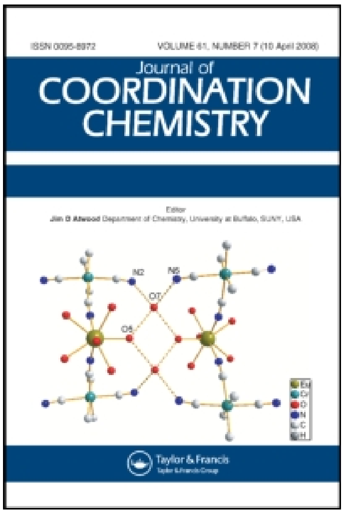

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Crystal structure and fluorescence of the supramolecular complex $[Dy(H_2L)(HL)(H_2O)_3]\cdot 0.5dipy\cdot 2H_2O$

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

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A novel dysprosium(III) complex of *N*-(2-propionic acid)salicyloylhydrazone (H_3L) and 2,2-dipyridyl (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 single-crystal X-ray diffraction methods. In the structure, Dy(III) is 9-coordinated by carboxyl O, acyl O atoms and azomethine N atoms of two ligands (H_2L and HL forms) and O atoms from three water molecules. H_2L and HL act as tridentate ligands, which form two stable five-numbered rings in the keto form, as indicated by the crystal structure and IR data. The coordination polyhedron around Dy(III) can be described as a monocapped square antiprism. A free 2,2-dipyridyl molecule and two water molecules are connected to coordinated water and ligands by hydrogen bonds to form a three-dimensional structural motif. The complex is highly fluorescent.

Keywords: Dysprosium(III); *N*-(2-propionic acid)salicyloylhydrazone; 2,2-Dipyridyl; Crystal structure; Fluorescence

1. Introduction

Development of polydentate ligands capable of forming stable lanthanide(III) complexes would not only allow further study of the coordination properties of rare earth metal ions but also enable chemists to explore certain important properties of these complexes [1]. Acylhydrazone ligands bearing both nitrogen and oxygen donors exhibiting both hard and soft base character would form more stable complexes than the polyoxo or polyaza ligands with lanthanide(III) cations [2]. For complexes of acylhydrazones, three coordination forms are reported, keto, enolic form and dehydrogenated conjugated [3–5], and the ligands can be variously charged [6–9]. Luminescent lanthanide complexes have found use as labels and sensors in the medical sciences [10] and dysprosium(III) 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 acylhydrazone and dipy ligands. Fluorescence properties were also investigated.

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2. Experimental

2.1. *Materials and measurements*

$Dy(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving Dy_2O_3 in 1 : 1 HNO_3 and crystallizing the product. All other chemicals used were of analytical grade. C, H, N analyses were obtained with a Perkin-Elmer 2400 system analyzer. The metal ion was determined by EDTA titration. IR spectra were recorded on an Equinox 55 spectrophotometer (KBr pellets). Molar conductance measurements were made using a DDS-11A conductivity meter. TG-DTG-DSC traces were obtained with a Netzsch STA 499C thermal analyzer with a heating rate of $10^{\circ}C\,min^{-1}$. X-ray intensity data were collected on a Bruker Smart-1000 CCD diffractometer. Fluorescence measurements were made using a Hitachi F-4500 spectrophotometer.

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

N-(2-propionic acid)salicyloylhydrazone (H_3L) was prepared according to the literature [9]. $Dy(NO_3)_3 \cdot 5H_2O$, H_3L and dipy in a 1 : 2 : 2 mole ratio were dissolved in aqueous ethanol and refluxed. Brilliant yellow rhombs were obtained from solution after several months. Yield: 62%. Anal. Calcd for $C_{25}H_{31}N_5O_{13}Dy$ (%): C, 38.89; H, 4.05; N, 9.07; Dy, 21.05. Found: C, 39.07; H, 3.98; N, 8.95; Dy, 21.08. The Λ_M value (DMF) of $4.8\,S\,cm^{-1}\,mol^{-1}$ is consistent with a non-electrolyte [12]. The complex is freely soluble in DMF and DMSO, sparingly soluble in methanol, but insoluble in water, ethanol and benzene.

