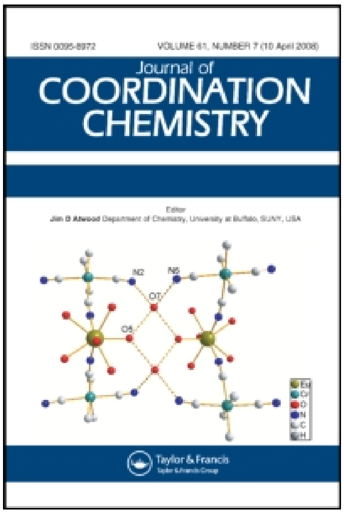

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Synthesis, Crystal structure and Fluorescence properties of a Binuclear Terbium(Iii) complex of *N*-(2-Pyridinyl)Ketoacetamide

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SYNTHESIS, CRYSTAL STRUCTURE AND FLUORESCENCE PROPERTIES OF A BINUCLEAR TERBIUM(III) COMPLEX OF *N*-(2-PYRIDINYL)KETOACETAMIDE

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A binuclear terbium(III) complex of *N*-(2-pyridinyl)ketoacetamide (HL) was synthesized and its crystal structure determined. Each terbium(III) binds to one *N*,*O*-bidentate HL, one *O*,*O*-bidentate L and two *N*,μ-*O*,*O*-tridentate bridging L ligands; the coordination polyhedron is a distorted square antiprism. The pyridine N and keto O atoms of the binucleating ligand are coordinated to each Tb with the amide O acting as a bridging atom. The adjacent $[Tb_2(HL)_2L_4]^{2+}$ units are bridged by double C(R)NH···ONO$_2$···HN(R)C hydrogen bonds to form an infinite 1-D chain, and a 2-D layer structure results from a rare near face-to-face π,π-stacking interaction between the pyridine rings of the adjacent chains. The crystal structure analysis reveals that the ligands completely shield the Ln(III) ions. Excited by the absorption band at 370 nm, the Tb(III) complex displays characteristic metal-centered fluorescence while the ligand fluorescence is completely quenched, showing that efficient ligand-to-metal energy transfer (antenna effect) occurs.

Keywords: Binuclear terbium(III) complex; *N*-(2-Pyridinyl)ketoacetamide; Crystal structure; Fluorescence; π,π-Stacking interactions

INTRODUCTION

Rare earth β-diketone complexes are highly functional compounds with outstanding optical, electric and magnetic properties. Optical properties have attracted quite a lot of attention since they can be used as fluorescence probes [1], as laser materials [2,3], and especially as electroluminescence materials [4,5] for their potential application in large-area displays. The organic β-diketone ligands play an important role in the high optical function of the complexes because they have a high coefficient of absorption. Excitation in ligand-based transitions causing the structural emission of rare earth

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complexes is called the "antenna effect" [6–10]. High energy transfer efficiency can be achieved when appropriate organic β-diketones are selected [11,12].

It has been reported that ligand-to-metal energy transfer of europium and terbium β-diketone chelates is affected significantly on changing substituents in the organic ligand. An increase in the conjugation by attaching aromatic substituents (*p*-phenyldibenzoyl methide, dinaphthoyl methides) to β-diketone can result in enhanced metallic emission [13]. *N*-(2-Pyridinyl)ketoacetamide is a potential ligand; a literature survey on this compound reveals that it is suited to formation of two stable six-membered chelate rings with a pair of metal ions [14].

In the present article, we describe the synthesis, crystal structure and fluorescence properties of the binuclear terbium(III) complex of *N*-(2-pyridinyl)ketoacetamide ligand (HL). The crystal structure of the complex indicates that two Tb^{3+} ions lie in an anhydrous and rigid structure, minimizing the ligand-to-water radiationless transition. There is a rare nearly face-to-face π–π interaction in this compound [15]. The fluorescence studies indicate that the Tb(III) complex displays the characteristic metal-centered fluorescence while the ligand fluorescence is completely quenched, showing that efficient ligand-to-metal energy transfer (antenna effect) occurs.

EXPERIMENTAL

Physical Measurements

Elemental analyses were determined on an Elementar Vario EL analyzer. IR-spectra were measured on Nicolet Nexus 670 FT-IR using KBr pellets in the range of 400–4000 cm^{-1}. The ^1H NMR spectra were recorded on a Bruker AM 200 spectrometer using $CDCl_3$ as solvent and Me_4Si as internal reference. Fluorescence measurements were performed on a Hitachi F-4500 spectrophotometer.

