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THE SYNTHESIS, CRYSTAL STRUCTURE AND SYNERGISTIC FLUORESCENCE EFFECT OF A HETERONUCLEAR LANTHANIDE COMPLEX (HLC) $\{Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O\}_n$

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Abstract—Sodium sulpho-salicylate ($C_7H_4SO_6Na_2$) reacts with terbium perchlorate to form $Tb(OH)(C_7H_3SO_6)H_2O$ (A) which reacts with lanthanum perchlorate to give the title complex $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**) whose crystal structure was determined. The Tb^{III} and La^{III} ions are bridged by tridentate and tetradentate carboxylic groups. The complex is a polymeric molecule formed by a repeating trinuclear HLC structural unit. Tb^{III} is eight-coordinated dodecahedral and La^{III} is 10-coordinated with a distorted bi-capped square antiprismatic configuration. The excitation and emission spectra showed that the maximum excitation wavelength of **A** is 356 nm, which is 12 nm greater than that of **B**, 344 nm. Both **A** and **B** have the same emission spectra at their excitation wavelengths 356 and 344 nm; the fluorescence intensity of **B** is 3.3 times that of **A** at the maximum emission wavelength 543 nm. The fluorescence enhancement of non-fluorescent ions (NFI) such as La^{III} for the fluorescent ions (FI) such as Tb^{III} in one molecule is known as "synergistic fluorescence effect", which is different from co-fluorescence resulting from the mixing of NFI complex with FI complex. The relationship between the structure and properties is discussed.

The lanthanide complexes of organic ligands as fluorescence materials have received extensive attention in laser liquid working materials,[1] environmental probing of biomolecules,[2] fluorescence plaster layers,[3] defect detection[4] and colour display parts.[5,6] In recent years, the commercial fluorescence materials have been mainly inorganic materials which have poor compatibility with organic media. The commercial use of the fluorescence organo-lanthanide complexes is limited by their high price. The key point is to lower the content of fluorescent ions in the complex such as Tb^{3+}, by substituting them with less expensive lanthanide ions such as La^{3+}, Y^{3+} or Gd^{3+}. The possibility that special fluorescence enhancement might be produced by tuning Ln–Ln′ electronic interactions with suitable heteronuclear chelates is particularly exciting. Ci Yunxiang studied the Gd^{3+}–Tiron–Tb^{3+} solution system and found that the Gd^{3+} ion can enhance the fluorescence intensity of Tb^{3+} and believed that a heteronuclear complex was formed.[7] We have used sulpho-salicylic acid (SSA) as ligand to synthesize the complex, Tb(OH) $(C_7H_3SO_6)H_2O$ (**A**) and the heteronuclear complex, $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**). Also, we have determined the crystal structure of **B** and studied the fluorescence spectra of both **A** and **B**. The relationship between the structure and properties is discussed.

EXPERIMENTAL

Sulpho-salicylic acid (SSA) was purchased from Beijing Chemicals. The lanthanum and terbium perchlorates were prepared by dissolving La_2O_3 and Tb_4O_7 (99.9%, from the Zhu Jiang Metal Refinery)

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in perchloric acid respectively. IR spectra were recorded on a Nicolet 7199B Fourier Transform Spectrometer (KBr pellet), the fluorescence intensity measurements were made on a Shimdazu Rf-540 Fluorescence Spectrometer.

Preparation of $Tb(OH)(C_7H_3SO_6)H_2O$ (A)

SSA (3 mmol) was dissolved in 6 mmol oxygen free NaOH solution and 1 mmol terbium perchlorate was added; a white precipitate was formed by heating and stirring for 5 min. The precipitate was filtered and dried. Found: Tb, 39.2; C, 20.2; H, 1.8. Calc. for $Tb(OH)(C_7H_3SO_6)H_2O$: Tb, 38.8; C, 20.7; H, 1.7%.

Preparation of $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**)

SSA (3 mmol) was dissolved in 6 mmol oxygen free NaOH solution and 1 mmol terbium perchlorate was added; a white precipitate was formed by heating and stirring the solution for 5 min, the 3 mmol NaOH and 1 mmol lanthanum perchlorate was added to the suspension, then the supernatant liquid became clear. The mixture was filtered, the filtrate was evaporated and crystals of **B** were obtained, which was unstable in the air. The ratio of La to Tb in the complex is 2.01 given by ICP analysis.