2.3. *X-ray crystallography*

A single crystal of dimensions $0.31 \times 0.20 \times 0.11\,mm^3$ was mounted on a Bruker Smart-1000CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm). By using the φ–ω scan technique at 298(2) K, some 7389 data were collected in the range $1.61 \leq \theta \leq 25.10^{\circ}$; of these, 5076 were independent and 4737 reflections with $I > 2.00\sigma(I)$ were refined. Data were corrected for Lp and absorption. The complex is triclinic, space group $P\bar{1}$, with $a = 0.94198(9)$, $b = 1.25000(12)$, $c = 1.36009(13)$ nm, $\alpha = 73.530(1)$, $\beta = 72.814(1)$, $\gamma = 77.549(1)^{\circ}$, $V = 1.4519(2)\,nm^3$, $Z = 1$, $\mu = 2.649\,mm^{-1}$, $D_c = 1.766\,Mg\,m^{-3}$, $F(000) = 772$. The structure was solved by direct methods and refined with full-matrix least-squares on F^2. The final R indices were $R = 0.0204$, $wR = 0.0575$, GOF = 1.098. The largest residual peak and hole in the final difference Fourier diagram were 0.939×10^3 and $-0.463 \times 10^3\,e\,nm^{-3}$. All calculations were performed with the SHELXTL-97 program.

3. Results and discussion

3.1. *Crystal structure*

Selected bond lengths and angles are listed in table 1. The molecular structure is shown in figure 1 and a crystal packing diagram in figure 2. The Dy atom is nine-coordinated

Table 1. Selected bond lengths ($\times 10^{-1}\,\mathrm{nm}^{-1}$) and bond angles (°) for the 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)		
Dy(1)–N(1)	2.539(2)	O(1)–C(1)	1.263(4)		
O(5)–Dy(1)–O(9)	79.09(7)	O(5)–Dy(1)–O(10)	75.84(7)	O(10)–Dy(1)–N(3)	126.49(7)
O(5)–Dy(1)–O(1)	151.88(7)	O(9)–Dy(1)–O(10)	68.79(7)	O(5)–Dy(1)–O(3)	77.73(7)
O(9)–Dy(1)–O(1)	89.71(7)	O(1)–Dy(1)–O(10)	76.06(7)	O(9)–Dy(1)–O(3)	74.63(8)
O(5)–Dy(1)–O(11)	92.10(8)	O(11)–Dy(1)–O(10)	70.69(7)	O(1)–Dy(1)–O(3)	124.27(6)
O(9)–Dy(1)–O(11)	139.46(8)	O(7)–Dy(1)–O(10)	139.82(7)	O(11)–Dy(1)–O(3)	142.37(7)
O(1)–Dy(1)–O(11)	79.73(7)	O(5)–Dy(1)–N(3)	63.89(7)	O(7)–Dy(1)–O(3)	82.11(7)
O(5)–Dy(1)–O(7)	126.57(7)	O(9)–Dy(1)–N(3)	130.10(8)	O(10)–Dy(1)–O(3)	138.03(7)
O(9)–Dy(1)–O(7)	140.60(7)	O(1)–Dy(1)–N(3)	137.73(7)	N(3)–Dy(1)–O(3)	66.04(7)
O(1)–Dy(1)–O(7)	77.57(7)	O(11)–Dy(1)–N(3)	76.88(7)	O(5)–Dy(1)–N(1)	134.22(7)
O(11)–Dy(1)–O(7)	75.20(8)	O(7)–Dy(1)–N(3)	62.68(7)	O(9)–Dy(1)–N(1)	71.42(7)
O(1)–Dy(1)–N(1)	62.96(7)	O(11)–Dy(1)–N(1)	132.78(8)	O(7)–Dy(1)–N(1)	69.57(7)
O(10)–Dy(1)–N(1)	121.78(7)	N(3)–Dy(1)–N(1)	111.56(7)	O(3)–Dy(1)–N(1)	61.33(7)