Preparation of Ligand

The ligand was prepared by the reaction of 2-aminopyridine with ethyl acetoacetate, as described previously [16]. Anal. Calcd. for $C_9H_{10}N_2O_2$(%): C, 60.67; H, 5.61; N, 15.73. Found: C, 60.58; H, 5.62; N, 15.71. ^1H NMR, δ: 2.31 (s, 3H), 3.61 (s, 2H, exchangeable), 7.07 (dt, 1H), 7.71 (dt, 1H), 8.21 (bd, 1H), 8.32 (dt, 1H), 9.68 (bs, 1H) ppm. IR (cm^{-1}) in KBr pellet: 1720, ν(CO) and 1685, ν(NH). M.p. = 109–110°C.

Synthesis of $[Tb_2(HL)_2L_4]\cdot 2NO_3\cdot 2C_2H_5OH$

$Tb(NO_3)_3\cdot 6H_2O$ (226.5 mg, 0.5 mmol) in 95% EtOH (10 mL) was added slowly to a solution of HL (267 mg, 1.5 mmol) in anhydrous EtOH (10 mL) at room temperature. The mixture was neutralized with aqueous $NH_3\cdot H_2O$ to pH = 7, and then stirred for 3 h. The resulting solution was left undisturbed at room temperature and allowed to evaporate slowly for crystallization. Colorless crystals of the title complex suitable for single-crystal X-ray structural determination were obtained in 10 d. The product obtained is soluble in many organic solvents, such as methanol and $CHCl_3$, and also in water. It exhibits good stability in the atmosphere over a long time.

TABLE I Crystal data and structure refinement for $[Tb_2(HL)_2L_4]\cdot 2NO_3\cdot 2C_2H_5OH$

Empirical formula	$C_{58}H_{68}N_{14}O_{20}Tb_2$
Formula weight	1599.10
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	9.881(1)
b (Å)	13.182(2)
c (Å)	14.848(4)
α (°)	109.03(2)
β (°)	102.36(2)
γ (°)	105.26(2)
Volume (Å^3)	1665.7(7)
Z	1
D_{calc} (Mg m^{-3})	1.594
Absorption coefficient (mm^{-1})	2.187
F(000)	804
Crystal size (mm)	0.58 × 0.40 × 0.40
θ range for data collection (°)	1.54–25.00
Index ranges	$0 \leq h \leq 11$, $-14 \leq k \leq 13$, $-17 \leq l \leq 17$
Reflections collected	6296
Independent reflections (*R*(int))	5713 (0.0157)
Absorption correction	Empirical
Max. and min. transmission	0.9825 and 0.6731
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5713/6/442
Goodness-of-fit on F^2	1.026
Final *R* indices *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0255, 0.0679
R indices *R*1, *wR*2 (all data)	0.0292, 0.0689
Extinction coefficient	0.0007(3)
Largest diff. Peak, hole (e Å^{-3})	0.595, −0.551

Crystal Structure Determination

Three-dimensional X-ray data were collected at 296(2) K in the $3.08 < 2\theta < 50°$ range on a Siemens P4 diffractometer by the ω scan method, using Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was made. The structure was solved by direct methods [17], which revealed the position of all nonhydrogen atoms, and refined on F^2 by full-matrix least-squares regression (SHELX97) [18]. All hydrogen atoms were located from difference maps and refined isotropically. Crystallographic data are listed in Table I and full details of the structure determination are given in the supporting information.

RESULTS AND DISCUSSION

Crystal Structure

The asymmetric unit consists of a binuclear cation $[Tb_2(HL)_2L_4]^{2+}$ formed by two symmetry related $Tb(HL)L_2$ moieties, two nitrate anions and two ethanol solvates. A diagram of the cation with the atom-numbering scheme is shown in Fig. 1. Three coordination modes of the ligand are observed: *N*,*O*-bidentate HL; *O*,*O*-bidentate L; and *N*,μ-*O*,*O*-tridentate bridging L. The two terbium atoms are bridged by the