Crystallography of $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**)

A crystal of approximate dimension 0.28 × 0.2 × 0.4 mm was sealed in a thin-walled glass capillary and mounted on a Siemens R3m/v four-circle diffractometer. Room-temperature intensity data were collected with a θ–2θ scan technique in the range $3° < 2\theta < 45°$ with Mo-K_α radiation under the conditions given in Table 1. Corrections for Lorentz and polarization effects were applied but not for absorption. The structure was solved by a combination of direct methods and difference Fourier technique. Full-matrix leasts square refinement of positional and thermal parameters led to convergence with $R = 6.4\%$.

RESULTS

Crystal structure

The selected bond lengths and angles are given in Table 2 and a projection with appropriate numbering scheme is presented in Fig. 1. The composition of complex **B** is $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**) in which terbium and two lanthanum ions are tridentate-bridged by two carboxylic groups and the other two carboxylic groups tetradentate-bridged the terbium, lanthanum and sodium ions.

Table 1. Crystallographic data for $Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O$ (**B**)

Formula	$[C_{28}H_{64}O_{50}S_4Na_3TbLa_2]$
Mol. wt.	1834
Crystal system	monoclinic
Space group	C2/c
Cell constants	
a (Å)	16.319(10)
b (Å)	18.374(8)
c (Å)	22.075(8)
β (°)	106.13(4)
V (Å^3)	6359(4)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.917
Temp. (K)	296
Radiation	Mo-K_α = 0.7103 Å
Monochromator	highly oriented graphite
Scan type	θ–2θ
Scan range (2θ max, °)	45
Total reflections	4517
Obs. data ($F > 4\sigma(F)$)	3560
R_f	0.064
R_w	0.0705
GOF	12.91

The structural data indicate that the two oxygen atoms O(23) and O(23a) of the two sulpho-groups coordinate to the La^{III} of the adjacent molecules in a unidentate mode to make the title complex into a chain polymer in the C2-axis direction. In addition, two oxygen atoms of the other two sulpho-groups O(22) and O(22a) coordinate to the Na ion located on the C2-axis to link the polymer chain forming a two dimensional molecule. The Tb^{III} and Na ions are located at (0, y, 1/4) and (0, 1/2, 0) respectively, while two La^{III} ions are located at both sides of the Tb^{III} ion. The Tb^{III} ion coordinates to eight oxygen atoms in a dodecahedron (Fig. 2). Four of these oxygen atoms O(16), O(16a), O(26), O(26a) are from the bridging oxygen atoms of the carboxylic groups, four O(14), O(14a), O(24), O(24a) of these from the hydroxy groups of SSA. The hydroxy group, the carboxylic group and the Tb^{III} ion form a six-membered chelate ring in which O(14), O(16), and O(17) are co-planar with the benzene ring. The La^{III} ion coordinates to 10 oxygen atoms, four of which are from carboxylic groups O(15), O(16), O(25), O(26) five from water molecules and one from the unidentate oxygen of the sulpho-group. They take an irregular bicapped square antiprism arrangement (Fig. 3), in which W(3), W(4), W(5)

Table 2. Selected bond lengths (Å) and angles (°)

