II}_2-Dy^{III}$ Complex

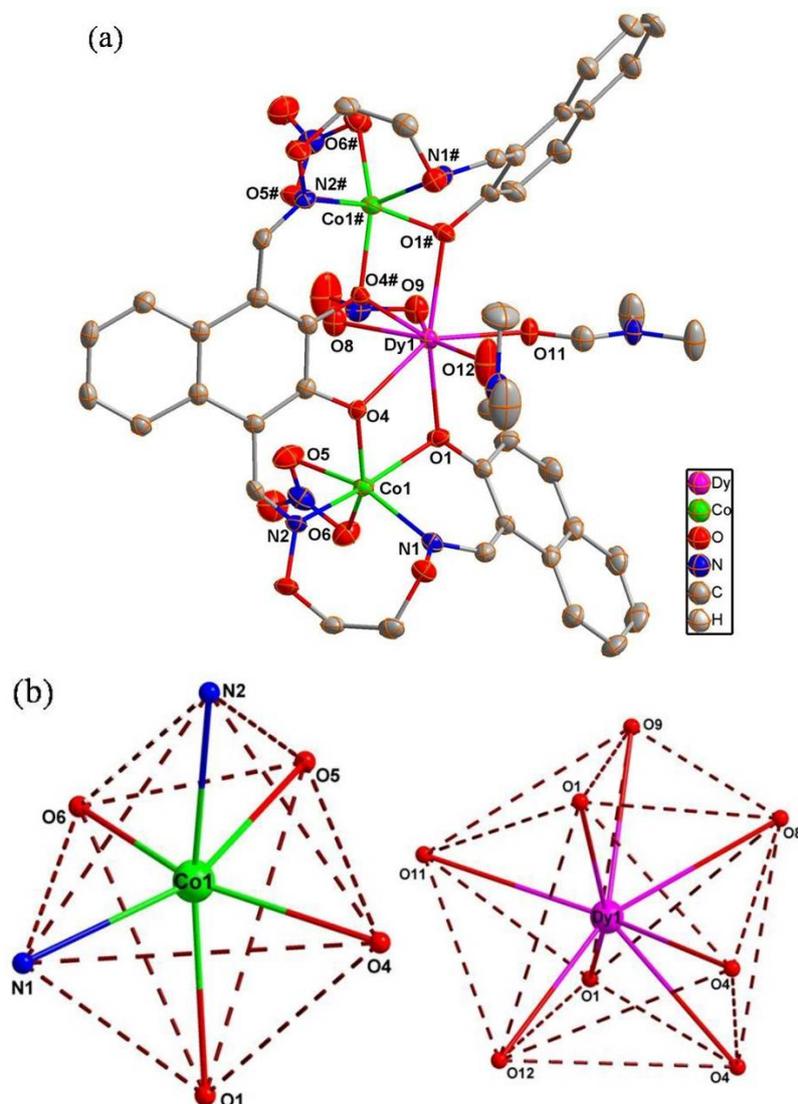
UV-Vis spectra of  $H_4L$  and its corresponding  $Co^{II}_2-Dy^{III}$  complex in mixed solutions (chloroform/methanol = 3:2,  $v/v$ ) at 298 K are shown in Figure 3. The spectrum of  $H_4L$  was almost consistent with the reported earlier [62]. In the UV-Vis titration experiments of  $Co^{II}_2-Dy^{III}$  complex, the color of the solution of  $Co^{II}$  complex in mixed solutions (chloroform/methanol = 3:2,  $v/v$ ) changed inconspicuously when the solution of  $Dy^{III}$  ion was added. However, the  $Co^{II}_2-Dy^{III}$  complex displayed three absorption bands at ca. 317, 374, and 419 nm, which shown red-shifted and indicate the coordination of  $H_4L$  with metal ions [70–74]. In addition, the molar absorption coefficient at 374 and 322 nm for the  $Co^{II}_2-Dy^{III}$  complex in mixed solutions (chloroform/methanol = 3:2,  $v/v$ ) are 29,200 and 18,900  $M^{-1}\cdot cm^{-1}$ , respectively. As in the case for the  $Co^{II}_2-Dy^{III}$  complex, although  $H_4L$  has two Salamo chelate units, the titration curves clearly indicated that the stoichiometry between  $Dy^{III}$  ion and  $[LCo_3]^{2+}$  was 1:1, and the isosbestic points (319, 351 and 401 nm) were observed.



