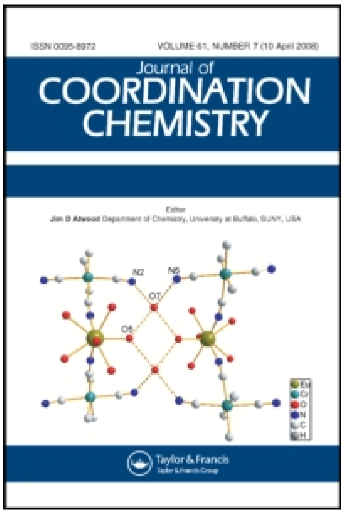

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Crystal structure and fluorescence properties of the supramolecule complex [$Dy(H_2L)(HL)(H_2O)_3$]·0.5dipy·$2H_2O$

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Crystal structure and fluorescence properties of the supramolecule complex $[Dy(H_2L)(HL)(H_2O)_3]\cdot 0.5dipy\cdot 2H_2O$

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A novel dysprosium(III) complex with N-(2-propionic acid)-salicyloyl hydrazone ($C_{10}H_{10}N_2O_4$, H_3L) and 2,2-dipyridyl ($C_{10}H_8N_2$, dipy) was prepared and characterized. The crystal structure of $[Dy(H_2L)(HL)(H_2O)_3]\cdot 0.5dipy\cdot 2H_2O$ was determined by X-ray single crystal diffractometry. The crystal complex crystallizes in the triclinic system with space group $P\bar{1}$. In the structure, Dy(III) is 9-coordinated by carboxyl O and acyl O atoms and azomethine N atoms of two ligands (H_2L and HL forms) and O atom from three water molecules. H_2L and HL act as tridentate ligands which form two stable five-numbered rings shared one side with keto-mode as indicated by the result of the crystal structure and infrared spectral analysis. The coordination polyhedron around Dy(III) was described as a monocapped square antiprism. One free 2,2-dipyridyl and two lattice waters connecting with coordinated water and ligands by hydrogen bonds lie in the crystal cell. The complex formed a three-dimensional super molecule in space through hydrogen bonds. The complex exhibits good fluorescence property.

Keywords: Dysprosium(III) complex; N-(2-Propionic acid)-salicyloyl hydrazone; 2,2-Dipyridyl; Crystal structure; Fluorescence property

1. Introduction

Development of the polydentate ligands capable of forming stable Lanthanide(III) complexes would not only allow further study of the coordination properties of the rare earth metal ions but also enable chemists to explore certain important properties of these complexes [1]. Acyl hydrazone ligands bearing both nitrogen and oxygen donors which exhibit both hard and soft base character would form more stable complexes than the polyoxa or polyaza ligands of these kinds with Lanthanide(III) cations [2]. For the complexes of acyl hydrazone, three coordination forms were reported by researches: keto-form, enolic form and dehydrogenation conjugation form [3–5]. The valence existence of acyl hydrazone is multiple [6–9]. Luminescent lanthanide complexes are

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found using as labels and sensors for natural and medical science [10]. Dysprosium(III)-based complexes have attracted considerable interest due to potential applications of their special fluorescent properties [11]. This article reports the crystal structure of a ternary Dy(III) complex with the acyl hydrazone and dipy ligands. The fluorescence property of the complex was investigated.

2. Experimental

2.1. *Main reagents and apparatus*

Pyruvic acid was biochemical reagent, $Dy(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving Dy_2O_3 (99.95%) in 1 : 1 HNO_3, and then crystallizing the products. All chemicals used were of analytical grade.

The C, H and N analyses were taken with a Perkin Elmer model 2400 element analyzer. IR spectra were recorded on an EQUINOX 55 IR spectrophotometer by using KBr pellets. Molar conductance measurement was made using a DDS-11A conductivity meter. TG-DTG-DSC curve is obtained with a NETZSCH STA 499C thermal analyzer with a heating rate of $10^{\circ}C\,min^{-1}$. The X-ray data for the crystal were collected on a Bruker Smart-1000 CCD X-ray single crystal diffractometer. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer.

