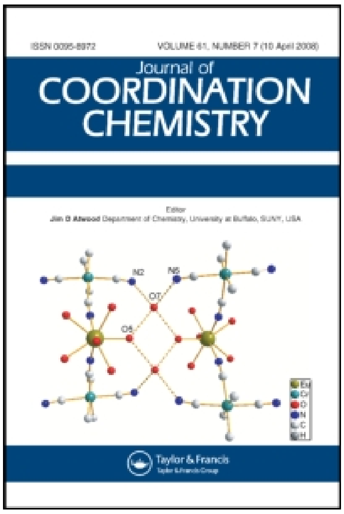

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis of a strongly luminescent dimeric dysprosium complex

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To cite this Article Bai, Yingying , Yan, Bing and Chen, Zhenxia(2005) 'Hydrothermal synthesis of a strongly luminescent dimeric dysprosium complex', Journal of Coordination Chemistry, 58: 10, 841 — 847

To link to this Article: DOI: 10.1080/00958970412331336312

URL: http://dx.doi.org/10.1080/00958970412331336312

Journal of Coordination Chemistry
Vol. 58, No. 10, 10 July 2005, 841–847

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Hydrothermal synthesis of a strongly luminescent dimeric dysprosium complex

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(Received in final form 23 July 2004)

The complex $[Dy(BAA)_2(phen)NO_3]_2$ (HBAA = phenylacetic acid, phen = 1,10-phenanthroline) was synthesized under hydrothermal conditions and characterized as by elemental analyses, IR, UV, fluorescence excitation and emission spectroscopy. A single-crystal X-rays structure determination diffraction indicates that the complex is dimeric and Dy has a coordination number of nine. The coordination polyhedron can be described as a distorted, monocapped, square antiprism. Pairs of adjacent metal atoms are bridged by four BAA groups in two coordination modes. The complex is triclinic system, space group $P\bar{1}$, with $a = 8.953(6)$, $b = 13.312(9)$, $c = 13.408(9)$ Å, $\alpha = 60.608(7)$, $\beta = 89.674(9)$, $\gamma = 72.165(9)^\circ$, $V = 1305.0(15)$ Å^3, $D_c = 1.718\,\mathrm{mg\,m^{-3}}$, $Z = 1$, $F(000) = 666$, $R_1 = 0.0424$.

Keywords: Dysprosium(III); Phenylacetic acid; 1,10-phenanthroline; Hydrothermal synthesis; Molecular assembly; X-ray structure; Luminescence

1. Introduction

Optical properties such as long decay-time luminescence, large Stokes' shifts, narrow emission bands and negligible concentration quenching make lanthanide complexes superior to traditional organic fluorophores [1–3]. This has led to much attention being paid to them with respect to applications as luminescent probes or labels for chemical or biological macromolecules. However, lanthanide *f–f* transitions are weak and direct excitation of lanthanide ions is difficult because of the forbidden nature of their transitions [4]. Therefore, the choice of suitable ligands that not only generate novel structural characteristics but also activate luminescence has been a central concern for the rational design and synthesis of new luminescent lanthanide complexes [5–8]. Apart from β-diketones, which have been acknowledged as being among the best activators, aromatic carboxylic acids have drawn considerable attention because of their fluorescence characteristics and thermal stability. These ligands readily lead to

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970412331336312

dimeric or infinite chain polymeric structures that are promising in terms of the development of new luminescent materials containing rare earth ions [9–16]. Furthermore, ternary or quaternary lanthanide complexes systems incorporating appropriate nitrogen-containing ligands such as bpy (2,2′-bipyridine) or phen (1,10-phenanthroline) are highly luminescent derivatives that are accessible via hydrothermal synthesis, rather than more traditional solution methods [17,18].

In this article, we report the hydrothermal synthesis of a novel luminescent quaternary dimeric complex, $[Dy(BAA)_2(phen)NO_3]_2$ (HBAA = phenylacetic acid), together with its crystal structure and photophysical properties.