**Figure 3.** (a) UV-Vis absorption spectra of  $H_4L$  ( $c = 1 \times 10^{-5} M$ ). (b) Absorption spectra of the  $Co^{II}_2-Dy^{III}$  complex in the presence of different concentrations of  $Dy^{III}$  ion in mixed solutions (chloroform/methanol = 3:2,  $v/v$ ) at 298 K.

### 3.3. Description of Crystal Structure of the $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$ Complex

The crystal structure of the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex and the coordination environment of  $\text{Co}^{\text{II}}$  and  $\text{Dy}^{\text{III}}$  atoms are shown in Figure 4. Selected bond lengths and angles are summed in Table 2.



**Figure 4.** (a) Molecular structure of the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex. (b) The coordination polyhedrons for  $\text{Co}^{\text{II}}$  and  $\text{Dy}^{\text{III}}$  atoms.

X-ray structure analysis showed the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex crystallizes in the monoclinic system, space group  $P_12_1/m_1$  with cell dimensions  $a = 9.2838(4)$ ,  $b = 24.9653(11)$ ,  $c = 12.7982(6)$ , and  $Z = 2$ . It is composed of two  $\text{Co}^{\text{II}}$  atoms, one  $\text{Dy}^{\text{III}}$  atom, one deprotonated  $(\text{L})^{4-}$  unit, three coordinated nitrate groups, and two coordinated  $N,N$ -dimethylformamide molecules resulting in a hetero-trinuclear  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex. In the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex, two terminal  $\text{Co}^{\text{II}}$  atoms are both six-coordinated with geometries of slightly distorted octahedron. The inner  $\text{N}_2\text{O}_2$  coordination spheres of Salamo moieties were occupied by two terminal Co1 and Co1# atoms, meanwhile, two bidentate nitrate groups coordinated two terminal  $\text{Co}^{\text{II}}$  atoms.  $\text{Dy}^{\text{III}}$  is sited in the  $\text{O}_4$  cavity that includes four phenoxy oxygen atoms (O1, O4, and O1#, O4#). Besides, the two coordinated DMF molecules provide two oxygen atoms (O11 and O12) and the bidentate nitrate groups provide remaining two oxygen atoms (O8 and O6), so  $\text{Dy}^{\text{III}}$  is eight-coordinated and possesses a distorted square antiprism geometry. Compared with

our previously reported Co<sup>II</sup> complex [62], Co<sup>II</sup> atoms are in N<sub>2</sub>O<sub>2</sub> coordination environments, and particularly the Co<sup>II</sup> atoms are chelated further with one bidentate nitrate group. The distance between the two terminal metal atoms Co1-Co1<sup>#</sup> is 6.322(3), in the previously reported Co<sup>II</sup> complex the distance of Co1-Co3 is 6.304(3). The distance of Co1-Co1<sup>#</sup> is longer than previously reported, because the larger radius Dy<sup>III</sup> atom replaced the central Co<sup>II</sup> atom. The angles of O2-N1-C11, O1-C1-C2 and C10-C11-N1 are 113.7(3), 116.8(4) and 123.3(4), respectively, indicating that the ligand H<sub>4</sub>L is more flexible.