2.2. *Synthesis of the complex $[Dy(H_2L)(HL)(H_2O)_3] \cdot 0.5dipy \cdot 2H_2O$*

The synthesis route and physical–chemical property of ligand N-(2-propionic acid)-salicyloyl hydrazone (H_3L) was reported in the literature 9. $Dy(NO_3)_3 \cdot 5H_2O$, H_3L and dipy in a 1 : 2 : 2 stoichiometry were dissolved in mixed solution of aqua-ethanol respectively and then mixed. The resultant solution was refluxed in 80°C water bath. Brilliant yellow rhombus single crystal was obtained from the mother solution after several months of standing. The yield is 62%. The metal ion was determined by EDTA titration. (Found: C, 39.07; H, 3.98; N, 8.95; Dy, 21.08 requires $C_{25}H_{31}N_5O_{13}Dy$: C, 38.89; H, 4.05; N, 9.07; Dy, 21.05.)

The molar electrical conductivity was measured in dimethylformamide (DMF). The Λ_M value ($4.8 S\,cm^{-1}\,mol^{-1}$) is consistent with the expected value for non-electrolyte [12]. The complex can be easily dissolved in DMF and dimethylsulfoxide (DMSO), sparingly soluble in methanol but not soluble in water, ethanol and benzene.

2.3. *Crystal structure measurement*

The single crystal $0.31 \times 0.20 \times 0.11\,mm^3$ in dimension was selected and mounted on a Bruker Smart-1000CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.071073\,nm$) using the ϕ–ω scan technique at 298(2) K. 7389 data were collected in a range of $1.61 \leq \theta \leq 25.10^{\circ}$, of which 5076 were independent data and 4737 reflections with $I > 2.00\sigma(I)$ were refined. Data were corrected for Lp and semiempirical method from equivalent absorption correction. The molecular structure crystallized in the triclinic space group $P\bar{1}$ with $a = 0.94198(9)$, $b = 1.25000(12)$,

$c = 1.36009(13)$ nm, $\alpha = 73.5300(10)$, $\beta = 72.8140(10)$, $\gamma = 77.5490(10)°$, $V = 1.4519(2)\,\mathrm{nm}^3$, $Z = 1$, $\mu = 2.649\,\mathrm{mm}^{-1}$, $D_c = 1.766\,\mathrm{Mg\,m}^{-3}$, $F(000) = 772$. The structure was solved with direct methods and refined with the full-matrix least-squares on F^2. The final R indices $R = 0.0204$, $\omega R = 0.0575$, GOF $= 1.098$. The largest residual peak and hole in the final difference Fourier diagram were $0.939 \times 10^3\,\mathrm{e\,nm}^{-3}$ and $-0.463 \times 10^3\,\mathrm{e\,nm}^{-3}$. All the calculation was performed with the SHELXTL-97 program.

3. Discussion

3.1. *Description of the crystal structure*

Selected bond lengths and bond angles of the crystal are listed in table 1. The molecule structure is shown in figure 1, and the crystal packing diagram is depicted in figure 2.

The X-ray study revealed that the crystal of $[\mathrm{Dy(H_2L)(HL)(H_2O)_3}] \cdot 0.5\mathrm{dipy} \cdot 2\mathrm{H_2O}$ was in the triclinic system with space group $\bar{P}1$. The Dy atom is nine-coordinated by two tridentate ligands and three water molecules. The linkage of the H_2L and HL ligand to the metal atom is accomplished through the acyl oxygen, carboxyl oxygen and imido nitrogen. Thus two five-membered chelate rings shared a same edge are formed. The coordination polyhedron of Dy can be described as a distorted monocapped square antiprism. Atoms O(3), O(5), O(11), O(7) and N(1), O(1), O(9), O(10) form lower and upper square plane respectively, the angle between two planes is 2.4°, the capping atom is N(3) for Dy. Non-coordinated dipy and two water molecules are found in the crystal lattice. From the perspective view of the complex shown in figure 1, the atoms of every N-(2-propionic acid)-salicyloyl hydrazone are almost located on the same plane. The two planes angle is 83.3°. The free dipy is approximately parallel with planes of Dy,

Table 1. Selected bond lengths ($\times 10^{-1}$ nm) and bond angles (°) for complex.

