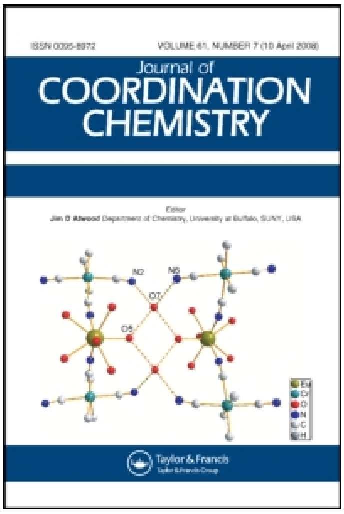

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Synthesis, structure, and properties of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_2$<i>_n · (<i>n</i>$H_5O_2$)(<i>n</i>$ZnCl_5$)(2<i>n</i>$ZnCl_4$) · (2<i>n</i>$H_2O$) with strong fluorescence

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Synthesis, structure, and properties of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_{2n}\cdot(nH_5O_2)(nZnCl_5)(2nZnCl_4)\cdot(2nH_2O)$ with strong fluorescence

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A 1-D metal-isonicotinato inorganic–organic hybrid complex $[Gd(C_6NO_2H_5)_3(H_2O)_2]_{2n}\cdot(nH_5O_2)(nZnCl_5)(2nZnCl_4)\cdot(2nH_2O)$ (**1**) has been synthesized via hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** is a 1-D polycationic chain-like structure with unprecedented $ZnCl_5^{3-}$. Optical absorption spectra of **1** reveal the presence of an optical gap of 3.35 eV. Photoluminescence investigations reveal that the complex **2** display a strong blue-light fluorescent emission band.

Keywords: Gadolinium; Lanthanide; Photoluminescence; Zinc

1. Introduction

Trivalent lanthanide complexes continue to be the active research area for remarkable physical properties and applications as magnetic functional materials, electroluminescent devices, catalysis, zeolite-like materials, and luminescent probes or labels in biological systems [1]. There is also an aesthetic perspective where the intriguing variety of architectures and topologies that can be obtained by self-assembling metal ions and multifunctional ligands attract chemists. Although 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]. Lanthanide-based inorganic–organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for applications. Metal complexes containing group 12 (IIB) elements have various coordination numbers and geometries, provided semiconductive properties and essential roles in biological systems of zinc. The isonicotinic anion is an interesting tecton in constructing extended structures because it is an unsymmetrical

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divergent ligand with a nitrogen at one side and two oxygens from the carboxylate at the other. The isonicotinic anion can link two metal centers by coordinating to a metal center with the nitrogen atom and, to the other one, with one or two carboxylate oxygens [4]. LN-IIB-based (LN = lanthanide) inorganic–organic hybrid materials with aromatic carboxylic acids as ligands may have novel structural topologies and properties, such as luminescence, semiconductivity, magnetism, electro and photochemistry, catalysis and thermochromism. Therefore, our group became interested in the crystal engineering of LN-IIB-based inorganic–organic hybrid materials with isonicotinic acid as ligand. We herein report the synthesis, crystal structure and properties of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_{2n} \cdot (nH_5O_2)(nZnCl_5)(2nZnCl_4) \cdot (2nH_2O)$ (**1**) with a 1-D polycationic chain-like structure and unprecedented $ZnCl_5^{3-}$ species.

2. Experimental

2.1. *Materials and instrumentation*

All reactants of A.R. grade were obtained commercially and used without purification. Infrared spectra were obtained with a PE Spectrum-One FT-IR spectrometer using KBr discs. The fluorescence data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer. UV–Vis spectra were recorded at room temperature on a computer-controlled PE Lambda 35 UV–Vis spectrometer equipped with an integrating sphere in the wavelength range 190–2500 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: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient which is wavelength independent when the particle size is larger than 5 µm, and R is the reflectance. The energy band gaps were determined by extrapolation from the linear portion of the absorption edge in a (α/S) *versus* energy plot from the UV–Vis diffuse spectra [5].

2.2. *Synthesis of $[Gd(C_6NO_2H_5)_3(H_2O)_2]_{2n} \cdot (nH_5O_2)(nZnCl_5)(2nZnCl_4) \cdot (2nH_2O)$ (1)*

The title complex was prepared by mixing $GdCl_3 \cdot 6H_2O$ (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^{-1}, colorless crystals suitable for X-ray analysis were obtained. The yield was 66% (based on zinc).