**Table 2.** Selected bond lengths (Å) and angles (°) for the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex.

Bond	Lengths	Bond	Lengths	Bond	Lengths
Dy1-O1 <sup>#1</sup>	2.339(3)	Dy1-O9	2.480(4)	Co1-O1	2.104(3)
Dy1-O1	2.339(3)	Dy1-O11	2.316(3)	Co1-O4	1.983(3)
Dy1-O4 <sup>#1</sup>	2.383(2)	Dy1-O12	2.275(5)	Co1-O5	2.210(3)
Dy1-O4	2.383(2)	Dy1-O12 <sup>#1</sup>	2.275(5)	Co1-O6	2.159(3)
Dy1-O8	2.400(4)	Dy1-N4	2.861(5)	Co1-N1	2.034(3)
Bond	Angles	Bond	Angles	Bond	Angles
O1 <sup>#1</sup> -Dy1-O1	158.66(13)	O9-Dy1-N4	26.13(13)	O12-Dy1-O11	76.66(17)
O1 <sup>#1</sup> -Dy1-O4	132.84(9)	O11-Dy1-O1 <sup>#1</sup>	80.97(6)	O12 <sup>#1</sup> -Dy1-O11	76.66(17)
O1-Dy1-O4	68.05(9)	O11-Dy1-O1	80.97(6)	O12 <sup>#1</sup> -Dy1-O12	18.2(5)
O1-Dy1-O4 <sup>#1</sup>	132.84(9)	O11-Dy1-O4	142.30(8)	O12-Dy1-N4	170.7(2)
O1 <sup>#1</sup> -Dy1-O4 <sup>#1</sup>	68.05(9)	O11-Dy1-O4 <sup>#1</sup>	142.30(8)	O12 <sup>#1</sup> -Dy1-N4	170.7(2)
O1-Dy1-O8	91.00(7)	O11-Dy1-O8	127.46(15)	O1-Co1-O5	100.03(12)
O1 <sup>#1</sup> -Dy1-O8	91.00(7)	O11-Dy1-O9	75.60(14)	O1-Co1-O6	91.67(12)
O1 <sup>#1</sup> -Dy1-O9	82.29(7)	O11-Dy1-N4	101.74(15)	O4-Co1-O1	80.49(11)
O1-Dy1-O9	82.29(7)	O12-Dy1-O1	102.3(2)	O4-Co1-O5	91.68(12)
O1-Dy1-N4	86.31(7)	O12 <sup>#1</sup> -Dy1-O1 <sup>#1</sup>	102.3(2)	O4-Co1-O6	147.62(12)
O1 <sup>#1</sup> -Dy1-N4	86.31(7)	O12-Dy1-O1 <sup>#1</sup>	84.4(2)	O4-Co1-N1	111.71(12)
O4 <sup>#1</sup> -Dy1-O4	64.84(12)	O12 <sup>#1</sup> -Dy1-O1	84.4(2)	O4-Co1-N2	87.13(12)
O4 <sup>#1</sup> -Dy1-O8	75.65(11)	O12-Dy1-O4 <sup>#1</sup>	79.37(18)	O6-Co1-O5	58.58(12)
O4-Dy1-O8	75.65(11)	O12 <sup>#1</sup> -Dy1-O4	79.37(18)	N1-Co1-O1	82.90(12)
O4-Dy1-O9	118.79(10)	O12 <sup>#1</sup> -Dy1-O4 <sup>#1</sup>	89.13(18)	N1-Co1-O5	156.54(14)
O4 <sup>#1</sup> -Dy1-O9	118.79(10)	O12-Dy1-O4	89.13(18)	N1-Co1-O6	98.23(13)
O4 <sup>#1</sup> -Dy1-N4	97.30(12)	O12 <sup>#1</sup> -Dy1-O8	154.48(18)	N1-Co1-N2	94.30(13)
O4-Dy1-N4	97.30(12)	O12-Dy1-O8	154.48(18)	N2-Co1-O1	165.20(12)
O8-Dy1-O9	51.86(14)	O12 <sup>#1</sup> -Dy1-O9	150.76(17)	N2-Co1-O5	88.34(13)
O8-Dy1-N4	25.73(14)	O12-Dy1-O9	150.76(17)	N2-Co1-O6	103.12(13)

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup> x, 1/2-y, z.