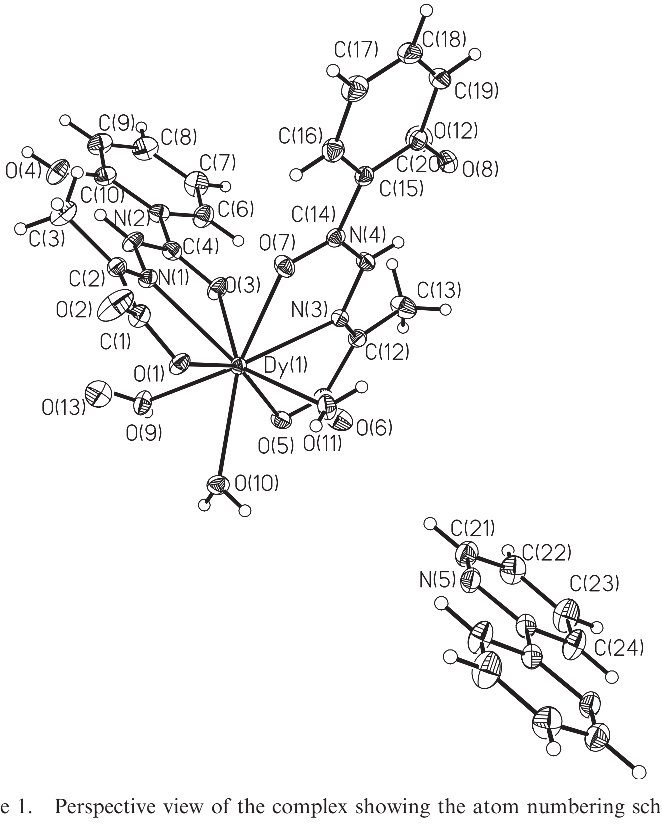

Figure 1. Perspective view of the complex showing the atom numbering scheme.

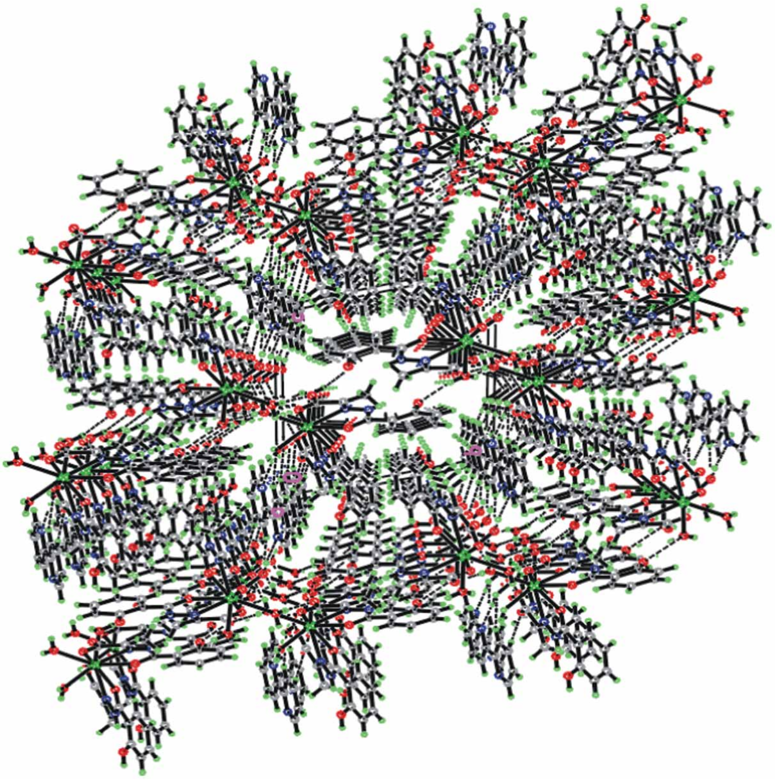

Figure 2. Packing diagram of the complex along the *a* axis.

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 atoms. Thus two sets of two coplanar five-membered chelate rings are formed, with a dihedral angle between the ligands of 83.3°. 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 planes, respectively, the angle between them being 2.4°; the capping atom is N(3). Non-coordinated dipy and two water molecules are present in the crystal lattice. The dipy molecule is approximately parallel with the plane formed by Dy, O(3), N(1) and O(1). The mean Dy–O bond length is 0.2405 nm, and that of Dy–N 0.2524 nm. Due to the oxophilic character of the lanthanide, Dy–O is shorter than Dy–N. Comparing the distances C–O (0.143 nm) and C=O (0.122 nm), the O(3)–C(4) and O(7)–C(14) bonds (0.1235 and 0.1246 nm, respectively) are formally double bonds, indicating that the ligands are in the keto form. The O(4)–C(10) bond (0.1369 nm) of the phenolic hydroxyl is longer than O(8)–C(20) (0.1317 nm), showing the bond strength of the latter is increased because of loss of hydrogen. Thus *N*-(2-propionic acid)salicyloylhydrazone coordinates both as a mono- and a divalent anion in the complex.

There are abundant hydrogen bonds in the lattice. Intramolecular hydrogen bonds are formed between the amido nitrogen atom and the oxygen atom of the phenol group. Intermolecular hydrogen are 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 others. 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)), in line with the ionization of the former. The 3D supramolecular network of hydrogen bonds provides extra stability for the crystal. The guest dipy molecule modulates the complex molecules and lies in a cavity (about 14.8% occupancy as calculated by PLATON [13]), and is stabilized by weak bonding interactions with the complex.

