SYNTHESIS, STRUCTURE AND PROPERTIES OF $[\text{Gd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (n\text{H}_3\text{O}_2^+)(n\text{ZnCl}_3^-)(2n\text{ZnCl}_4^{2-}) \cdot (2n\text{H}_2\text{O})$ WITH STRONG FLUORESCENCE

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(Received: November 28, 2007 - Accepted: December 22, 2008)

ABSTRACT

A novel one-dimensional metal-isonicotinato inorganic-organic hybrid complex $[\text{Gd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (n\text{H}_3\text{O}_2^+)(n\text{ZnCl}_3^-)(2n\text{ZnCl}_4^{2-}) \cdot (2n\text{H}_2\text{O})$ (**1**) has been successfully synthesized via hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** is characteristic of a novel one-dimensional polycationic chain-like structure and unprecedented ZnCl_3^{3-} species. Optical absorption spectra of **1** reveal the presence of an optical gap of 3.35 eV. Photoluminescent investigation reveals that the title complex displays a strong blue-light fluorescent emission band.

Keywords: gadolinium, lanthanide, photoluminescence

INTRODUCTION

Currently, the increasing interest in the field of the crystal engineering of inorganic-organic hybrid materials is justified by the potential applications of these materials as catalysis, zeolite-like materials, biology, magnetic functional materials, and so on.¹ There is also an aesthetic perspective: for the vast amount of inorganic-organic hybrid materials, the intriguing variety of the architectures and topologies that can be obtained by self-assembling metal ions and multifunctional ligands attract chemists. In recent years, although the synthesis of inorganic-organic hybrid materials based on transition metals has become widespread,² there are relatively few reports on lanthanide-based inorganic-organic hybrid materials despite their potential applications in luminescence and other fields.³ To our knowledge, lanthanide-based inorganic-organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Besides, LN-TM-based (LN = lanthanide, TM = Transition Metal) inorganic-organic hybrid materials with aromatic carboxylic acids as ligands maybe have novel structural topologies and properties, such as luminescence, semiconductivity, magnetism, electro- and photochemistry, catalysis, thermochromism and so forth. Therefore, our group recently became interested in the crystal engineering of LN-TM-based inorganic-organic hybrid materials with isonicotinic acid as ligand. Herein we reported the synthesis, crystal structure and properties of $[\text{Gd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (n\text{H}_3\text{O}_2^+)(n\text{ZnCl}_3^-)(2n\text{ZnCl}_4^{2-}) \cdot (2n\text{H}_2\text{O})$ (**1**) with a novel one-dimensional polycationic chain and unprecedented ZnCl_3^{3-} species.

Synthesis:

The title complex was prepared by mixing $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.373 g), ZnCl_2 (1 mmol, 0.136 g), isonicotinic acid (1 mmol, 0.123 g) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 7 days. After being slowly cooled to room temperature at 6 °C/h, colorless crystals suitable for X-ray analysis were obtained. The yield was 86%.

X-Ray Diffraction study:

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) 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™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. CCDC 664484.

Fluorescent analysis:

The fluorescent studies were conducted at room temperature on an Edinburgh FLS920 fluorescence spectroscopy instruments.

UV-vis spectroscopy study:

The UV-vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength range 190–1100 nm. BaSO_4 plate was used as a

reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: $a/S = (1-R)^2/2R$, a is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance.

RESULTS AND DISCUSSION

Crystal and Molecular Structure:

Table 1 presents relevant crystallographic and refinement data. X-ray diffraction analysis reveals that the structure of the title complex consists of one $[\text{Gd}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n}^{6+}$ cationic chains, H_3O_2^+ cations, ZnCl_3^{3-} and ZnCl_4^{2-} anions, and isolated water molecules, as shown in Fig. 1. The Zn1 atom is tetrahedrally bounded 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,⁴ no complex containing ZnCl_5^{3-} anion was reported thus far, although one complex containing ZnCl_4^{4-} anion has been reported.⁵ Therefore, it is first time to document ZnCl_5^{3-} moieties. The bond lengths of Zn-Cl range from 2.081(2) to 2.390(2) Å with an average value of 2.255(2) Å, which are normal and comparable with the counterparts found in the literature.⁶ The Zn2 atom is positional disordered and the occupancy of Zn2 must be set to 0.5 to get rational structure model and thermal displacement parameters. The gadolinium atom is octahedrally coordinated by eight oxygen atoms, of which two are from two water molecules and six are from six isonicotinic acid ligands, yielding a distorted square anti-prism with the top and bottom planes defined by O(6)(1-x, y, 1/2-z), O(2)(1-x, y, 1/2-z), O(1), O(5), and O(4)(1/2-x, -1/2-y, -z), O(2W), O(3) and O(1W) atoms, respectively. The bond lengths of Gd-O_{isonicotinato} range from 2.344(3) to 2.394(2) Å with an average value of 2.372(3) Å, which is obviously shorter than that of Gd-O_{water} being of 2.449(2) and 2.496(2) Å, indicating that isonicotinato ligand has a stronger affinity to Gd^{III} ion than that of water. The gadolinium atoms are alternately bridged by two or four μ_2 -isonicotinic acid ligands in a 2-4-2 (the number indicates the number of the bridges) mode to construct a 1D polycationic chain with the Gd...Gd distances of ca. 4.992 and 4.554 Å, respectively (Fig. 2 and Scheme 1d). It is noteworthy that, up to date, the types of the chains formed by LN and isonicotinic acid that have been documented are mainly 1-1-1, 2-1-2 and 2-2-2 types (Scheme 1a, b and c, respectively). However, the 2-4-2 type is very rare. In **1**, no $\pi \dots \pi$ stacking interactions were established between the adjacent isonicotinato ligands. The 1D chains, ZnCl_5^{3-} moieties and water molecules are linked by hydrogen bonds to yield a 3D network with ZnCl_5^{3-} anions located in the cavities (Fig. 3). It is proposed that O3W hydrogen bonds to its symmetry-related O3W' to form a H_3O_2^+ moiety. Other crystallographic independent water molecules cannot form the H_3O_2^+ moiety, because they cannot hydrogen bond to their symmetry-related water molecules. The position of the proton between O3W and its symmetry-related O3W' could not be structurally located due to the existence of the heavy gadolinium and zinc atoms. However, the existence of H_3O_2^+ has been confirmed by the MS spectra showing H_3O_2^+ at $m/z = 37.0211$.

Table 1. Crystal data and structure refinement for (1)

Empirical formula	C ₃₆ H ₄₇ Cl ₁₃ Gd ₂ N ₆ O ₂₀ Zn ₃
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal Size (mm)	0.45 × 0.30 × 0.20
Crystal system	Monoclinic
Space group	C2/c
a (Å)	23.878(5)
b (Å)	20.558(5)
c (Å)	15.339(4)
beta (°)	127.329(5)
Volume(Å ³)	5987(2)
Z	4
Formula weight	1855.26
Density(cal.)(g/cm ³)	2.058
Absorption coefficient(mm ⁻¹)	4.022
F(000)	3616
Theta range (°)	2.59 to 25.06
Index ranges	-28<= <i>h</i> <=28, -23<= <i>k</i> <=24, -18<= <i>l</i> <=17
Data Completeness measured	0.988
Reflections measured	17951
Independent reflections	5262 (Rint = 0.0253)
Empirical Absorption Correction	Sphere (Rigaku CrystalClear)
Relative Transmission Factor	0.6542 - 1.0000
Refinement Method	Full-matrix least-squares on F ²
Parameter/Data	386 / 4506
Final R indices (obs.)	R1 = 0.0378, wR2 = 0.0945
R indices (all)	R1 = 0.0432, wR2 = 0.0993
Goodness-of-fit	0.997
Largest and Mean Delta/Sigma	0.001, 0
Largest difference peak(e.Å ⁻³)	1.705, -2.060

Table 2. Selected bond lengths (Å).