### 3.4. Supramolecular Interactions of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> Complex

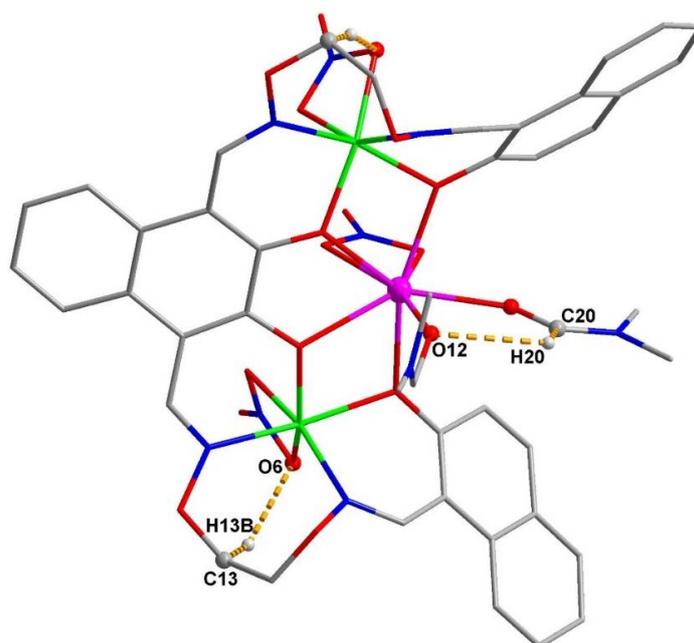
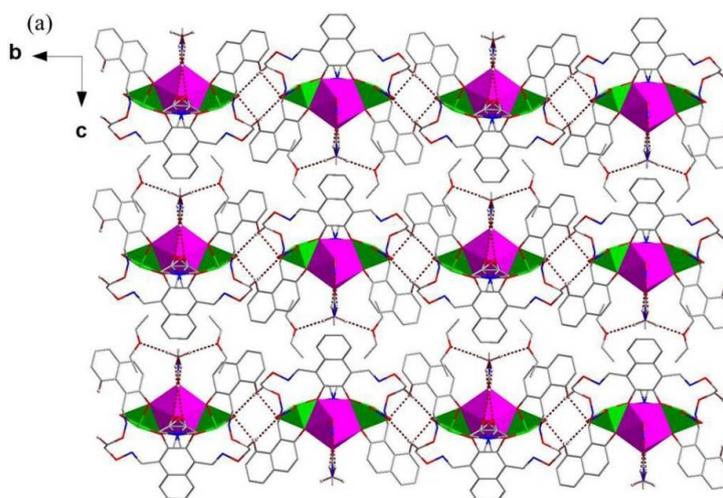
Notably, there are various intra- and inter-molecular hydrogen bond interactions in the crystal structure of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex. The hydrogen bond parameters are summed in Table 3. As shown in Figure 5.

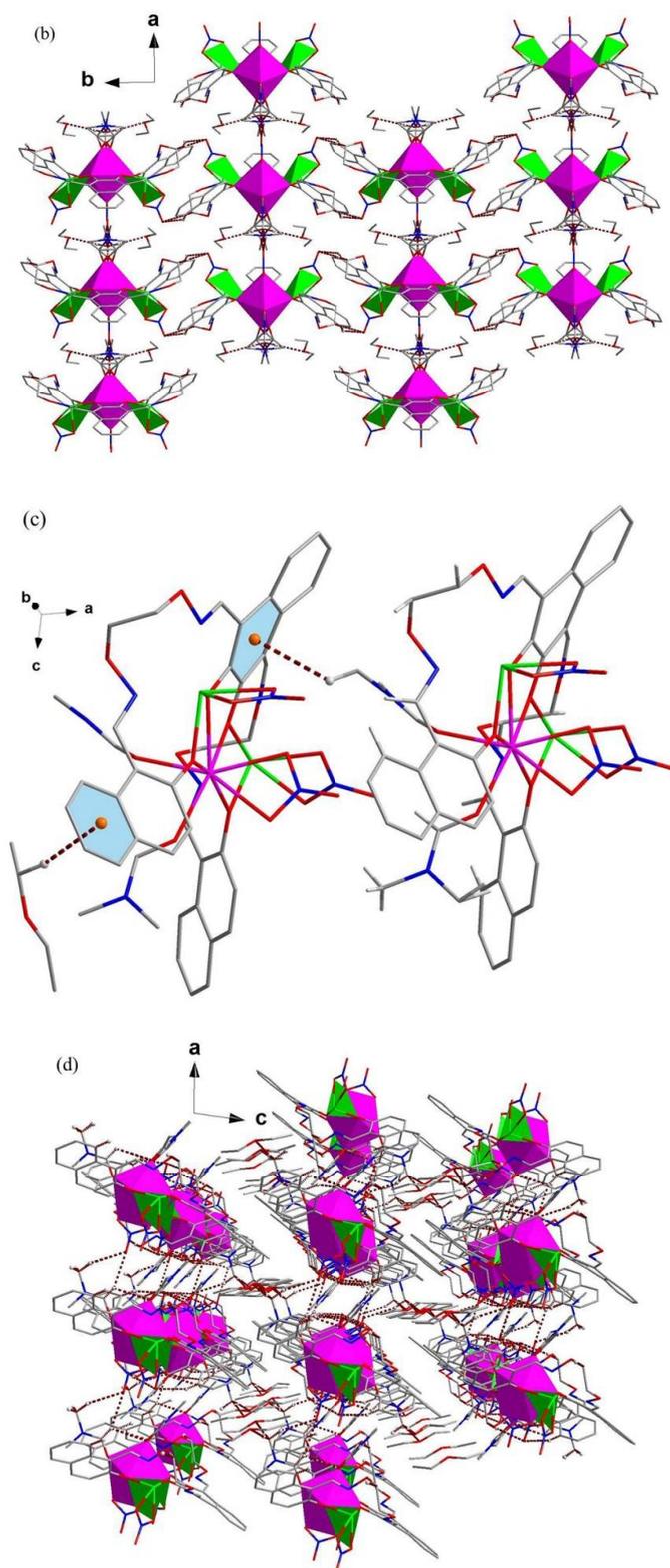
There are three pairs of intra-molecular hydrogen bond interactions (C13-H13B...O6, C20-H20...O12 and C22-H22B...O11) [75,76]. Besides, the structure of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex is stabilized by inter-molecular O-H...O, C-H...O and C-H...π hydrogen bond interactions. As a result, the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex possesses a self-assembling infinite 2D and 3D supra-molecular structure [77] via the inter-molecular hydrogen bonds, respectively (Figure 6). The 3D supra-molecular structure of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex includes two parts. The former is linked via inter-molecular O-H...O and C-H...O hydrogen bond interactions. The latter is composed of the C-H...π interactions. The inter-molecular hydrogen bonding of the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex makes its structure variable and stable. There is no π...π interactions in the Co<sup>II</sup><sub>2</sub>-Dy<sup>III</sup> complex because the distance between ring centroids was 5.953(2) which beyond the specified range.