2. Experimental

2.1. *Synthesis*

All reagents were of analytical grade and used without further purification, except for the stock solution of dysprosium nitrate, prepared by reaction of Dy_2O_3 and nitric acid. The complex was prepared by mixing dysprosium nitrate, phenylacetic acid and 1,10-phenanthroline (2 : 3 : 2 mol ratio) in a small volume of deionized water, and adjusting the pH of the mixture to 3–4 with aqueous 0.2 M NaOH. After stirring the mixture for two hours, a white precipitate formed and this was transferred to a 25 cm^3 Teflon-lined reactor and heated at 433 K for 3 days. The resulting yellow elongated prisms were suitable for X-ray diffraction analysis. The filtrate remaining after the crystals were filtered off was further evaporated to yield a yellow solid used for IR, fluorescence excitation and emission spectroscopy. (1349.97) Anal. Calc. For $[Dy(BAA)_2(phen)NO_3]_2$ (%): C, 50.69; H, 3.32; N, 6.34 %. Found: C, 49.93; H, 3.41; N, 6.19%. Characteristic IR: 1412 cm^{-1} (ν_{sCOO-}), 1548 cm^{-1} (ν_{asCOO-}).

2.2. *X-ray crystallography*

X-ray measurements for a crystal of dimensions 0.10 × 0.10 × 0.05 mm were performed with graphite-monochromated Mo Kα radiation on a CCD detector four-circle diffractometer using the ω–2θ scan technique. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were added geometrically and not refined. All calculations were performed with SHELXS-97 and SHELXL-97 [19,20]. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 235444. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. *Physical measurements*

Elemental analyses of C, H and N were carried out on an Elementar Cario EL instrument. Infrared spectra were recorded on a Nexus 912 AO446 FTIR spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. Ultraviolet absorption spectra were obtained with an Agilent 8453 spectrophotometer. Excitation and emission spectra for a solid sample of the complex were recorded with a Perkin–Elmer LS-55 spectrophotometer.

3. Results and discussion

3.1. *Crystal structure*

The dysprosium compound crystallizes in the triclinic system, space group $P\bar{1}$, with all atoms lying in general positions. Crystallographic data and final atomic coordinates for non-hydrogen atoms are given in tables 1 and 2, and the molecular structure with the atom numbering scheme is shown in figure 1. The crystal consists of dimers of $[Dy(BAA)_2(phen)NO_3]_2$ units related by the inversion centre. Each Dy ion achieves a coordination number of nine by bonding to five oxygen atoms of four bridging BAA anions, two oxygen atoms from a bidentate nitrate group and two nitrogen atoms from chelated 1,10-phenanthroline. Of the four carboxylate groups, two show bidentate bridging and two show tridentate chelating–bridging modes; the Dy···Dy distance is 3.892(2) Å. Around Dy(1), N(1), N(2), O(1) and O(2A) form a plane as illustrated by addition of bond angles O(2A)–Dy(1)–O(1) (138.19(18)°), O(2A)–Dy(1)–N(1) (76.89(19)°), O(1)–Dy(1)–N(2) (78.0(2)°) and N(2)–Dy(1)–N(1) (64.3(2)°). The two carboxylic oxygen atoms O(3) and O(4) coordinating to Dy(1) in the μ-bridging fashion and C(9) form a perfectly planar four-membered ring and the parallelogram consisting of Dy(1), Dy(2), O(3A) and O(3) is constrained to lie in this plane, due to the inversion

Table 1. Crystal data and structure refinement for $[Dy(BAA)_2(phen)NO_3]_2$.

Complex	$[Dy(BAA)_2(phen)NO_3]_2$
Formula	$C_{56}H_{44}N_6O_{14}Dy_2$
M	1349.97
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	Mo Kα
Crystal system	$P\bar{1}$
Space group	Triclinic
Unit dimensions	$a = 8.953(6)$ Å $b = 13.312(9)$ Å $c = 13.408(9)$ Å $\alpha = 60.608(7)^\circ$ $\beta = 89.674(8)^\circ$ $\gamma = 72.165(9)^\circ$
Volume	1305.0(15) Å^3
Z	1
Calculated density	1.718 mg m^{-3}
Absorption coefficient	2.915 mm^{-1}
F(000)	666
θ range for data collection	1.77–25.01°
Reflections collected/unique	5508/4530 [R(int) = 0.0179]
Completeness to $2\theta = 25.01$	98.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4530/0/352
Goodness-of-fit on F^2	1.165
Final *R* indices [$I > 2((I)$]	$R_1 = 0.0424$, $wR_2 = 0.1078$
Largest diff. peak and hole	2.010 and -1.166 e Å^{-3}

