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STUDIES ON A NEW TYPE OF TERBIUM COMPLEX WITH SULPHONATED CATECHOLATE. THE MOLECULAR STRUCTURE AND FLUORESCENCE PROPERTIES OF $[Tb_2(C_6H_3S_2O_8)_2\cdot 6DMF]_n$

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Abstract—Reaction of sulphonated catecholate $Na_2C_6H_4S_2O_8$ (Tiron) and terbium perchlorate with a 3 : 2 mole ratio in hot water resulted in the precipitation of crystalline $Tb_2(C_6H_3S_2O_8)_2\cdot 5H_2O$ (**A**) which was recrystallized in water–DMF mixed solvent to obtain the title complex $Tb_2(C_6H_3S_2O_8)_2\cdot 6DMF$ (**B**). The X-ray crystal structure determination of **B** indicates that Tiron and terbium ion form a chain polymer with a 1 : 1 mole ratio. The unique structural unit is a dimer in which two terbium ions are bridged by one oxygen atom from a deprotonated hydroxyl group of Tiron. The distance between terbium ions is 3.385 Å. The terbium ion is eight-coordinated dodecahedral. The elemental analysis data and thermographic data show that compound **B** loses one DMF molecule in air to become $Tb_2(C_6H_3S_2O_8)_2\cdot 5DMF$ (**B′**). The fluorescence spectra of A and **B′** have been studied. Both A and **B′** have the same maximum excitation wavelength (318 nm) at which the emission fluorescence intensity of **B′** is 2.5 times that of A at 543 nm. The thermogravimetric analysis and IR spectra of A and **B′** have been studied.

Tiron has been used as a chelating reagent for heavy metals.[1] The anti-blood coagulation properties of complex Tiron with lanthanide was investigated.[2] Raymond synthesized the complex of Tiron with Ce^{IV}, $Na_{12}[Ce(C_6H_2S_2O_8)_4](H_2O)_9(DMF)_6$ and determined its structure.[3] The complex of Tiron with terbium has a strong fluorescence emission of Tb^{III} ion when it absorbs UV light, and this was employed to analyse the Tb^{III} ion.[4] The structure is unknown, though it is essential to understand the energy transfer from Tiron to the central terbium atom. Here we report the synthesis and crystal structure of the title complex. The fluorescence spectra, IR spectra and thermostability of these complexes were studied as well.

EXPERIMENTAL

IR spectra were recorded on a Nicolet 7199B FTIR spectrometer. The thermogravimetric analysis was recorded by an LT-1 model thermobalance under atmosphere. The fluorescence intensity measurements were made on a Shimdazu RF-540 fluorescence spectrophotometer. Tiron was purchased from Shanghai Third Chemical Reagent Factory. Terbium perchlorate was prepared by dissolving Tb_4O_7 (99.9%) in perchloric acid.

Preparation of $Tb_2(C_6H_3S_2O_8)_2\cdot 5H_2O$ (A)

Tiron (3 mmol) was dissolved in 3 mmol oxygen-free NaOH solution; 2 mmol terbium perchlorate

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was added under heating and stirring. White crystalline **A** was precipitated after refluxing for 3 h. The solution was filtered and the precipitate was washed with ethanol. Found: C, 14.5; H, 1.6. Calc. for $Tb_2(C_6H_3S_2O_8)_2 \cdot 5H_2O$ (**A**): C, 15.3; H, 1.6%.

Preparation of $Tb_2(C_6H_3S_2O_8)_2 \cdot 6DMF$ (***B***)

Part of **A** was dissolved in a mixed solvent of water and DMF with the volume ratio 2:3. The solution was evaporated at 35°C; 7 days later, regular shaped crystals of **B** were obtained, which were unstable in air. Found: C, 26.6; H, 3.5; N, 6.0. Calc for $Tb_2(C_6H_3S_2O_8)_2 \cdot 5DMF$ (**B′**): C, 26.6; H, 3.4; N, 5.8%.

Crystallography of ***B***

A crystal of approximately $0.2 \times 0.2 \times 0.2$ mm was sealed in a thin-walled glass capillary and mounted on a Rigaku RASA-IIS four-circle diffractometer. Room-temperature intensity data were collected with a θ–2θ scan technique in the range of $3 < 2\theta > 50$ 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 position of terbium was located by using the Patterson method and subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. Full matrix least-squares refinement of positional and thermal parameters led to convergence with $R_f = 6.9\%$, in which the hydrogen atoms contributions are not included.