Gd(1)-O(1)	2.367(2)
Gd(1)-O(2)#1	2.344(3)
Gd(1)-O(3)	2.354(3)
Gd(1)-O(4)#2	2.385(2)
Gd(1)-O(5)	2.394(2)
Gd(1)-O(6)#1	2.385(2)
Gd(1)-O(1W)	2.449(2)
Gd(1)-O(2W)	2.496(2)
Zn(1)-Cl(1)	2.267(1)
Zn(1)-Cl(2)	2.312(1)
Zn(1)-Cl(3)	2.266(1)
Zn(1)-Cl(4)	2.265(1)
Zn(2)-Cl(5)	2.180(3)
Zn(2)-Cl(5)#3	2.269(3)
Zn(2)-Cl(6)	2.263(3)
Zn(2)-Cl(7)	2.390(2)
Zn(2)-Cl(7)#3	2.081(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2; #2 -x+1/2, -y-1/2, -z; #3 -x+1, y, -z+3/2.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (Å²).

atom	x	y	z	U(eq)
Gd(1)	0.381129(7)	-0.257427(8)	0.118074(10)	0.01921(4)
Zn(1)	0.289518(19)	-0.02490(2)	0.58444(3)	0.03433(11)
Zn(2)	0.51281(4)	-0.28149(5)	0.72952(6)	0.0419(3)
Cl(1)	0.23890(4)	0.03937(5)	0.63915(7)	0.0476(3)
Cl(2)	0.40183(4)	0.01428(4)	0.66537(6)	0.0351(2)
Cl(3)	0.29588(5)	-0.12811(5)	0.64164(7)	0.0502(3)
Cl(4)	0.23243(5)	-0.02303(5)	0.40092(6)	0.0465(3)
Cl(5)	0.48742(15)	-0.17847(12)	0.71756(14)	0.0850(10)
Cl(6)	0.52918(10)	-0.26583(10)	0.60033(15)	0.1228(7)
Cl(7)	0.40495(6)	-0.33946(8)	0.64815(11)	0.0893(5)
O(1)	0.42390(11)	-0.17821(12)	0.25708(15)	0.0347(7)
O(2)	0.53699(10)	-0.19963(12)	0.38872(16)	0.0345(6)
O(3)	0.28886(11)	-0.25117(11)	0.13308(17)	0.0303(6)
O(4)	0.17929(11)	-0.23713(12)	0.07509(16)	0.0328(7)
O(5)	0.43465(10)	-0.31781(12)	0.28444(15)	0.0316(7)
O(6)	0.55031(10)	-0.33916(12)	0.38770(16)	0.0331(6)
N(1)	0.47354(16)	-0.05488(17)	0.5695(2)	0.0534(10)
N(2)	0.31581(16)	-0.20092(18)	0.4714(2)	0.0507(10)
N(3)	0.47563(17)	-0.45065(17)	0.5833(2)	0.0676(10)
C(1)	0.48094(15)	-0.17141(16)	0.3511(2)	0.0267(8)
C(2)	0.47805(14)	-0.12636(16)	0.4266(2)	0.0244(8)
C(3)	0.53566(17)	-0.12247(19)	0.5356(2)	0.0363(10)
C(4)	0.5309(2)	-0.0860(2)	0.6052(3)	0.0506(12)
C(5)	0.41566(18)	-0.0567(2)	0.4633(3)	0.0502(11)
C(6)	0.41843(16)	-0.09243(18)	0.3903(2)	0.0354(10)
C(7)	0.24395(15)	-0.23978(16)	0.1480(2)	0.0233(8)
C(8)	0.26919(14)	-0.22774(16)	0.2648(2)	0.0242(8)
C(9)	0.33805(18)	-0.23983(19)	0.3512(3)	0.0386(11)
C(10)	0.3612(2)	-0.2261(3)	0.4564(3)	0.0598(15)
C(11)	0.24869(19)	-0.1911(2)	0.3896(3)	0.0492(11)
C(12)	0.22390(16)	-0.20432(19)	0.2837(2)	0.0378(10)
C(13)	0.49026(15)	-0.34351(15)	0.3636(2)	0.0247(8)
C(14)	0.48411(15)	-0.38410(16)	0.4398(2)	0.0283(8)
C(15)	0.5433(2)	-0.4026(2)	0.5411(3)	0.0500(12)
C(16)	0.5365(2)	-0.4368(2)	0.6107(3)	0.0651(14)
C(17)	0.4168(2)	-0.4356(2)	0.4865(3)	0.0708(13)
C(18)	0.41977(17)	-0.4015(2)	0.4122(3)	0.0466(11)
O(1W)	0.31712(11)	-0.36088(11)	0.05777(18)	0.0372(7)
O(2W)	0.32819(10)	-0.14877(11)	0.03688(16)	0.0293(6)
O(3W)	0.42163(12)	-0.52380(13)	0.67643(18)	0.0463(8)
O(4W)	0.28205(16)	-0.10218(17)	-0.1636(2)	0.0916(11)