Tb—O(14)	2.335(9)	Tb—O(16)	2.357(10)
Tb—O(24)	2.350(9)	Tb—O(26)	2.376(9)
Tb—O(14A)	2.335(9)	Tb—O(16A)	2.357(10)
Tb—O(24A)	2.350(9)	Tb—O(26A)	2.376(9)
La—O(15)	2.667(9)	La—O(16)	2.648(9)
La—W(1)	2.538(9)	La—O(25)	2.642(11)
La—O(26)	2.628(10)	La—W(2)	2.569(11)
La—W(3)	2.655(11)	La—W(4)	2.575(10)
La—W(5)	2.599(13)	La—O(23A)	2.560(11)
Na(1)—O(22A)	2.507(14)	Na(1)—O(22B)	2.507(14)
Na(1)—W(7A)	2.399(23)	Na(1)—W(7B)	2.399(23)
Na(1)—W(8A)	2.417(21)	Na(1)—W(8B)	2.417(21)
Na(2)—O(15)	2.283(14)	Na(2)—W(3)	2.515(12)
Na(2)—W(6)	2.415(19)	Na(2)—W(13)	2.373(47)
Na(2)—W(6A)	2.530(16)		
O(14)—Tb—O(16)	71.6(3)	O(14)—Tb—O(14A)	104.8(4)
O(24)—Tb—O(24A)	99.6(5)	O(16)—Tb—O(16A)	129.0(5)
O(26)—Tb—O(26A)	129.7(3)	O(26)—Tb—O(14A)	77.5(3)
O(24)—Tb—O(16A)	80.3(3)	O(16)—Tb—O(14A)	77.9(3)
O(15)—La—O(16)	48.3(3)	O(16)—La—O(26)	59.5(3)
O(26)—La—O(25)	48.5(3)	O(25)—La—W(4)	69.2(4)
O(25)—La—W(2)	70.3(4)	W(4)—La—W(2)	81.5(4)
O(26)—La—W(2)	74.9(3)	W(4)—La—W(5)	69.7(4)
W(3)—La—O(23A)	67.9(4)	O(15)—La—O(23A)	69.1(3)
W(1)—La—O(15)	72.9(3)	O(16)—La—W(1)	71.5(3)
W(1)—La—W(5)	70.7(3)	W(2)—La—W(3)	72.2(3)
W(7A)—Na(1)—W(8B)	85.8(7)	W(7A)—Na(1)—W(8A)	94.2(7)
O(22A)—Na(1)—W(7A)	86.0(8)	O(22A)—Na(1)—W(8B)	82.3(7)
W(3)—Na(2)—W(6A)	161.4(6)	O(15)—Na(2)—W(6A)	104.7(5)
W(6)—Na(2)—W(6A)	86.2(6)	W(13)—Na(2)—W(6A)	89.2(11)

and O(23b) form square plane 1 and W(1), W(2) O(15), O(25) form plane 2. The mean atom deviations are 0.275 and 0.178 Å respectively. The angle between these two planes is 4.0°. It is very interesting to note that the two capping atoms (O(26), O(16)) are both capping plane 2. This irregularity may be due to the rigidity of the two-dimensional structure. There are two coordination types for the Na ions in the molecule. Na(1) is located on a C2 axis and coordinates to six oxygen atoms, two of these O(22a), O(22b) are from two unidentate sulpho groups, four from water molecules. Na(2) is located in a general position and coordinates to five oxygen atoms, one of these O(15) from the tetradentate carboxylic group and four from water molecules.

IR spectra

The IR spectra of SSA, **A** and **B** were measured. Compared to the IR spectra of SSA, the stretching vibration of the carboxylic group of **A** shifts from 1673 to 1647 cm^{-1}, and two new strong peaks appear at 1509 and 1553 cm^{-1}, while in complex **B**, 1673 cm^{-1} disappears and two new strong peaks appear at 1522 and 1553 cm^{-1}, which indicates that the coordination modes of the carboxylic acids are different in **A** and **B**. In addition, the asymmetric vibration of $S{=}O$, 1211 cm^{-1}, is split into 1207 and 1268 cm^{-1} in **B**, which indicates that the $S{=}O$ locates in an asymmetric coordination environment. The IR spectra analysis demonstrates that the coordination mode of SSA in **B** is more complicated than that in **A**.

Synergistic fluorescence of the hetero lanthanide complex

Fixing the emission wavelength of the Tb^{III} ion at 543 nm, the excitation spectra of both **A** and **B** were obtained in the range 250–400 nm (Fig. 4). The maximum excitation wavelength of **A** and **B** are 356 and 344 nm respectively, and the intensity of absorbance of **B** at 344 nm is 2.0 times that of A at 356 nm. Fixing the maximum excitation of **A** and **B** at 356 and 344 nm, the emission spectra of **A** and