Table 1. Crystallographic data for **B**

Formula	$[C_{12}H_6O_{16}S_4Tb_2][C_{18}H_{42}N_6O_6]$
Mol. wt	1290
Crystal system	monoclinic
Space group	$P21/n$
Cell constants	
a (Å)	25.696(5)
b (Å)	9.651(2)
c (Å)	9.464(3)
β (°)	96.82(2)
V (A^3)	2330.4(10)
Z	2
D_{calc} (g cm^{-3})	1.771
Temp. (K)	296
μ_{calc} (cm^{-1})	33.0
Radiation	Mo-K_α = 0.71073 Å
Monochromator	highly oriented graphite
Scan type	θ–2θ
Scan range (2θ max, °)	50
Scan speed (° min^{-1})	8
Total reflections	3698
Obsd data	2142
No. of variables	289
R_f	0.069
R_w	0.079
GOF	1.830

RESULTS AND DISCUSSION

Thermal stability of A and ***B′***

Thermogravimetric analysis of **A** and **B′** showed that one water molecule was lost from **A** and one DMF from **B′** below 169°C, and the cumulative loss is 2.22% (calc. 1.91%) for **A** and 5.75% (calc. 5.99%) for **B′**. The remaining four solvent molecules were lost in the range 169–200°C for **A** and 169–342°C for **B′**, and the cumulative weight loss was 7.77% (calc. 7.64%) for **A** and 22.99% (calc. 23.99%) for **B′**. It could be assumed that the first water or DMF were lattice molecules and the latter four water or DMF molecules were coordinated to the terbium ion, which was confirmed by the crystal structure data.

IR spectra

IR spectra of Tiron and complexes **A** and **B′** were measured. Compared to Tiron, the asymmetric vibration absorption peak of the sulpho group at 1200 cm^{-1} was split into 1200 and 1149 cm^{-1} for **A** and 1194 and 1164 cm^{-1} for **B′**, which indicated that the sulpho groups were involved in the coordination to the terbium ion and located in an asymmetric environment. The ν(C—O) at 1235 cm^{-1} was split into 1286 and 1254 cm^{-1} in **A** and 1277 and 1250 cm^{-1} in **B′**. The δ(OH) at 1379 cm^{-1} was shifted to 1402 cm^{-1} in **A** and 1384 cm^{-1} in **B′**. These IR spectral data showed that all the Tiron groups were coordinated to terbium ion in the complex.

Structure of ***B***

Selected bond lengths and angles are given in Table 2. The Tb^{III} ion is eight-coordinated with dodecahedral geometry. Complex **B** is a polymer in which the unique structural unit is a dimer, $Tb_2(C_6H_3S_2O_8)_2 \cdot 4DMF$. The ORTEP view of the dimer with approximate numbering scheme is presented in Fig. 1.

The two Tb^{III} ions are bridged by oxygens [O(1), O(1a)] from the deprotonated hydroxyl group of two Tirons. The distance between the two Tb^{III} ions is 3.385(9) Å. The other hydroxyl group [O(6)] of

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

Tb—O(1)	2.369(13)	O(6)—C(1)	1.332(22)
Tb—O(1a)	2.367(12)	O(11)—C(9)	1.23(4)
Tb—O(2)	2.319(16)	N(1)—C(7)	1.48(4)
Tb—O(3)	2.328(15)	N(1)—C(8)	1.40(4)
Tb—O(4)	2.320(16)	N(1)—C(9)	1.35(4)
Tb—O(5)	2.460(13)	N(2)—C(13)	1.32(4)
Tb—O(6)	2.423(13)	N(2)—C(14)	1.46(4)
Tb—O(7)	2.464(14)	N(2)—C(15)	1.40(4)
S(1)—O(5)	1.430(17)	N(3)—C(10)	1.28(4)
S(1)—O(7)	1.471(15)	N(3)—C(11)	1.47(6)
S(1)—O(10)	1.426(14)	N(3)—C(12)	1.42(5)
S(1)—C(5)	1.711(20)	C(1)—C(2)	1.425(25)
S(2)—O(3)	1.455(16)	C(1)—C(6)	1.39(3)
S(2)—O(8)	1.409(18)	C(2)—C(3)	1.39(3)
S(2)—O(9)	1.442(18)	C(3)—S(2)	1.787(19)
O(1)—C(6)	1.342(22)	C(3)—C(4)	1.37(3)
O(2)—C(13)	1.25(3)	C(4)—C(5)	1.41(3)
O(4)—C(10)	1.17(3)	C(5)—C(6)	1.42(3)
C(6)—O(1)	1.342(22)		
O(1)—Tb—O(1′)	69.7(4)	O(2)—Tb—O(4)	89.3(6)
O(1)—Tb—O(2)	92.3(6)	O(2)—Tb—O(5)	72.6(5)
O(1)—Tb—O(3)	96.5(5)	O(2)—Tb—O(6)	78.8(5)
O(1)—Tb—O(4)	151.2(5)	O(2)—Tb—O(7)	128.8(5)
O(1)—Tb—O(5)	75.9(4)	O(3)—Tb—O(4)	94.3(6)
O(1)—Tb—O(6)	136.8(4)	O(3)—Tb—O(5)	132.8(5)
O(1)—Tb—O(7)	75.3(5)	O(3)—Tb—O(6)	78.4(5)
O(1′)—Tb—O(2)	81.5(6)	O(3)—Tb—O(7)	76.7(5)
O(1′)—Tb—O(3)	79.2(5)	O(4)—Tb—O(5)	77.2(5)
O(1′)—Tb—O(4)	138.8(5)	O(4)—Tb—O(6)	71.6(5)
O(1′)—Tb—O(5)	135.6(5)	O(4)—Tb—O(7)	81.4(5)
O(1′)—Tb—O(6)	67.2(4)	O(5)—Tb—O(6)	137.5(5)
O(1′)—Tb—O(7)	134.4(5)	O(5)—Tb—O(7)	56.2(5)
O(2)—Tb—O(3)	154.5(5)	O(6)—Tb—O(7)	141.4(5)