2.3. *X-ray structure determination*

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) by using a ω-scan technique. Crystal Clear software was used for data reduction and empirical absorption corrections [6]. The structure was solved by the direct method using the Siemens

SHELXTL™ Version 5 package of crystallographic software [7]. The difference Fourier maps based on these atomic positions yield the other nonhydrogen atoms. The hydrogen atom positions were generated theoretically, except for those on the lattice water molecules that is yielded by the difference Fourier maps, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in table 1. Selected bond lengths are listed in table 2.

3. Results and discussion

X-ray diffraction analysis reveals that the structure of **1** consists of one $[Gd(C_6NO_2H_5)_3(H_2O)_2]_2^{6+}$, $H_5O_2^+$ cations, $ZnCl_5^{3-}$ and $ZnCl_4^{2-}$ anions, and isolated water molecules, as shown in figure 1. The Zn1 is tetrahedrally bound by four chlorides to form a $ZnCl_4^{2-}$ anion, while the Zn2 is coordinated by five chlorides to form a $ZnCl_5^{3-}$ anion. In contrast to the numerous complexes containing $ZnCl_4^{2-}$ [8], no complex containing $ZnCl_5^{3-}$ was reported thus far, although one complex containing $ZnCl_6^{4-}$ has

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{47}Cl_{13}Gd_2N_6O_{20}Zn_3$
Temperature (K)	298(2)
Wavelength(Å)	0.71073
Crystal size (mm^3)	0.45 × 0.30 × 0.20
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions (Å, °)	
a	23.878(5)
b	20.558(5)
c	15.339(4)
β	127.329(5)
V (Å^3)	5987(2)
Z	4
Formula weight	1855.26
D_{Calcd} (g cm^{-3})	2.058
Absorption coefficient (mm^{-1})	4.022
F(000)	3616
θ range (°)	2.59 to 25.06
Index ranges	$-28 \le h \le 28$, $-23 \le k \le 24$, $-18 \le l \le 17$
Data completeness measured	0.988
Reflections measured	17951
Independent reflections	5262 ($R_{int} = 0.0253$)
Empirical absorption correction	Sphere (Rigaku Crystal Clear)
Relative transmission factor	0.6542–1.0000
Refinement method	Full-matrix least-squares on F^2
Parameter/data	386/4506
Final *R* indices (obs.)	$R_1 = 0.0378$, $wR_2 = 0.0945$
R indices (all)	$R_1 = 0.0432$, $wR_2 = 0.0993$
Goodness-of-fit	0.997
Largest and mean delta/sigma	0.001, 0
Largest difference peak (e A^{-3})	1.705, −2.060

Table 2. Selected bond lengths (Å).

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

Note: 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, $-z+3/2$.

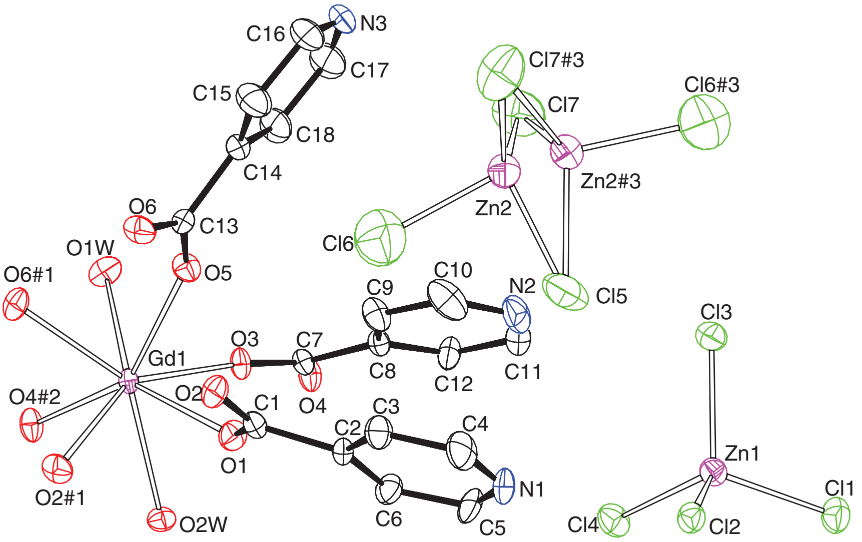


Figure 1. ORTEP-plot of **1** with 35% thermal ellipsoids. Lattice water molecules, hydrogen atoms and disordered Cl5#3 are omitted for clarity. The occupancies of Zn2 and Cl5 are equal to 0.5 (symmetry codes: #1: $1-x$, y, $1/2-z$; #2: $1/2-x$, $-1/2-y$, $-z$; #3: $1-x$, y, $3/2-z$).