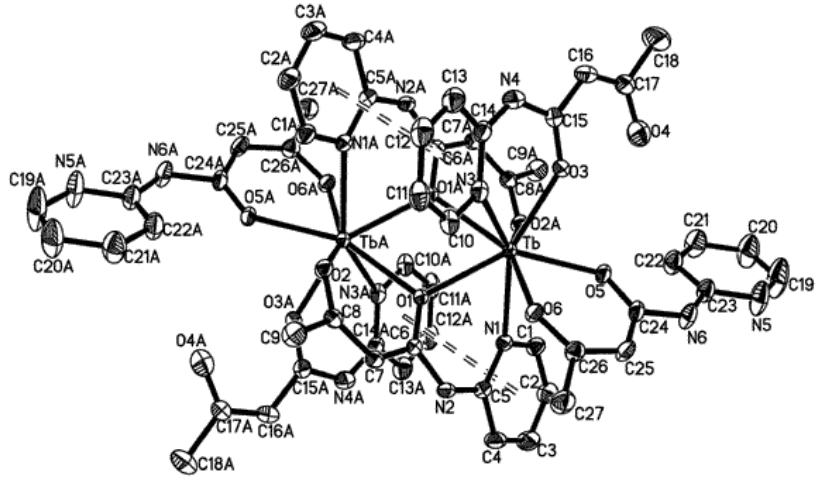


FIGURE 1 A diagram of $[Tb_2(HL)_2L_4]^{2+}$ (thermal ellipsoids at 20% probability level and the dashed lines show π,π-stacking interaction).

TABLE II Selected bond distances (Å), bond angles (°) and hydrogen bonds for $[Tb_2(HL)_2L_4] \cdot 2NO_3 \cdot 2C_2H_5OH$

Tb–O(6)	2.256(2)	Tb–O(5)	2.337(2)	Tb–N(1)	2.562(3)
Tb–O(3)	2.307(3)	Tb–O(1)	2.403(2)	Tb–N(3)	2.603(3)
Tb–O(2)#1	2.330(2)	Tb–O(1)#1	2.414(2)		
Tb–O(1)–Tb#1	113.45(8)	O(1)–Tb–O(1)#1	66.55(8)	O(2)#1–Tb–N(1)	79.14(9)
O(6)–Tb–O(5)	74.44(9)	O(6)–Tb–N(3)	78.04(10)	O(3)–Tb–N(3)	68.05(10)
O(3)–Tb–O(5)	73.26(9)	O(2)#1–Tb–O(1)#1	71.29(8)	O(1)–Tb–N(1)	67.40(9)
O(4)–H(4)···O(3)		0.82	2.08	2.755(5)	139.0
N(4)–H(4N)···O(10)		0.86	2.30	3.106(6)	155.8
N(2)–H(2N)···O(7)#3		0.86	2.22	3.073(5)	173.9
N(6)–H(6N)···O(7)#4		0.86	2.41	3.249(6)	165.5

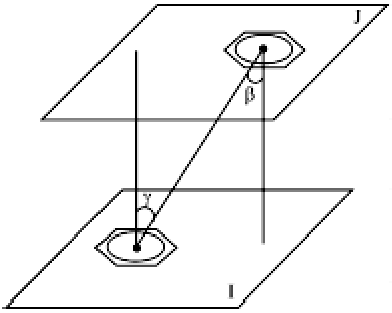
Symmetry code: #1 $-x+2$, $-y+1$, $-z+1$; #2 $-x+2$, $-y+1$, $-z$; #3 x, y, $1+z$; #4 $-x+2$, $-y$, $-z$.

amino oxygen atoms [O(1) and O(1A)] of two binucleating ligands with a *trans* arrangement forming a coplanar Tb_2O_2 moiety. This coordination mode is identical to that observed for a binuclear Cu(II) complex of this ligand [14], however, the organic ligands are arranged approximately coplanar to the central Cu_2O_2 moiety in the binuclear copper(II) complexes while the ligands in this terbium(III) complex are distorted and deviate distinctly from the dimeric plane.