each Tiron is also coordinated to Tb^{III}. The Tb—O(6) bond length is 0.05 Å longer than that of Tb—O(1) or Tb—O(1a), which may be due to the rigidity of the skeleton of the benzene. The two sulpho groups are coordinated to terbium in different forms; one is bidentate, the other is in unidentate form. The dimers are bridged by the oxygen atom from a unidentate sulpho group to form a chain polymer molecule. The DMF molecules in the crystal structure have two forms; four DMFs are coordinated to Tb^{III} through the oxygen atom and the other two are lattice molecules, existing between the chain polymer and parallel to the (110) plane. From the elemental analysis, thermogravimetric analysis and IR spectral data, it can be concluded that complexes **A** and **B′** are similar in structure; the only difference is the presence of lattice molecules in **A**.

So far only a few structures of catechol complexes and their derivatives with lanthanides have been reported. Sofen *et al.* reported the structure of $Na_4[M(C_6H_4O_2)_4]\cdot 2H_2O$ (M = Ce^{IV}, Hf^{IV}) in which the two hydroxyl groups were coordinated to the M^{IV} ions and Ce^{IV} was eight-coordinate.[5] Raymond *et al.* reported the structure of $Na_5[Gd(C_6H_4O_2)_4]\cdot 19.2H_2O$ and $Na_6[Gd(C_6H_4O_2)_4]\cdot 20H_2O$.[6] The former was obtained when the ratio Gd^{III}/catechol was 0.5 and the latter was a dimer obtained when the ratio was greater than 0.5. In addition, in the complex $Na_{12}[Ce(C_6H_2S_2O_8)_4](H_2O)_9(DMF)_6$, the Ce^{IV} ion was eight-coordinate and only two hydroxyl groups were coordinated to the Ce^{IV} ion, the sulpho groups were not. The crystal structure was a monomer which was obtained when the ratio Ce^{IV}/Tiron was 0.25. In the case of complex **B**, a chain polymer molecule with novel structure was obtained when the ratio of Tb^{III}/Tiron was 2 : 3.