Scheme 1. Important chain-like structural types of isonicotinic acid bridging LN centers: (a) 1-1-1; (b) 2-1-2; (c) 2-2-2 and (d) 2-4-2 types, in which the number indicates the number of the bridges.

Fig. 1. ORTEP-plot of **1** with 35% thermal ellipsoids. Lattice water molecules, hydrogen atoms and disordered Cl5#3 are omitted for clarity. The occupancies of Zn2 and Cl5 are equal to 0.5. (Symmetry codes: #1 1-x, y, 1/2-z; #2 1/2-x, -1/2-y, -z; #3 1-x, y, 3/2-z).

Fig. 2. The 1D cationic chain-like structure of **1**.

Fig. 3. Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): O1W...Cl1(1/2-x, -1/2+y, 1/2-z) 3.197(3), O2W...Cl2(x, -y, -1/2+z) 3.228(2), O2W...O4W 2.735(4), O3W...Cl4(1/2-x, -1/2-y, 1-z) 3.252(3), O3W...O3W(1-x, y, 3/2-z) 2.976(4), O3W...N3 2.864(5), O4W...Cl3(x, y, -1+z) 3.243(4), O4W...Cl4(x, -y, -1/2+z) 3.230(4), N1...Cl2 3.189(4), N1...Cl5 3.288(4) and N2...Cl3 3.285(4).

UV-vis spectroscopy

Optical absorption spectrum of **1** reveals the presence of an optical gap of 3.35 eV (Fig. 4), which suggests that complex **1** shows a wide-gap semiconductor property and is consistent with the color of the crystal, as the case found in the reference.⁷ The gradual slope of the optical absorption edge for **1** is indicative of the existence of indirect transitions.⁸ The optical absorption of **1** is likely originated from the charge-transfer excitations mainly from the valence band of the chlorine atoms to the conduction band of the zinc center, similar to those reported in the references.⁹

Fig. 4. The solid-state diffuse reflectance spectrum for **1**.

Fluorescence

The solid-state emission spectra of the title complex were investigated at room temperature (Fig. 5). The fluorescent spectrum study shows that the title complex exhibits a strong blue-light emission band with a maximum wavelength of 415 nm upon photo-excitation at 350 nm. The emission should probably be assigned to the LMCT transition (charge transfer from isonicotinic acid ligand to LN metal). Thus, this compound may be a candidate for blue-light luminescent materials.

Fig. 5. Solid-state emission and excitation spectra of 1 at room temperature. Red solid line: emission spectrum; green dashed line: excitation spectrum.

CONCLUSION

In brief, we have successfully prepared a metal-isonicotinato inorganic-organic hybrid complex via hydrothermal reaction. The crystal structure of the title complex is characteristic of a novel one-dimensional polycationic chain-like structure and unprecedented ZnCl_5^{2-} species. This complex exhibits a strong blue-light fluorescent emission band, and it may be used as a blue-light luminescent material. Optical absorption spectra show that the title compound may be a candidate for potential photoelectric material. It is believed that more and more LN-TM-based inorganic-organic hybrid complexes with good physical properties can be developed.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the NSF of China (50572030), the Foundations of Overseas Chinese Affairs Office of the State Council (07QZR05) and the NSF of Fujian Province (2004HZ01-3).