Selected bond lengths, bond angles and hydrogen bonds of this complex are given in Table II. The Tb···Tb separation is 4.027 Å and the Tb–O–Tb angle is 113.45(8)°; larger than those of $Tb_2(tod)_6$ (tod = 2,2,7-trimethyl-3,5-octanedione), in which ligands coordinate in a similar planar fashion while terbium(III) is seven-coordinate [19]. An approximately tetrahedral geometry is observed about each of the terbium atoms in their coordination to the equatorial binucleating ligands. Thus Tb is coordinated to the amido oxygen O(1) and pyridine nitrogen N(1) of one ligand [Tb–O(1) 2.403(2) Å and Tb–N(1) 2.562(3) Å] as well as to the ketonic oxygen O(2A) and amido oxygen O(1A) of the other [Tb–O(2A) 2.330(2) Å and Tb–O(1A) 2.414(2) Å]. The Tb–O bond distances agree with those observed in $Tb_2(tod)_6$ [2.3330(18)–2.3996(17) Å] [19].

Of the remaining four ligands, one *N*,*O*-bidentate HL and *O*,*O*-bidentate L are bound to each Tb(III) atom resulting a distorted square antiprismatic geometry about each terbium atom. It is noteworthy that these four ligands are also distorted and not coplanar. The Tb–O bond distances [2.256(3)–2.337(2) Å] are similar to those found for Tb(III) complexes of β-ketones [20]. As shown in Fig. 1, pyridyl rings involving N(1)[N(1A)] and N(3A)[N(3)] atoms [ring 1 (1A) and 2A (2)] stack, dictated by the coordination of the nitrogen atoms to Tb and Tb(A). Analysis of this stacking interaction gives the structural parameters as follows: centroid–centroid distance is 3.8295 Å and the dihedral angle between stacked rings α and angles β, γ of the centroid–centroid vector to the normal to the ring planes (see Scheme 1 below) are $\alpha = 5.63$, $\beta = 22.5$ and $\gamma = 22.46°$. The perpendicular distance from ring 1 (1A) to the plane 2A (2) is 3.539 Å, and that from the ring 2A (2) to the plane 1 (1A) is 3.457 Å. Such a structure has a σ,π-contribution [15].

As shown in Fig. 2, all the amide groups are involved in intermolecular hydrogen bonding interactions (Table II). An infinite 1-D chain along the *b* axis is formed by two bridging nitrates involved in the double amide–nitrate–amide hydrogen bonds N2–H2N···O7···H6N–N6 [N2···O7 3.073(5) Å, N6···O7 3.249(6) Å]. This type of hydrogen bonding linkage system can be formulated as Tb(A)–O=C(R)NH···ONO$_2$···HN(R)C=O–Tb. Pyridine rings (rings 2 and 2A) involving N(3) and N(3A)



SCHEME 1 β and γ angles in a ring–ring π,π-stacking interaction.

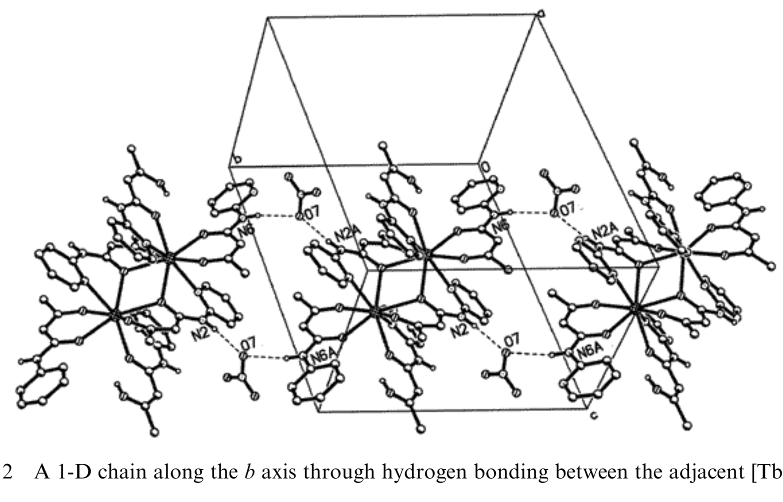


FIGURE 2 A 1-D chain along the *b* axis through hydrogen bonding between the adjacent $[Tb_2(HL)_2L_4]^{2+}$ units.