Table 2. Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Dy(BAA)_2(phen)NO_3]_2$.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Dy(1)	955(1)	8733(1)	1598(1)	32(1)
N(1)	140(8)	7808(6)	3615(5)	38(2)
N(2)	2476(8)	6449(6)	3004(6)	43(2)
N(3)	3747(9)	8836(7)	2571(6)	49(2)
O(1)	1936(7)	8069(5)	354(4)	47(1)
O(2)	991(7)	9595(5)	−1504(4)	44(1)
O(3)	−1302(7)	9541(5)	−53(4)	40(1)
O(4)	−1019(7)	7862(5)	1594(5)	49(2)
O(5)	3872(7)	8349(5)	1958(5)	54(2)
O(6)	2363(8)	9208(6)	2779(5)	54(2)
O(7)	4869(9)	8986(6)	2924(6)	70(2)
C(1)	1744(10)	8491(7)	−723(7)	41(2)
C(2)	2391(12)	7550(8)	−1091(7)	52(2)
C(3)	2701(11)	8046(7)	−2317(7)	45(2)
C(4)	1687(15)	8205(12)	−3172(10)	79(3)
C(5)	2054(19)	8657(13)	−4324(11)	95(4)
C(6)	3392(18)	8892(11)	−4531(11)	82(4)
C(7)	4377(16)	8760(12)	−3697(11)	89(4)
C(8)	4047(13)	8314(11)	−2589(10)	73(3)
C(9)	−1773(10)	8652(7)	598(7)	40(2)
C(10)	−3286(10)	8595(8)	158(7)	47(2)
C(11)	−2833(10)	7551(8)	−94(7)	45(2)
C(12)	−2099(12)	7634(9)	−1012(9)	59(2)
C(13)	−1739(15)	6700(12)	−1260(11)	83(3)
C(14)	−2122(17)	5669(12)	−568(13)	90(4)
C(15)	−2844(18)	5579(11)	343(12)	91(4)
C(16)	−3214(14)	6517(9)	589(9)	68(3)
C(17)	−1064(12)	8429(8)	3892(8)	54(2)
C(18)	−1567(13)	7919(10)	4961(9)	66(3)
C(19)	−780(13)	6711(9)	5771(8)	60(3)
C(20)	497(11)	6019(8)	5533(7)	45(2)
C(21)	1383(13)	4733(9)	6327(7)	59(3)
C(22)	2556(12)	4089(8)	6031(7)	58(3)
C(23)	3000(11)	4634(7)	4916(7)	48(2)
C(24)	4202(13)	3980(9)	4561(9)	64(3)
C(25)	4500(12)	4555(8)	3455(9)	63(3)
C(26)	3625(11)	5781(8)	2719(8)	55(2)
C(27)	2159(11)	5891(7)	4104(7)	45(2)
C(28)	922(11)	6580(7)	4420(6)	41(2)

centre. Table 3 shows the selected bond lengths and bond angles for this complex. It thus follows that the Dy–carboxyl(tridentate chelating-bridging)–Dy network is completely planar, with coordinated phen ligands lying parallel to each in the crystal. It is noted that Dy(1)–O(3) (2.555(6) Å) as the longest Dy–O(carboxylate) distance, is much longer than Dy(1)–O(3A) (2.329(5) Å). This is possibly related to non-bonded steric interactions [20]. Obviously, the coordination polyhedron is not a tricapped trigonal prism. However, provided that N(1), N(2), O(5) and O(6) are sited at the corners of a square, the geometry can be viewed in terms of a distorted, monocapped, square antiprism, in which the capping vertex is occupied by one of the chelating oxygen atoms O(3) and the capped face is formed by O(1), O(2A), O(3A) and O(4) from four BAA groups.

Dy completes its coordination sphere by bonding to water molecules and since the four BAA groups bind only to the central dysprosium ion, adjacent units are linked

Table 3. Selected bond distances (Å) and bond angles (°) for $[Dy(BAA)_2(phen)NO_3]_2$.