REFERENCES

- 1.- (a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **116**, 1151, (1994).
(b) K. M. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **45**, 283, (1997).
(c) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* 375, (1999).
(d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reinecke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **34**, 319, (2001).
- 2.- (a) M. J. Zaworotko, *Chem. Soc. Rev.* 283, (1994).
(b) G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature*. **374**, 792, (1995).
(c) C. Janiak, *Angew. Chem., Int. Ed. Engl.* **36**, 1431, (1997).
(d) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **31**, 474, (1998).
(e) S. R. Batten, R. Robson, *Angew. Chem., Int. Ed. Engl.* **37**, 1460, (1998);
(f) W. Lin, O. R. Evans, R.-G. Xiong, Z. Wang, *J. Am. Chem. Soc.* **120**, 13272, (1998).
(g) O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem., Int. Ed. Engl.* **38**, 536, (1999).
- 3.- T. M. Reinecke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **121**, 1651, (1999).
- 4.- (a) J. Valdes-Martinez, M. D. Rio-Ramirez, S. Hernandez-Ortega, C. B. Aakeroy, B. Helfrich, *Cryst. Growth Des.* **1**, 485, (2001).
(b) R. J. M. K. Gebbink, R. T. Jonas, C. R. Goldsmith, T. D. P. Stack, *Inorg. Chem.* **41**, 4633, (2002).
(c) J.-Y. Shin, D. Dolphin, B. O. Patrick, *Cryst. Growth Des.* **4**, 659, (2004).
(d) D. Schnieders, M. Merkel, S. M. Baldeau, B. Krebs, *Z. Anorg. Allg. Chem.* **630**, 1210, (2004).
(e) D. V. Shevchenko, S. R. Petrusenko, V. N. Kokozyay, I. Svoboda, J. Kozisek, *Inorg. Chem. Commun.* **8**, 665, (2005).
(f) D. M. D'Alessandro, P. H. Dinolfo, M. S. Davies, J. T. Hupp, F. R. Keene, *Inorg. Chem.* **45**, 3261, (2006).
- 5.- R. J. Deeth, M. A. Hitchman, G. Lehmann, H. Sachs, *Inorg. Chem.* **23**, 1310, (1984).
- 6.- (a) A. Bino, F. A. Cotton, Z. Dori, M. Shaia-Gottlieb, M. Kapon, *Inorg. Chem.* **27**, 3592, (1988).
(b) A. J. Dickie, D. C. R. Hockless, A. C. Willis, J. A. McKeon, W. G. Jackson, *Inorg. Chem.* **42**, 3822, (2003).
(c) Z. Tao, Q.-J. Zhu, S.-F. Xie, W. G. Jackson, Z.-Y. Zhou, X.-G. Zhou, *Polyhedron*. **22**, 1603, (2003).
(d) A. Dogan, B. Sarkar, A. Klein, F. Lissner, T. Schleid, J. Fiedler, S. Zalis, V. K. Jain, W. Kaim, *Inorg. Chem.* **43**, 5973, (2004).
- 7.- E. A. Axtell, Y. Park, K. Chondroudis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **120**, 124, (1998).
- 8.- F. Q. Huang, K. Mitchell, J. A. Ibers, *Inorg. Chem.* **40**, 5123, (2001).
- 9.- (a) J.-H. Liao, M. G. Kanatzidis, *Chem. Mater.* **5**, 1561, (1993).
(b) T. J. McCarthy, X. Zhang, M. G. Kanatzidis, *Inorg. Chem.* **32**, 2944, (1993).
(c) E. A. Axtell, Y. Park, K. Chondroudis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **120**, 124, (1998).