

Hydrothermal Synthesis, Crystal Structure and Photoluminescence of $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n n[\text{HgCl}_2]_n(\text{C}_6\text{NO}_2\text{H}_5)$

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The first example of isonicotinic acid compounds with infinite mercury halide chains, $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n n[\text{HgCl}_2]_n(\text{C}_6\text{NO}_2\text{H}_5)$ (**1**), was synthesized through hydrothermal reactions and structurally characterized by X-ray single crystal diffraction. Compound **1** features a one-dimensional (1-D) motif, based on infinite 1-D $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains, neutral HgCl_2 moieties and isolated isonicotinic acid molecules. The $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains, HgCl_2 moieties and isonicotinic acid molecules are interlinked by hydrogen bonds and π - π interactions to give a two-dimensional supramolecular layer. Photoluminescent investigation reveals that the title compound exhibits a strong emission in blue region. The emission band is identified as the π - π^* transitions of the isonicotinic acid moieties.

Keywords: Crystal structure, Hydrothermal reaction, Isonicotinic acid, Mercury, Photoluminescence

INTRODUCTION

The increasing interest in the field of the crystal engineering of inorganic-organic hybrid materials has been justified by the potential applications of these materials as biological materials, magnetic functional materials, catalysts, zeolite-like materials, and so forth [1]. To our knowledge, transition metal compounds containing group 12 elements are particularly attractive for many reasons, such as, semiconductive properties, the variety of coordination numbers and geometries provided by the d^{10} configuration of the group 12 metal, photoluminescence properties, and so on. Moreover, isonicotinic acid has gained increased attention recently due to its common character-delocalized π -electrons of the pyridyl rings which makes it an excellent candidate for the preparation of light emitting compounds with potential in

various technical applications.

Fluorescent materials, particularly blue fluorescent materials, have been of intense interest because blue fluorescence is one of the key color components required for full-color EL displays and blue fluorescent materials are still rare. Therefore, we recently became interested in the crystal engineering of group 12-based materials with isonicotinic acid. We herein report the hydrothermal synthesis, crystal structure and photoluminescence of $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n n[\text{HgCl}_2]_n(\text{C}_6\text{NO}_2\text{H}_5)$ (**1**), which is the first example of isonicotinic acid compounds with infinite mercury halide chains and displays fluorescent activities in the blue range.

EXPERIMENTAL

Instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification. The fluorescent data

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were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

X-Ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction [2]. The structure was solved by the direct methods using the Siemens SHELXTLTM Version 5 package of crystallographic software [3]. Different Fourier maps based on the atomic positions yielded 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. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective

parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Synthesis

[HgCl₂(C₆NO₂H₅)]_nn[HgCl₂]_n(C₆NO₂H₅) (1). The title compound was prepared by mixing HgCl₂ (1 mmol, 0.272 g), isonicotinic acid (1 mmol, 0.123 g) and 10 ml distilled water in a 23 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 78%.

Table 1. Summary of Crystallographic Data and Structure Analysis for **1**

Empirical formula	C ₁₂ H ₁₀ Cl ₄ Hg ₂ N ₂ O ₄
Formula weight	789.20
X-Rays	MoK α
Crystal system	Monoclinic
Space group	<i>Pc</i>
Unit cell dimensions	$a = 3.9032(3) \text{ \AA}$ $b = 18.518(2) \text{ \AA}$ $c = 12.843(1) \text{ \AA}$ $\beta = 92.148(1)^\circ$
<i>Z</i>	2
<i>V</i>	927.6(1) \AA^3
<i>D_x</i>	2.825 mg m ⁻³
Absorption coefficient	17.124 mm ⁻¹
Crystal size	0.14 × 0.07 × 0.05 mm
No. of reflections collected/unique	5096/2858 [$R_{\text{(int)}} = 0.0551$]
Refinement	Full matrix least squares on F^2
Goodness-of-fit on F^2	1.006
Data/restraints/parameters	2637/20/217
Final <i>R</i> indices	$R_1 = 0.0388$, $wR_2 = 0.0812$
<i>R</i> indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.0822$
Index ranges	$-4 \leq h \leq 4$, $-22 \leq k \leq 22$, $-15 \leq l \leq 15$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	Graphite
Structure determination	Siemens SHELXTL