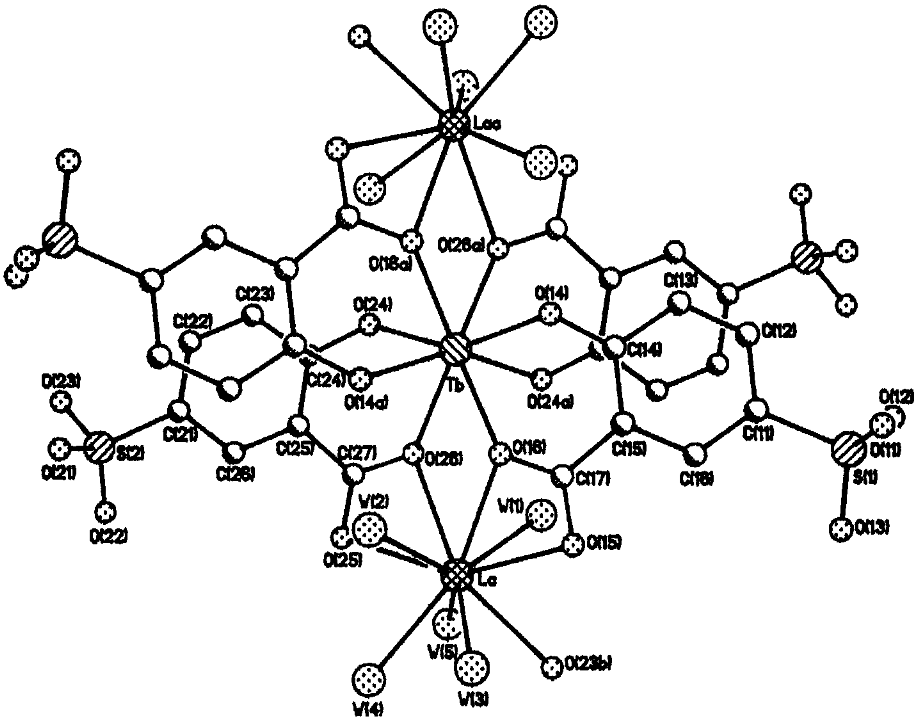

Fig. 1. The view of the anion $\{TbLa_2(C_7H_3SO_6)_4\cdot 10H_2O\}^{3-}$.

B were obtained (Fig. 5), from which it can be seen that there are three emission fluorescence spectra bands at 490, 543 and 586 nm, which are assigned to $^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$ and $^5D_4$–$^7F_4$ electron transfers of the Tb^{III} ion. The fluorescence intensity of **B** is 3.3 times that of **A** at 543 nm.

The green fluorescence of the solution of compound **A** was not observed under sunlight, but when a solution containing La^{III} was added to the solution of **A**, a strong green fluorescence of Tb in the solution was observed under sunlight. It was assumed that the HLC of Tb^{III} and La^{III} was formed. In order to confirm this assumption, a few crystals of **B** were dissolved in water, and the same green fluorescence of Tb was observed under sunlight at once. To our knowledge, this is the first example for terbium complexes that the fluorescence enhancement can be seen under the excitation of sunlight. We have named the fluorescence enhancement of NFI to FI in one molecule the

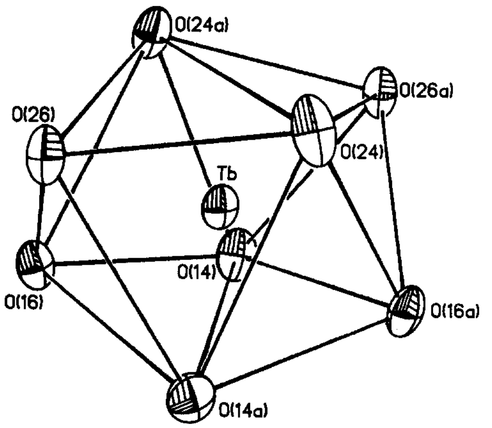

Fig. 2. Polyhedron of Tb in the complex anion $\{TbLa_2(C_7H_3SO_6)_4\cdot 10H_2O\}^{3-}$.

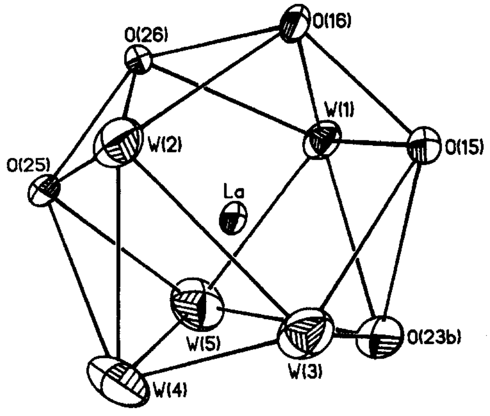

Fig. 3. Polyhedron of La in the complex anion $\{TbLa_2(C_7H_3SO_6)_4\cdot 10H_2O\}^{3-}$.

