

КРАТКИЕ СООБЩЕНИЯ

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STRUCTURE AND LUMINESCENCE OF $[\text{Tb}_{0.5}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_3\text{O})_{4n}(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n}$

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A novel bimetallic 4f–3d metal-isonicotinic acid inorganic-organic hybrid complex $[\text{Tb}_{0.5}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_3\text{O})_{4n}(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n}$ (**1**) is synthesized. It has a one-dimensional polycationic chain-like structure. Photoluminescent investigation reveals that it displays interesting emissions in the violet, blue, green, and yellow regions.

Keywords: crystal structure, terbium, lanthanide, photoluminescence.

The research of lanthanide complexes continues to be an active research area, which may be ascribed to their remarkable properties and potential applications as electroluminescent devices and luminescent probes [1, 2]. For inorganic-organic hybrids, the intriguing variety of topologies that can be obtained by self-assembling of metal ions and multifunctional ligands attracts chemists. Although the synthesis of inorganic-organic hybrids based on transition metals has become widespread [3, 4]; there are relatively few reports on lanthanide inorganic-organic hybrids [5]. Furthermore, the isonicotinate anion is a quite interesting tecton in constructing extended structures because it can link two metal centers [6]. We suggest that LN—IIB (LN = lanthanide) inorganic-organic hybrids with aromatic carboxylic acids as ligands may have novel topologies and properties. So, we have recently become interested in the crystal engineering of LN—IIB inorganic-organic hybrids with isonicotinic acid as ligand. We report here the synthesis, structure, and luminescence of **1**.

Experimental. Instrumentation. All reactants were obtained commercially and used without further purification.

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ V-5 package of crystallographic software. The structure was refined by a full-matrix least-squares refinement on F^2 .

Synthesis. $[\text{Tb}_{0.5}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_3\text{O})_{4n}(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n}$ (**1**). The title complex was prepared by mixing $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.374 g), ZnCl_2 (1 mmol, 0.136 g), isonicotinic acid (1 mmol, 0.123 g) and 10 ml of distilled water in a 25-ml Teflon-lined stainless steel autoclave and heated at 180 °C for 7 days.

Results and discussion. Table 1 presents the crystal data. X-ray diffraction analysis reveals that its structure consists of one $[\text{Tb}_{0.5}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n}^{3n+}$ polycationic chain, H_3O^+ cations, ZnCl_5^{3-} and ZnCl_4^{2-} anions (Fig. 1). The Zn1 atom is tetrahedrally bound by four chlorine atoms to form a ZnCl_4^{2-} anion, while the Zn2 atom is coordinated by five chlorine atoms to form a ZnCl_5^{3-} anion. In contrast to the numerous complexes containing ZnCl_4^{2-} anion [7–9], no complex containing

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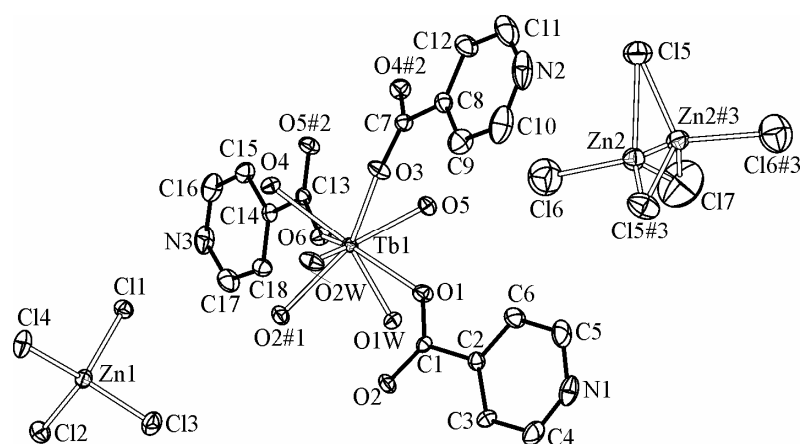


Fig. 1. ORTEP plot of **1** with 35 % thermal ellipsoids. Lattice water molecules and disordered Cl5B and Cl7B are omitted for clarity. The occupancies of Tb1, Zn2 and Cl7 are 0.5

ZnCl_5^{3-} anion was reported thus far, although one complex containing the ZnCl_6^{4-} anion has been reported [10]. Therefore, it is the first time to document ZnCl_5^{3-} moieties. The Zn-Cl bond lengths range from 2.149(9) to 2.436(1) Å (Table 2) with an average value of 2.269(9) Å, which are normal and comparable with the counterparts [11, 12]. The Zn2 atom is positionally disordered and the occupancy of Zn2 must be set to 0.5 to get a rational structure model and thermal displacement parameters.