Dy(1)–O(5)	2.341(2)	N(1)–C(2)	1.277(4)	O(2)–C(1)	1.225(4)
Dy(1)–O(9)	2.343(2)	N(1)–N(2)	1.369(3)	O(3)–C(4)	1.235(3)
Dy(1)–O(1)	2.3798(19)	N(2)–C(4)	1.347(4)	O(4)–C(10)	1.369(4)
Dy(1)–O(11)	2.396(2)	N(3)–C(12)	1.271(4)	O(5)–C(11)	1.270(4)
Dy(1)–O(7)	2.413(2)	N(3)–N(4)	1.366(3)	O(6)–C(11)	1.239(4)
Dy(1)–O(10)	2.472(2)	N(4)–C(14)	1.346(4)	O(7)–C(14)	1.246(3)
Dy(1)–O(3)	2.507(2)	N(5)–C(21)	1.341(4)	O(8)–C(20)	1.317(4)
Dy(1)–N(3)	2.505(2)	N(5)–C(25)	1.344(4)	O(10)–Dy(1)–N(3)	126.49(7)
Dy(1)–N(1)	2.539(2)	O(1)–C(1)	1.263(4)	O(5)–Dy(1)–O(3)	77.73(7)
O(5)–Dy(1)–O(9)	79.09(7)	O(5)–Dy(1)–O(10)	75.84(7)	O(9)–Dy(1)–O(3)	74.63(8)
O(5)–Dy(1)–O(1)	151.88(7)	O(9)–Dy(1)–O(10)	68.79(7)	O(1)–Dy(1)–O(3)	124.27(6)
O(9)–Dy(1)–O(1)	89.71(7)	O(1)–Dy(1)–O(10)	76.06(7)	O(11)–Dy(1)–O(3)	142.37(7)
O(5)–Dy(1)–O(11)	92.10(8)	O(11)–Dy(1)–O(10)	70.69(7)	O(7)–Dy(1)–O(3)	82.11(7)
O(9)–Dy(1)–O(11)	139.46(8)	O(7)–Dy(1)–O(10)	139.82(7)	O(10)–Dy(1)–O(3)	138.03(7)
O(1)–Dy(1)–O(11)	79.73(7)	O(5)–Dy(1)–N(3)	63.89(7)	N(3)–Dy(1)–O(3)	66.04(7)
O(5)–Dy(1)–O(7)	126.57(7)	O(9)–Dy(1)–N(3)	130.10(8)	O(5)–Dy(1)–N(1)	134.22(7)
O(9)–Dy(1)–O(7)	140.60(7)	O(1)–Dy(1)–N(3)	137.73(7)	O(9)–Dy(1)–N(1)	71.42(7)
O(1)–Dy(1)–O(7)	77.57(7)	O(11)–Dy(1)–N(3)	76.88(7)	O(7)–Dy(1)–N(1)	69.57(7)
O(11)–Dy(1)–O(7)	75.20(8)	O(7)–Dy(1)–N(3)	62.68(7)	O(3)–Dy(1)–N(1)	61.33(7)
O(1)–Dy(1)–N(1)	62.96(7)	O(11)–Dy(1)–N(1)	132.78(8)		
O(10)–Dy(1)–N(1)	121.78(7)	N(3)–Dy(1)–N(1)	111.56(7)		

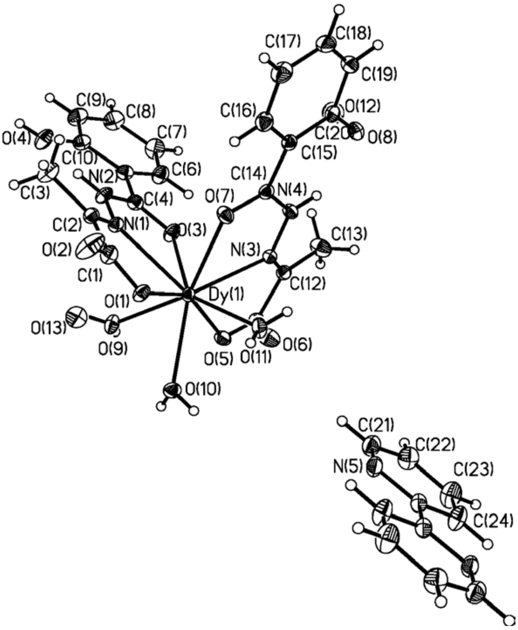

Figure 1. Perspective view of molecule for the complex.