Dy(1)–O(1)	2.301(5)	Dy(1)–O(5)	2.504(6)
Dy(1)–O(2)#1	2.314(5)	Dy(1)–N(2)	2.554(6)
Dy(1)–O(3)#1	2.329(5)	Dy(1)–O(3)	2.555(6)
Dy(1)–O(4)	2.395(6)	Dy(1)–N(1)	2.573(6)
Dy(1)–O(6)	2.446(6)		
O(1)–Dy(1)–O(2)#1	138.19(18)	O(4)–Dy(1)–N(2)	78.8(2)
O(1)–Dy(1)–O(3)#1	76.7(2)	O(6)–Dy(1)–N(2)	88.9(2)
O(2)#1–Dy(1)–O(3)#1	74.57(19)	O(5)–Dy(1)–N(2)	69.7(2)
O(1)–Dy(1)–O(4)	83.5(2)	O(1)–Dy(1)–O(3)	71.19(19)
O(2)#1–Dy(1)–O(4)	90.2(2)	O(2)#1–Dy(1)–O(3)	72.49(19)
O(3)#1–Dy(1)–O(4)	127.08(19)	O(3)#1–Dy(1)–O(3)	75.0(2)
O(1)–Dy(1)–O(6)	128.1(2)	O(4)–Dy(1)–O(3)	52.13(17)
O(2)#1–Dy(1)–O(6)	77.7(2)	O(6)–Dy(1)–O(3)	146.89(19)
O(3)#1–Dy(1)–O(6)	83.5(2)	O(5)–Dy(1)–O(3)	140.67(19)
O(4)–Dy(1)–O(6)	143.0(2)	N(2)–Dy(1)–O(3)	123.5(2)
O(1)–Dy(1)–O(5)	77.1(2)	O(1)–Dy(1)–N(1)	137.2(2)
O(2)#1–Dy(1)–O(5)	122.9(2)	O(2)#1–Dy(1)–N(1)	76.89(19)
O(3)#1–Dy(1)–O(5)	75.5(2)	O(3)#1–Dy(1)–N(1)	146.12(19)
O(4)–Dy(1)–O(5)	145.7(2)	O(4)–Dy(1)–N(1)	70.4(2)
O(6)–Dy(1)–O(5)	51.4(2)	O(6)–Dy(1)–N(1)	72.8(2)
O(1)–Dy(1)–N(2)	78.0(2)	O(5)–Dy(1)–N(1)	106.0(2)
O(2)#1–Dy(1)–N(2)	141.1(2)	N(2)–Dy(1)–N(1)	64.3(2)
O(3)#1–Dy(1)–N(2)	140.6(2)	O(3)–Dy(1)–N(1)	113.0(2)

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

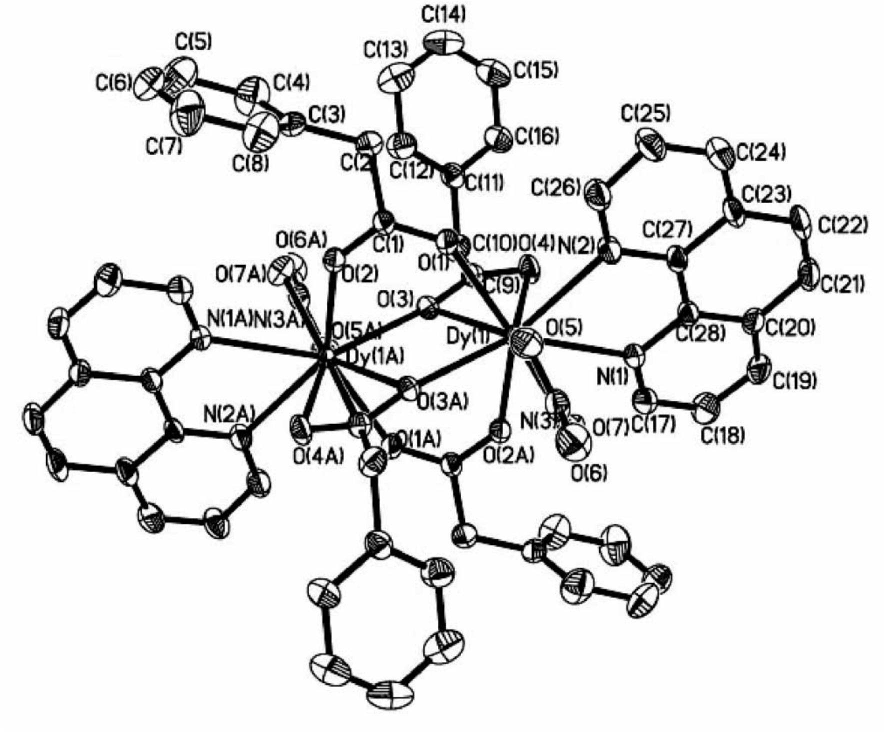

Figure 1. Molecular structure of $[Dy(BAA)_2(phen)NO_3]_2$ showing the atom numbering scheme.