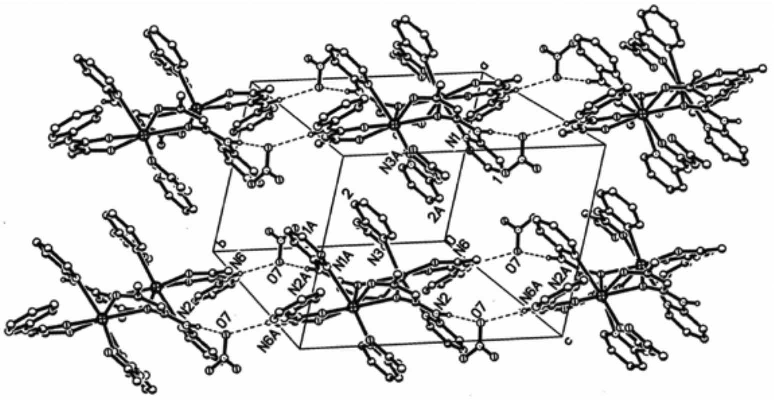


FIGURE 3 A 2-D layer structure through π,π-stacking interaction between the pyridine rings of the adjacent chains.

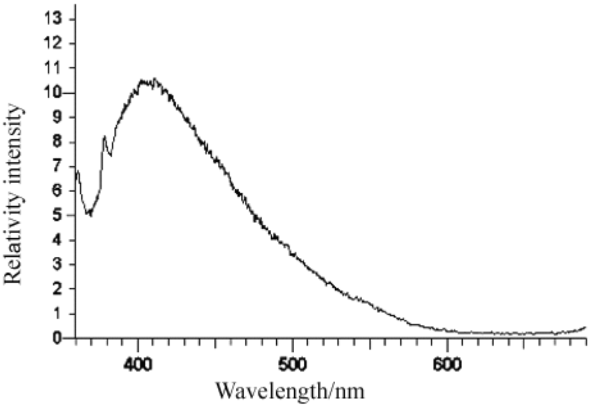


FIGURE 4 The emission spectra of the ligand in the solid state.

atoms belonging to adjacent chains, lie parallel and stacked (dihedral angle between planes $\alpha = 0.03°$) at a distance of 3.50 Å resulting in a 2-D layer structure (Fig. 3). This π,π-interaction has small displacement between the stacked rings (angles of the c–c vector with the perpendicular to each stacked ring plane $\beta = \gamma = 8.32°$; see Scheme 1) and comes near to a face-to-face alignment [15], a rarely observed phenomenon.

Fluorescence Properties

Among rare earth complexes, the terbium(III) complexes are of special interest for their fluorescence properties. As shown in Fig. 4, a powder of the free ligand gave a broad band emission at $\lambda_{max} = 412$ nm upon excitation at 350 nm. The emissions of the complex resulting from excitation at 370 nm are all characteristic of the Tb(III) ion, as shown in Fig. 5. Four narrow emission peaks centered at 490, 546, 584 and 620 nm, assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions, respectively,

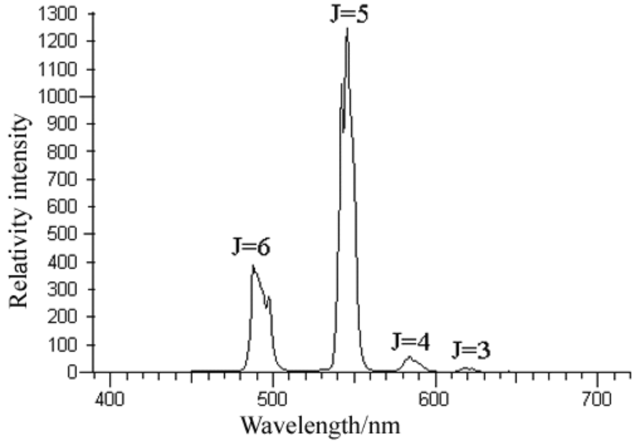


FIGURE 5 The emission spectra of the complex in the solid state.

were obtained. It is noteworthy that the ligand emission is totally quenched in the emission spectra of the complex, indicating an efficient ligand-to-metal energy transfer process (antenna effect) [8–12]. From the emission spectra of complexes, we can conclude that the triplet energy of the ligand is at a very appropriate level. Analysis of the crystal structure indicates the ligand can effectively shield the Tb(III) ions from external interactions. We may deduce that the comparatively good fluorescence properties of our complex are due, in part, to these two points. A detailed fluorescence study is in progress.

Supplementary Data

Supplementary crystallographic data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition number 195539.

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