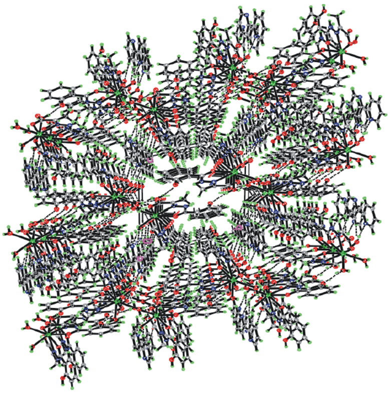

Figure 2. Packing diagram of the complex along a axis.

O(3), N(1) and O(1). The mean bond length of Dy–O is 0.2405 nm, and that of Dy–N is 0.2524 nm. Due to the oxophilic character of lanthanide, the bond length of Dy–O is shorter than that of Dy–N. Comparing the distances to C–O (0.143 nm) and C=O (0.122 nm), that the bond lengths of O(3)–C(4), and O(7)–C(14) are 0.1235 and 0.1246 nm respectively, indicate that these bonds are double linkage and ligand functions as a keto form. In the same environment, the bond length of O(4)–C(10) (0.1369 nm) of phenolic hydroxyl is longer than that of O(8)–C(20) (0.1317 nm), showing the bond intensity of O(8)–C(20) is increased because of loss of hydrogen connected with O(8). So N-(2-propionic acid)-salicyloyl hydrazone

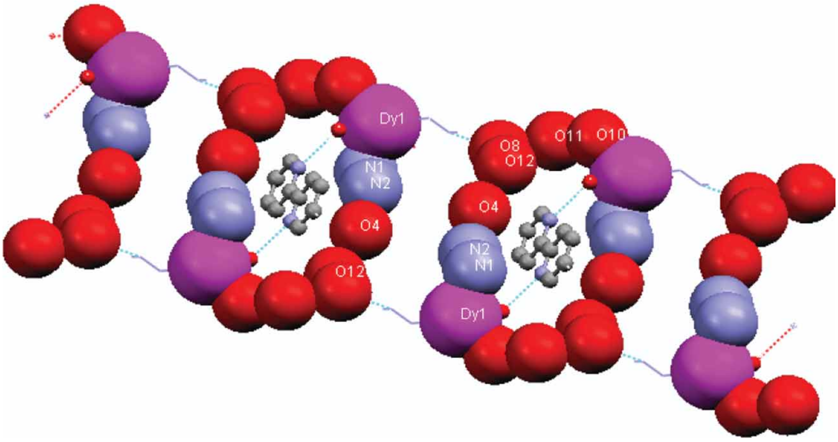

Figure 3. A diagram seed orientation face (2, 0, 1) and the other atoms was omitted for clarity.

was coordinated with Dy(III) by negative univalent (H_2L) and bivalent (HL) in complex.

The tridentate ligand can form two five-membered rings shared the same edge, indicating its coordination ability is strong. The space of Dy(III) is crowded with two coordinated N-(2-propionic acid)-salicyloyl hydrazone. The rare earth elements are oxophilic, the oxygen of water is more liable to coordinate to Dy than nitrogen of dipy. In addition, the steric hindrance effect of dipy is more unfavorable to coordination than that of water. Therefore dipy is free in the crystal cell. In one moleculer, H_2L and HL are like two butterfly wings, the bonds of Dy–O(9) and Dy–O(10) are just as two antennae. So the whole complex look like two butterflies face to face.