been reported [9]. 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 [10]. The Zn2 is position disordered and the occupancy of Zn2 must be set to 0.5 to get rational structure model and thermal displacement parameters. The gadolinium is coordinated by eight oxygens, two from water molecules and six from isonicotinic acid ligands, in 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 shorter than $Gd–O_{water}$, 2.449(2) and 2.496(2) Å. The gadoliniums are alternately bridged by two or four μ_2-isonicotinic acid ligands in a 2-4-2 (the number indicates the number of bridges) mode to construct a 1-D polycationic chain with the Gd · · · Gd distances of ca 4.992 and 4.554 Å [figure 2 and scheme 1(d)]. The types of chains formed by LN and

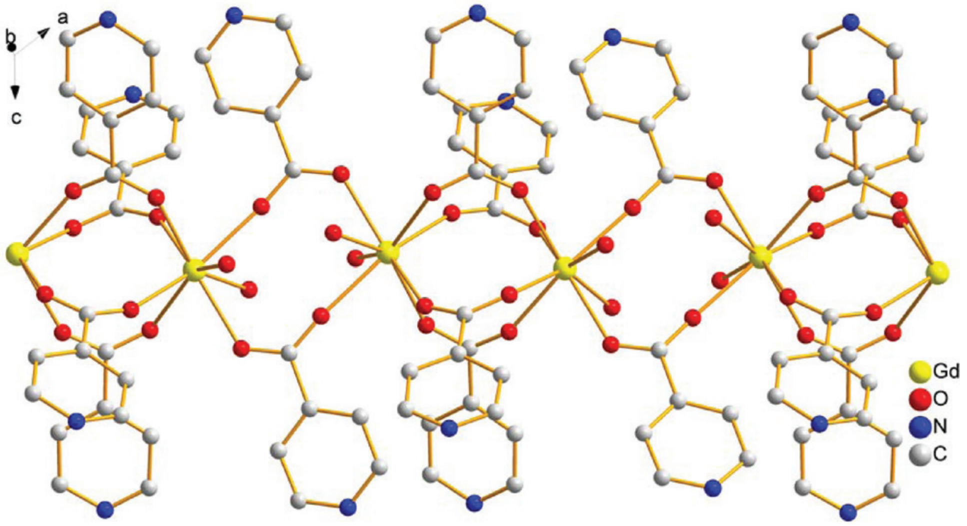
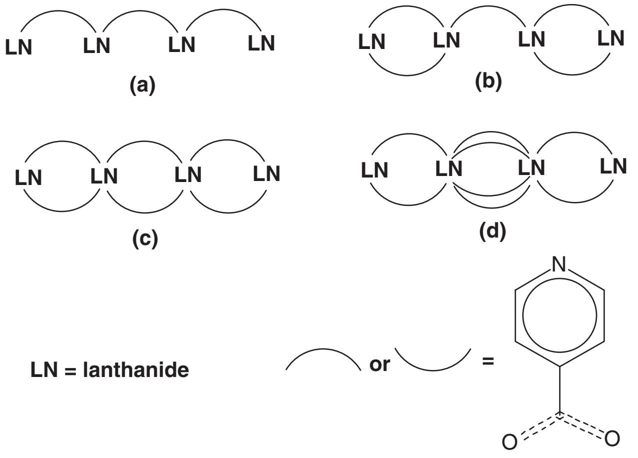


Figure 2. The 1D cationic chain-like structure of **1**.



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 bridges.

isonicotinic acid documented are mainly 1-1-1, 2-1-2, and 2-2-2 types [scheme 1(a), (b), and (c), respectively]. The 2-4-2 type is very rare. In **1**, no $\pi \cdots \pi$ stacking interactions exist between adjacent isonicotinato ligands. The 1-D chains, $ZnCl_4^{2-}$ and water molecules are linked by hydrogen bonds to yield a 3-D network with $ZnCl_5^{3-}$ located in the cavities (Supplemental Material).

Optical absorption spectrum of **1** reveals an optical gap of 3.35 eV (figure 3), suggesting that **1** shows a wide-gap semiconductor property and is consistent with the color of the crystal [11]. The gradual slope of the optical absorption edge for **1** is indicative of the existence of indirect transitions [12]. The optical absorption of **1** is likely due to absorption centered in the isonicotinate.