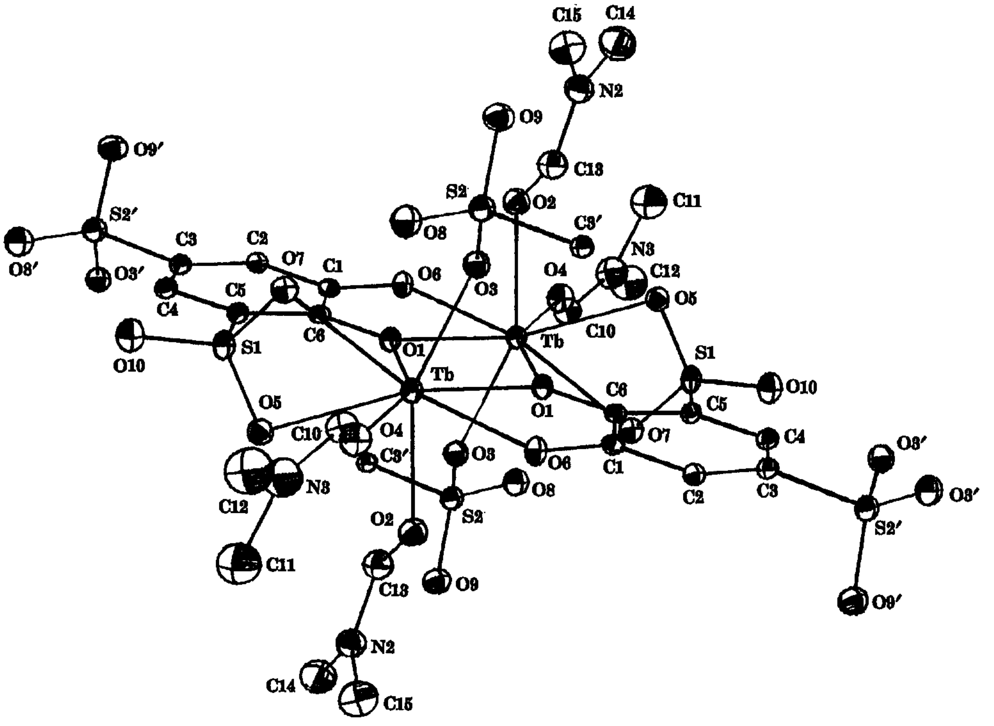

Fig. 1. The ORTEP view of $Tb_2(C_6H_3S_2O_8)_2 \cdot 4DMF$.

*The fluorescence spectra of A and **B'***

Excitation spectra. Fixing the emission wavelength of terbium at 543 nm, the excitation spectra of both A and **B'** were obtained in the range of 250–400 nm (Fig. 2). The maximum excitation wavelengths of A and **B'** were both at 318 nm, and the absorption peak of **B'** is 2.9 times that of A.

Emission spectra. Fixing the maximum excitation wavelength of A and **B'** at 318 nm, the emission spectra of A and **B'** were obtained in the range 450–600 nm (Fig. 3). There are three emission peaks at 490, 543 and 586 nm, which were assigned to the electronic transfer of $^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$, $^5D_4$–$^7F_4$ of terbium, respectively. The fluorescence intensity of **B'** was 2.5 times that of A at 543 nm.

Generally, the fluorescence intensity of a complex was increased greatly when the water donors were substituted by organic donors. There are two reasons for this. The first is that the energy received by the ligands is partly lost when it is transferred to the high frequency vibrating O—H of water mol-

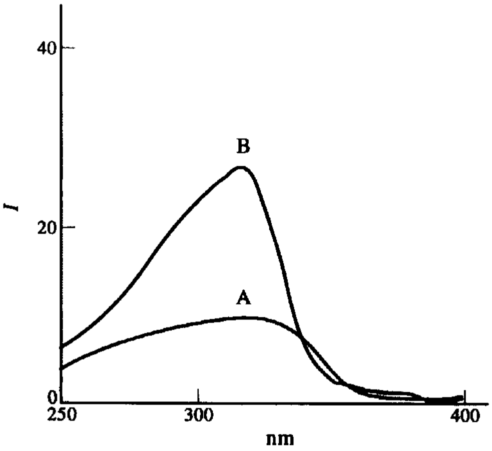

Fig. 2. The excitation spectra of A and **B'**.

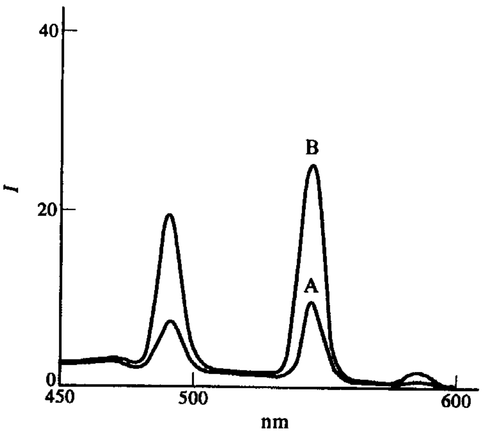

Fig. 3. The emission spectra of A and **B'**.

ecules, which results in the decreasing of fluorescence quantum yield. The second is that the organic donors are involved in the energy transfer to the fluorescent ions. From the DMF structure, we believe that the first reason is responsible for our case.

Supplementary material available: tables of atomic coordinates and complete bond distances and angles and thermal parameters; Listings of observed and calculated structure factors. Ordering information is given on any current masthead page.

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