Table 1

Crystal Data

Empirical formula	$\text{C}_{36}\text{H}_{50}\text{Cl}_{13}\text{N}_6\text{O}_{20}\text{TbZn}_3$
Formula weight	1702.70
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions $a, b, c, \text{Å}; \beta, \text{deg.}$	23.900(3), 20.5531(9), 15.285(1); 127.544(3)
Z	4
$V, \text{Å}^3$	5953(1)
$d_x, \text{g/cm}^3$	1.900
Absorption coefficient, mm^{-1}	3.024
Crystal size, mm	0.48×0.25×0.20
No. of reflections collected/unique	18131/5189 [$R_{\text{int}} = 0.0248$]
Goodness-of-fit on F^2	1.031
Final R indices	$R_1 = 0.0426, wR_2 = 0.1150$
R indices (all data)	$R_1 = 0.0462, wR_2 = 0.1182$
$(\Delta/\sigma)_{\text{max}}$	0.001

Table 2

Selected Bond Lengths (Å)

Tb(1)—O(1)	2.337(2)	Tb(1)—O(5)	2.311(2)	Zn(1)—Cl(1)	2.3144(7)	Zn(2)—Cl(5)	2.436(1)
Tb(1)—O(2)#1	2.298(2)	Tb(1)—O(6)	2.321(2)	Zn(1)—Cl(2)	2.2672(9)	Zn(2)—Cl(5)#2	2.197(1)
Tb(1)—O(3)	2.352(2)	Tb(1)—O(1W)	2.465(2)	Zn(1)—Cl(3)	2.2664(8)	Zn(2)—Cl(6)	2.262(2)
Tb(1)—O(4)	2.350(2)	Tb(1)—O(2W)	2.417(2)	Zn(1)—Cl(4)	2.2679(8)	Zn(2)—Cl(7)	2.149(9)

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

Fig. 2. Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å)

The terbium atom is octahedrally coordinated by eight oxygen atoms, yielding a distorted square anti-prism. The Tb—O_{isonicotinic acid} bond lengths range from 2.298(2) to 2.352(2) Å, which are shorter than that of Tb—O_{water} of 2.417(2) and 2.465(2) Å, indicating that the isonicotinic acid ligand has a stronger affinity to the Tb^{III} ion. The terbium atoms are alternately bridged by two or four μ_2 -isonicotinic acid ligands to construct a 1D polycationic chain. The 1D polycationic chains, ZnCl₄²⁻ moieties, ZnCl₅³⁻ anions, and water molecules are hydrogen bonded to yield a 3D network (Fig. 2).

Taking into account the excellent luminescent property of the Tb³⁺ ion, the luminescence was investigated (Fig. 3). The excitation spectra show that the effective energy absorption mainly takes place in the long-wavelength ultraviolet, violet, and blue regions. The excitation bands under the emission of 545 nm possess two main peaks. We further measured the corresponding emission spectra by selective excitation with different excitation wavelengths, and they showed a similar emission position except a small difference in intensities. The emission spectra show three bands under the excitation of 355 nm (489 nm, 545 nm, and 588 nm) corresponding to the characteristic emission ⁵D₄—⁷F_J transitions (*J* = 6, 5, 4) of Tb³⁺ ions. This indicates that effective energy transfer took place and that conjugated systems formed between the ligands and chelated lanthanide ions. Among three characteristic ⁵D₄—⁷F_J transitions (*J* = 6, 5, 4), the green luminescent intensity of the ⁵D₄—⁷F₅ transition is the strongest. Except these emission bands, upon the photoexcitation of 355 nm, the fourth intensive band with a maximum wavelength of 403 nm is found, which is stronger than the characteristic ⁵D₄—⁷F_J transitions (*J* = 6, 5, 4). This strong emission is tentatively assigned to the $\pi \rightarrow \pi^*$ charge-transfer interaction of the isonicotinic acid ligands.