**Table 3.** Hydrogen bonding interactions ( $\text{\AA}$ ,  $^\circ$ ) for the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex <sup>a</sup>.

D–H...A	H...A	D...A	D–H...A	Symmetry Codes
C13–H13B... O6	2.58	3.497(6)	158	
C20–H20... O12	2.53	3.041(8)	115	
O8–H8...O7	2.57	3.378(6)	145	1-x, 1-y, -z
O12–H12A...O7	2.51	3.476(6)	174	1-x, 1-y, -z
C20–H20... O10	2.54	3.403(7)	154	-1+x, y, z
C21–H21A... O10	2.46	3.358(9)	155	-1+x, y, z
C21–H21C... O13	2.46	3.421(6)	176	x, 1/2-y, z
C13–H13A... Cg1	2.79		140	1-x, 1-y, -z
C27–H27A... Cg2	2.70		167	x, y, z
C24–H24C... Cg3	2.72		122	-1+x, 1/2-y, z
C22–H22B... Cg4	2.97		107	x, 1/2-y, 1+z

<sup>a</sup> Cg1, Cg2, Cg3 and Cg4 for the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex are the centroids of C1–C4, C9, C10; C4–C9; C15, C16, C16<sup>#</sup>, 15<sup>#</sup>, C17<sup>#</sup>, C17 and C17–C19, 19<sup>#</sup>–C17<sup>#</sup> atoms, respectively.