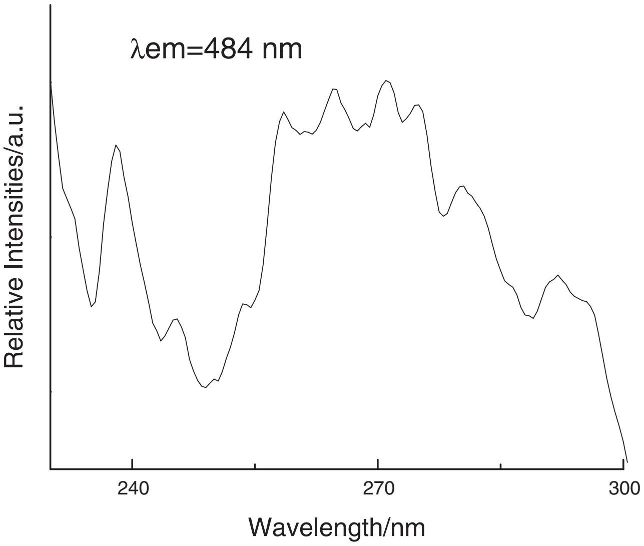

Figure 2. Excitation spectrum for solid $[Dy(BAA)_2(phen)NO_3]_2$ at 77 K.

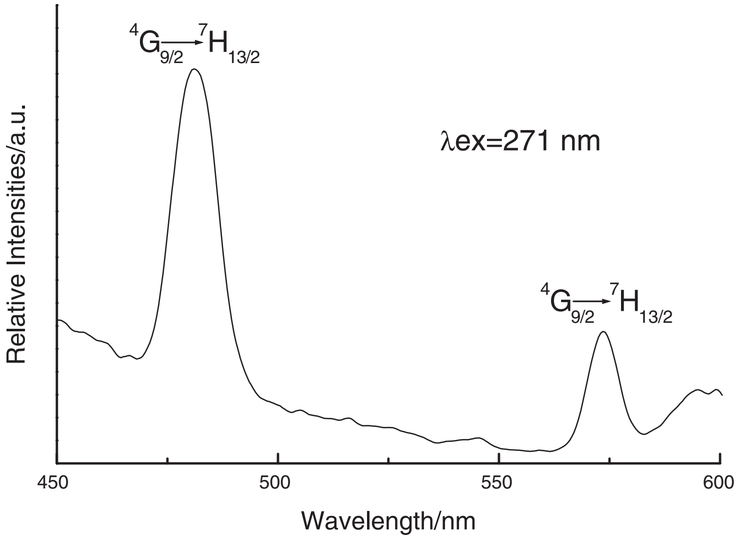

Figure 3. Emission spectrum for solid $[Dy(BAA)_2(phen)NO_3]_2$ at 77 K.

solely through weak intermolecular forces. In particular, coordinated phen molecules lie parallel to each other and associated π–π stacking interactions serve to stabilize the lattice.

3.2. *Photophysical properties*

In the ultraviolet absorption spectrum of $[Dy(BAA)_2(phen)NO_3]_2$ (10^{-4} M dimethylsulfoxide solution), maximum absorption attributed to BAA was observed at 257 nm, showing a slight Einstein shift (from 254 nm). This implies that BAA ligands transfer energy to the lanthanide ion by intersystem crossing processes. The shoulder at 266 nm can be assigned to absorption by phen. The excitation spectrum for the solid complex is shown in figure 2. Excitation at 484 nm gives rise to a broad and intense band at 200–300 nm, covering the ligand absorption band. Figure 3 shows the emission spectrum of $[Dy(BAA)_2(phen)NO_3]_2$ at 77 K under excitation at 271 nm. The two intense peaks at 484 and 575 nm correspond to the characteristic $^4F_{9/2} \rightarrow {}^6H_J$ ($J=$ 15/2, 13/2) emission transitions of the Dy(III) ion. Both ultraviolet absorption and fluorescence spectra indicate that BAA is an efficient sensitiser for Dy^{3+}.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (20301013).

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