In conclusion, we have prepared a metal-isonicotinic acid inorganic-organic hybrid. The structure features a novel 1D polycationic chain-like structure. The investigation on the luminescence shows that it displays interesting emissions in the violet, blue and yellow regions.

Supplementary material. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 669716. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

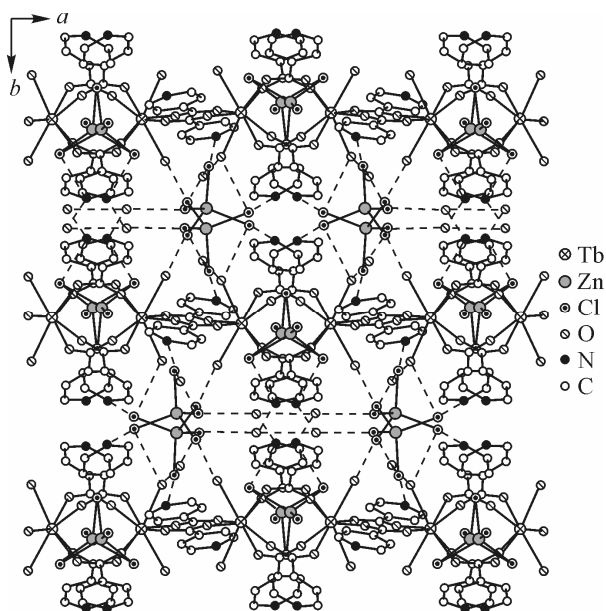
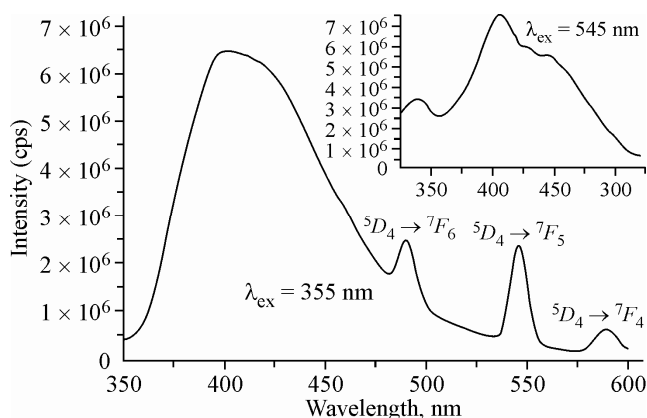


Fig. 3. Luminescent emission spectrum (inset: excitation spectrum)



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REFERENCES

1. Eddaoudi M., Moler D.B., Li H. *et al.* // *Acc. Chem. Res.* – 2001. – **34**. – P. 319.
2. Kido J., Okamoto Y. // *Chem. Rev.* – 2002. – **102**. – P. 2357.
3. Zaworotko M.J. // *Chem. Soc. Rev.* – 1994. – P. 283.
4. Yaghi O.M., Li H., Davis C. *et al.* // *Acc. Chem. Res.* – 1998. – **31**. – P. 474.
5. Reineke T.M., Eddaoudi M., Fehr M. *et al.* // *J. Am. Chem. Soc.* – 1999. – **121**. – P. 1651.
6. Chapman M.E., Ayyappan P., Foxman B.M. *et al.* // *Cryst. Growth Des.* – 2001. – **1**. – P. 159.
7. Gebbink R.J.M.K., Jonas R.T., Goldsmith C.R., Stack T.D.P. // *Inorg. Chem.* – 2002. – **41**. – P. 4633.
8. Shevchenko D.V., Petrusenko S.R., Kozoy V.N. *et al.* // *Inorg. Chem. Commun.* – 2005. – **8**. – P. 665.
9. D'Alessandro D.M., Dinolfo P.H., Davies M.S. *et al.* // *Inorg. Chem.* – 2006. – **45**. – P. 3261.
10. Deeth R.J., Hitchman M.A., Lehmann G., Sachs H. // *Inorg. Chem.* – 1984. – **23**. – P. 1310.
11. Dickie J., Hockless D.C.R., Willis A.C. *et al.* // *Inorg. Chem.* – 2003. – **42**. – P. 3822.
12. Dogan A., Sarkar B., Klein A. *et al.* // *Inorg. Chem.* – 2004. – **43**. – P. 5973.
13. McCarthy T.J., Zhang X., Kanatzidis M.G. // *Inorg. Chem.* – 1993. – **32**. – P. 2944.