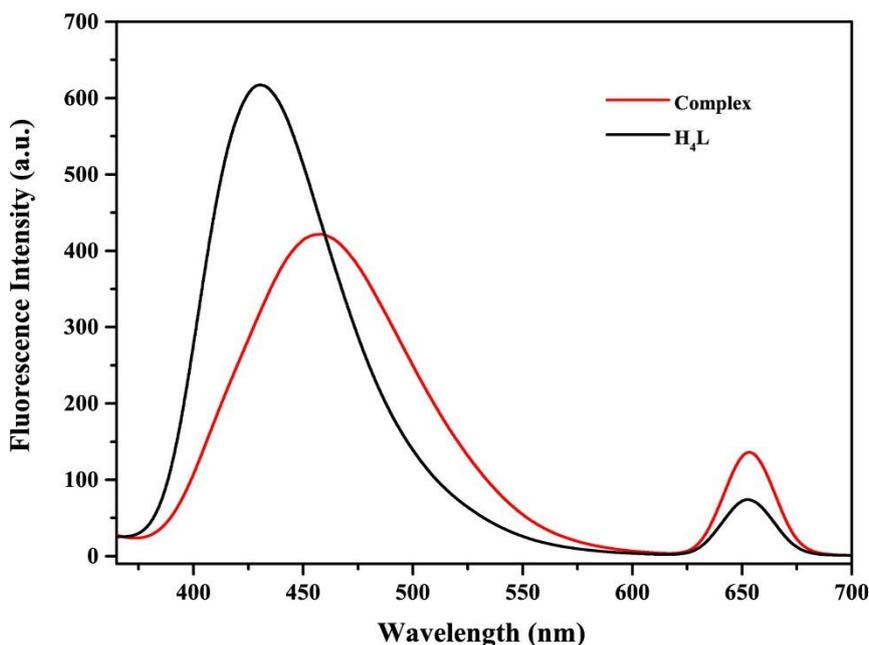
**Figure 5.** Intramolecular hydrogen bonding interactions of the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex.**Figure 6.** Cont.



**Figure 6.** Part of the infinite 2D supra-molecular structure along  $a$  axis (a);  $c$  axis (b); C-H... $\pi$  (c) and 3D (d) supra-molecular structure of the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex with intermolecular hydrogen bondings (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

### 3.5. Fluorescence Properties of the $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$ Complex

The emission spectra of  $\text{H}_4\text{L}$  and its  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex in dilute DMF solution at room temperature are depicted in Figure 7.  $\text{H}_4\text{L}$  showed an intense photoluminescence with maximum emission at ca. 431 nm when excited at ca. 372 nm, which can be attributed to intra-ligand  $\pi\text{-}\pi^*$  transitions. Meanwhile, compared with  $\text{H}_4\text{L}$ , the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex showed slightly weaker fluorescence intensity with maximum emissions at ca. 421 nm upon excitation at ca. 372 nm, which are attributed to the intra-ligand  $\pi\text{-}\pi^*$  transition and exhibiting that the fluorescent behaviour has been affected by the  $\text{Co}^{\text{II}}$  atoms [78]. The bathochromic indicates the hetero-trinuclear structure led to a larger conjugate system [72].



**Figure 7.** Fluorescence spectra of  $\text{H}_4\text{L}$  and its  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex ( $c = 1 \times 10^{-5}$  M) upon excitation at ca. 372 nm in mixed solutions (chloroform/methanol = 3:2,  $v/v$ ) at 298 K.

## 4. Conclusions

We have newly designed a novel hetero-trinuclear  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex with a multi-naphthol-based bis(Salamo)-like tetraoxime  $\text{H}_4\text{L}$ . The  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex has been characterized via X-ray diffraction and physicochemical methods. In the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex, two terminal  $\text{Co}^{\text{II}}$  atoms, sited in the  $\text{N}_2\text{O}_2$  cavities of the Salamo units, bear distorted octahedral geometries, and the central  $\text{O}_4$  coordination environment was occupied by the  $\text{Dy}^{\text{III}}$  atom bearing a distorted square antiprism. Significantly, the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex possesses a self-assembling infinite 2D and 3D supra-molecular structure through the inter-molecular hydrogen bondings which make its structure variable and stable. Compared with  $\text{H}_4\text{L}$ , the  $\text{Co}^{\text{II}}_2\text{-Dy}^{\text{III}}$  complex exhibited slightly lower fluorescence intensity, and shifted to higher wavelength, indicating the hetero-trinuclear structure led to a larger conjugate system.

**Supplementary Materials:** The crystallographic data is available online at <http://www.mdpi.com/2073-4352/8/4/174/s1>.

**Acknowledgments:** This work was supported by the National Natural Science Foundation of China (21761018) and the Program for Excellent Team of Scientific Research in Lanzhou Jiaotong University (201706), both of which are gratefully acknowledged.

**Author Contributions:** Yu-Hua Yang and Jing Hao performed most of the experiments. Xiao-Yan Li and Yang Zhang contributed to the writing of the manuscript. Wen-Kui Dong designed the project. All authors reviewed the manuscript.

**Conflicts of Interest:** The authors declare no competing financial interests.

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