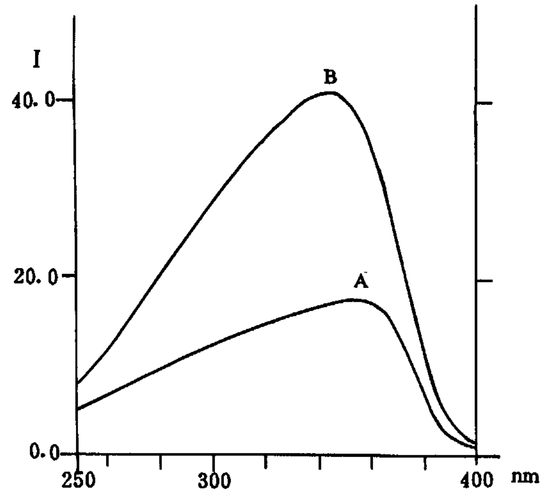

Fig. 4. The excitation spectra of **A** and **B**.

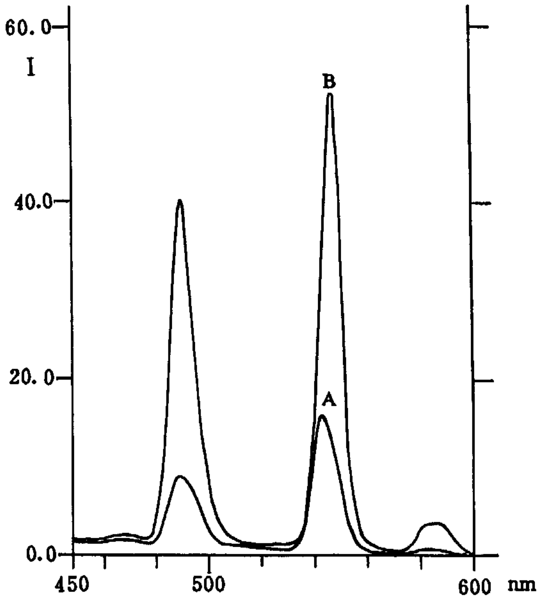

Fig. 5. The emission spectra of **A** and **B**.

"synergistic fluorescence effect", which is different from co-fluorescence resulting from the mixing of NFI complex with FI complex.[8]

DISCUSSION

Certain lanthanide chelates, when irradiated with light absorbed by the organic ligand, emit light with the energy distribution spectra characteristic of the lanthanide ion. The mechanism for this intramolecular energy transfer from ligand to central atom has been proposed by Crosby and associates.[1,9] It appears that the energy transfer is dependent on the characteristics of the central atom and the energy level matching between the central ion and ligand. In this work, complexes **A** and **B** have the same ligand SSA and the same fluorescence central atom Tb, but the excitation and emission spectra are different. The fluorescence intensity of **A** is enhanced greatly by the addition of a non-fluorescence ion La^{III} to form a heteronuclear complex **B**. From the structure of **B** we can explain the synergistic fluorescence as follows: firstly, the crystal structure data show that the complex **B** is a relatively rigid two-dimensional molecule, all the functional groups of SSA are involved in the coordination to metal atoms which prevents the energy loss by molecular vibration. Secondly, in complex **B** the coordinated groups, carboxylic and hydroxy chelate the Tb ion to form a six membered ring which enlarges the conjugated system of the molecule, and makes the energy transfer from ligand to Tb ion more efficient. For example, acetylacetone is not aromatic but its complex with the Tb ion has a relatively strong fluorescence intensity due to the formation of a six membered chelating ring. Thirdly, from Fig. 1, it can be seen that the Tb ion coordinates only to the carboxylic and hydroxy groups of SSA, and not to water molecules. In other words, the Tb ion is located in a water free environment, which is advantageous to the fluorescence enhancement. Usually, in the fluorescence analysis of lanthanide ions, in order to improve the sensitivity of detection, a surfactant is employed to form a colloidal membrane around the lanthanide complex to avoid the collision between the complex and water molecules.[7] Thus more excited electrons of Tb ion may undergo a radiative transition to a lower energy level resulting in characteristic line emission after the indirect excitation by energy transfer. Fourthly, the La^{III} ion does not have 4*f* electrons, and it does not receive the energy from the ligand, this means that energy transfer from the ligand to metal ions focuses only on the Tb^{III} ion.

CONCLUSION

A heteronuclear fluorescence complex containing Tb and La ions was isolated from a high pH value water solution. In the complex a network structure were formed through the coordination of all the functional groups of SSA. The structural studies demonstrated that the fluorescence intensity is not only dependent on the selection of an appropriate complexing agent and the addition of an appropriate non-fluorescent lanthanide ion, but also on the water free environment of central ions and the enlargement of the conjugated system, which has a relatively rigid structure.

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Supplementary materials available. Tables of complete atom coordinates and thermal parameters, bond distances and angles (2 pages); Listings of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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