3.2. *Thermal and spectroscopic properties*

Upon heating under nitrogen, the complex undergoes three major stages of weight loss. The first occurs at 60–216°C. The DSC curve shows two narrow endothermic peaks at 83 and 165°C. Associated weight losses (4.8, 6.9%) are consistent with values calculated for the removal of two lattice and three coordinated water molecules (4.7, 7.0%). Decomposition occurs in a stepwise manner above 220°C as the complex completely decomposes.

IR bands for the complex at 1616 and 1359 cm^{-1} are assigned to $\nu_{\mathrm{s\,COO^-}}$ and $\nu_{\mathrm{as\,COO^-}}$, respectively. The shifts suggest that the carboxylate groups of the ligand act as monodentate ligands [14]. IR spectra of the ligand show three strong amide bands at 1680, 1552 and 1298 cm^{-1}. These are shifted to 1620 (amide I), 1552 (amide II) and 1327 cm^{-1} (amide III) in the complex, respectively. The shifts are consistent with the coordination of the keto form of the ligand [1]. The complex gives a broad band between 3500 and 3000 cm^{-1}, reasonably attributable to –OH and –NH groups involved in hydrogen bonding [15]. In-plane and out-of-plane vibrations of water were observed in the spectrum of the complex at 774 and 581 cm^{-1}; these are associated with coordinated water molecules [16].

Solid state fluorescence of the complex was measured at room temperature with an excitation wavelength of 350 nm. Spectra exhibit a broad band around 430 nm, attributed to the ligand and dipy. Three other 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(III), respectively [17]. The fluorescence enhancement of Dy(III) reflects efficient energy transfer from the conjugated π-electron system of the ligand to the Dy^{3+} ion, as compared to $\mathrm{Dy(NO_3)_3 \cdot 5H_2O}$ under the same conditions. Since the excitation wavelength is fixed in π–π* transitions ($\lambda_{\max}$ of the complex in the UV) the characteristic emissions of Dy(III) demonstrate intramolecular energy transfer by a resonance coupling effect [10].

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 602985. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] X.H. Bu, M. Du, L. Zhang, X.B. Song, R.H. Zhang, T. Clifford. *Inorg. Chim. Acta*, **308**, 143 (2000).
[2] D.S. Kumar, V. Alexander. *Inorg. Chim. Acta*, **238**, 63 (1995).
[3] D.G. Paschalidis, I.A. Tossidis, M. Gdaniec. *Polyhedron*, **19**, 2629 (2000).
[4] Z.Y. Yang, R.D. Yang, F.S. Li, K.B. Yu. *Polyhedron*, **19**, 2599 (2000).
[5] R.W. Deng, J.G. Wu, Z.N. Chen. *Synth. React. Met.- Org. Chem.*, **22**, 1295 (1992).
[6] P.K. Singh, B. Singh. *Indian J. Chem., Sect. A: Inorg. Bioinorg. Phys. Theor. Anal. Chem.*, **37A**, 331 (1998).
[7] X. Shen, Y.Y. Xie, H.L. Jiang. *Synth. React. Inorg. Met. Org. Chem.*, **25**, 511 (1995).
[8] M.X. Wang, H.Q. Den, W.D. Shan. *Chin. Chem. Lett.*, **2**, 587 (1991).
[9] S.Y. He, Y. Liu, J.S. Zhao, H.A. Zhao, R. Yang, R.Z. Hu, Q.Z. Shi. *Chin. J. Chem.*, **21**, 139 (2003).
[10] Y.W. Wang, W.S. Liu, N. Tang, M.Y. Tan. *Spectrochim. Acta*, **A60**, 2459 (2004).
[11] L.J. Zhang, Y.S. Zhou, L. Xu, Z. Yu, I.A. Razak, S. Chantrapromma, H.K. Fun, X.Z. You. *Inorg. Chem. Commun.*, **4**, 368 (2001).
[12] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[13] A.L. Spek. *Platon. A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands (1998).
[14] S. Gao, Z. Shi, J. Hua, S.H. Feng, R.R. Xu, S.X. Liu, L.H. Huo, P.G. Chen. *Chem. J. Chin. Univ.*, **21**, 177 (2000).
[15] G. Singh, P.S.S.J. Shastry, R.K. Lonibala, T.R. Rao. *Synth. React. Inorg. Met. Org. Chem.*, **22**, 1041 (1992).
[16] N. Kazuo. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 199, Chemical Industry Press, Beijing (1986).
[17] D.K. Sardar, W.M. Bradley, R.M. Yow, J.B. Gruber, Z. Zandi. *J. Luminesc.*, **106**, 195 (2004).