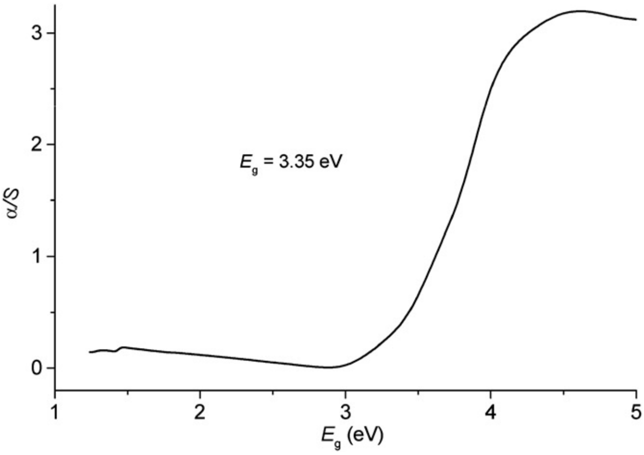


Figure 3. The solid-state diffuse reflectance spectrum for **1**.

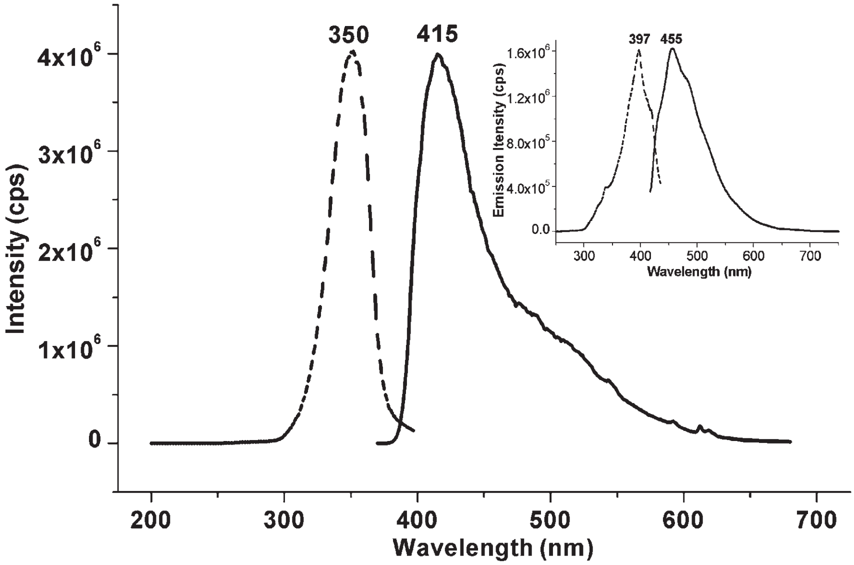


Figure 4. Solid-state emission and excitation spectra of **1** (inner plot: pure isonicotinic acid ligand). Red solid line: emission spectrum; green dashed line: excitation spectrum (color online only).

The solid-state luminescence of **1** was investigated at room temperature (figure 4). The excitation spectra of **1** show that the effective energy absorption takes place in the ultraviolet region from 300 to 400 nm. The excitation band of **1** possesses one main peak at 350 nm. The corresponding emission spectrum shows one main and intense emission band in the blue region with the maximum wavelength of 415 nm upon photo-excitation at 350 nm. To understand the luminescence of **1**, the luminescence spectra of pure isonicotinic acid were also measured under the same conditions. For pure isonicotinic acid, the emission spectra show an intense emission band in the blue region with maximum wavelength of 455 nm upon photo-excitation at 397 nm (inner plot of figure 4). The similarity of the luminescence spectra of **1** and pure isonicotinic acid suggests that the emission spectra of **1** should be assigned as an intraligand π–π^* transition of isonicotinic acid ligand. The absence of the characteristic emissions of Gd^{3+} and the existence of the ligand-based emissions in the luminescent spectra of **1** implies that isonicotinic acid ligand is not suitable for sensitization of Gd^{3+}. The absence of characteristic emissions of Gd^{3+} is probably due to Gd^{3+} possessing a relatively stable half-filled 4f shell. This complex may be a candidate for blue-light luminescent materials.

4. Conclusion

We have prepared a gadolinium isonicotinato inorganic–organic hybrid via a hydrothermal reaction. The crystal structure of **1** is characteristic of a 1-D polycationic chain and unprecedented $ZnCl_5^{3-}$ species. This complex exhibits a strong blue-light fluorescence emission band, and it may be used as a blue-light luminescent material. Optical absorption spectra show that the title compound may be a photoelectric material. More LN-TM-based inorganic–organic hybrid complexes with good physical properties may be developed.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 664484. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk).

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