There are abundant hydrogen bonds in the molecule. The intramolecular hydrogen bonds have been formed between nitrogen atom of amido and oxygen atom of the phenol hydroxyl. The intermolecular hydrogen bonds have been formed by N(5)···H–O(9), O(1)···H–O(10), O(2)···H–O(13), O(5)···H–O(13), O(6)···H–O(10), O(10)···H–O(11) and O(9)···H–O(13) and so on. The hydrogen bonds of O(8) with O(11), O(12) and N(4) are more extensive than those of O(4) with O(12) and N(2), showing electron density of O(8) is decreased and hydrogen atom is easier to lose, which agreed with what was described above. The 3 dimensional supramolecule network of hydrogen bonds provides an extra stability for the crystal. A diagram showing this network is displayed in figure 2. The guest dipy molecule modulates the complex molecules to attain the most stable accommodation into the cavity, The complex molecules are laterally shifed away from each other to create the cavity fitted to the shape of the guest molecules. As the result, dipy fills cavities to about 14.8% occupancy calculated by PLATON [13] and is stabilized by the interaction with the complex molecules (see figure 3).

3.2. *Infrared spectra*

IR spectra of the complex at 1616 and 1359 cm^{-1} were assigned to $\nu_s(\mathrm{COO}^-)$ and $\nu_{as}(\mathrm{COO}^-)$, respectively. The shifts suggest that the carboxylate groups of the ligand act

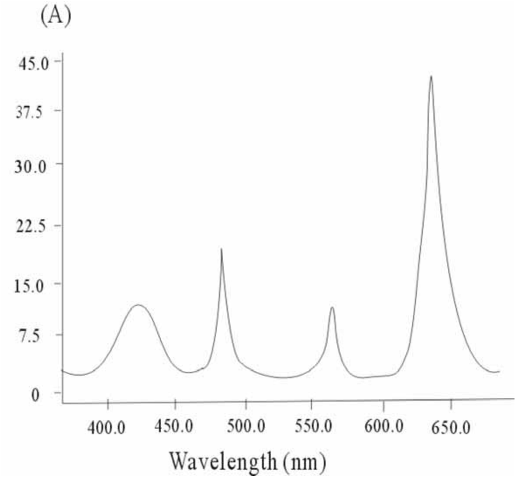

Figure 4. The fluorescence spectrum of the solid complex at room temperture.

as a monodentate ligand coordinating to the Dy(III) [14]. IR spectra of the ligand show three strong amide bands at 1680, 1552 and 1298 cm^{-1}. However, the bands were shifted to 1620 (amide I), 1552 (amide II) and 1327 cm^{-1} (amide III) for complex respectively. These shifts indicate that the coordination involving the keto-form of the ligand [1]. The complex shows a wide band between 3500 to 3000 cm^{-1}, and this band could be reasonably attributable to the –OH and –NH groups involved in intermolecular hydrogen bonding [15]. The in-plane and out-of-plane vibrations of water were observed in the spectrum of the complex at 774 and 581 cm^{-1}, which was associated with the coordinated water molecules [16]. This IR spectroscopic analysis is in agreement with the X-ray crystal structure of the complex.

3.3. *Thermal behaviors*

Upon heating under nitrogen ($\beta = 10\,K\,min^{-1}$), the complex undergoes three major stages of weight loss. The first weight loss occurs over 60–216°C. The DSC curve shows two narrow endothermic peaks in this temperature at 83 and 165°C, The value of the weight loss at this stage (4.8%, 6.9%) is agree with the value calculated for the removal of two lattice water molecules and three coordinated waters (4.7%, 7.0%). The decomposition occurs in stepwise manner when heated to above 220°C.

3.4. *Fluorescence property*

The solid state fluorescence characteristic of the Dy complex was measured in room temperature. The excitation wavelength is 350 nm. The spectra of the complex was given in figure 4. The broad band around 430 nm can be attributed to ligand and dipy. The other three peaks at 480, 575 and 645 nm can be attributed to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions of Dy^{3+}, respectively [17]. The fluorescence enhancement of Dy^{3+} reflects the efficient energy transfer from the π-electron conjugated system to the Dy^{3+} compared to $Dy(NO_3)_3 \cdot 5H_2O$ under the same condition. Since the excitated wavelength is fixed in $\pi - \pi^*$ transitions $\lambda_{\max}$ of the complex in UV, The existence of the characteristic emissions of Dy^{3+} demonstrate intramolecule energy transfer process by intramolecule resonance coupling effection [10].

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