Table 2. Selected Bond Lengths and Bond Angles of **1**

Bond lengths (Å)		Bond angles (°)	
Hg(1)-Cl(1)	2.365(1)	Cl(1)-Hg(1)-Cl(2)	164.20(4)
Hg(1)-Cl(2)	2.351(1)	Cl(1)-Hg(1)-Cl(2)#1	90.05(3)
Hg(1)-Cl(2)#1	2.960(1)	Cl(1)-Hg(1)-N(1)	96.03(8)
Hg(1)-N(1)	2.414(4)	Cl(2)-Hg(1)-N(1)	99.37(8)
Hg(2)-Cl(3)	2.302(1)	Cl(2)-Hg(1)-Cl(2)#1	93.92(3)
Hg(2)-Cl(4)	2.302(1)	N(1)-Hg(1)-Cl(2)#1	88.29(8)
O(1)-C(6)	1.341(5)	Cl(3)-Hg(2)-Cl(4)	177.18(4)
O(2)-C(6)	1.234(5)	Hg(1)-Cl(2)-Hg(1)#2	93.92(3)
O(3)-C(12)	1.278(5)		
O(4)-C(12)	1.228(4)		

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

RESULTS AND DISCUSSION

X-Ray diffraction analysis shows that the structure of the title compound consists of infinite 1-D $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains, $[\text{HgCl}_2]$ moieties and isolated isonicotinic acid molecules. The mercury atoms are grouped into two kinds. Hg1 atom is coordinated by three chlorine atoms and one nitrogen atom to yield a HgCl_3N tetrahedron, with the bond lengths of Hg-Cl ranging from 2.351(1) to 2.960(1) Å and the average value of 2.558(1) Å which is comparable with those reported previously [4]. On the contrary, Hg2 atom is twofold coordinated with two chlorine atoms in an approximately linear arrangement $[\text{Cl}3\text{-Hg}2\text{-Cl}4 = 177.18(4)^\circ$, which is comparable with that of isolated HgCl_2 moieties in the literature [5]. Each HgCl_3N tetrahedron connects to two neighboring ones *via* corner-sharing to form a 1-D $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains appended by terminally coordinating isonicotinate ligands (Fig. 1).

Unlike the ligating isonicotinate ligands, there are some isolated isonicotinic acid molecules coexisting in the crystal structure. For C6-containing carboxyl group, the bond length of O(1)-C(6) is 1.341(5) Å, obviously longer than that of O(2)-C(6) which is 1.234(5) Å, indicating that O(1)-C(6) is a single bond while O(1) bonds to a hydrogen atom. For C12-containing carboxyl group, the bond lengths of O(3)-C(12) and O(4)-C(12) are close with the values of 1.278(5) and 1.228(4) Å, respectively, suggesting that both of them are double bonds. Result of the bond valence calculation indicates

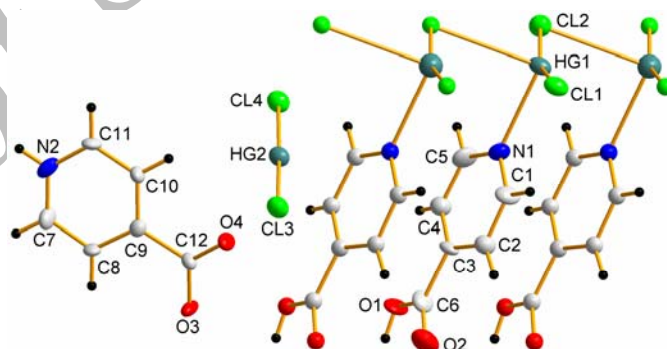


Fig. 1. ORTEP drawing of **1** with 30% thermal ellipsoids. Hydrogen atoms were represented as black small spheres.

that the mercury is in +2 oxidation state (Hg1: 1.987, Hg2: 1.739) [6]. In **1**, some $\pi \dots \pi$ stacking interactions (centroid to centroid distance is *ca.* 3.903 Å) are established between the adjacent isonicotinic acid moieties. For every two neighboring isonicotinic acid moieties, they are perfectly coplanar with the dihedral angle of 0° . As shown in Figs. 2 and 3, the $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains, $[\text{HgCl}_2]$ moieties and isolated isonicotinic acid molecules are interconnected together through hydrogen bonds to give a 2-D supramolecular layer parallel to the *ac* plane. These layers stack along the *b* axis to complete the 3-D structure (Fig. 3).

For the structure of **1**, a Flack *x* parameter of 0.02(1) was calculated, indicating a correct absolute structure [7]. It is

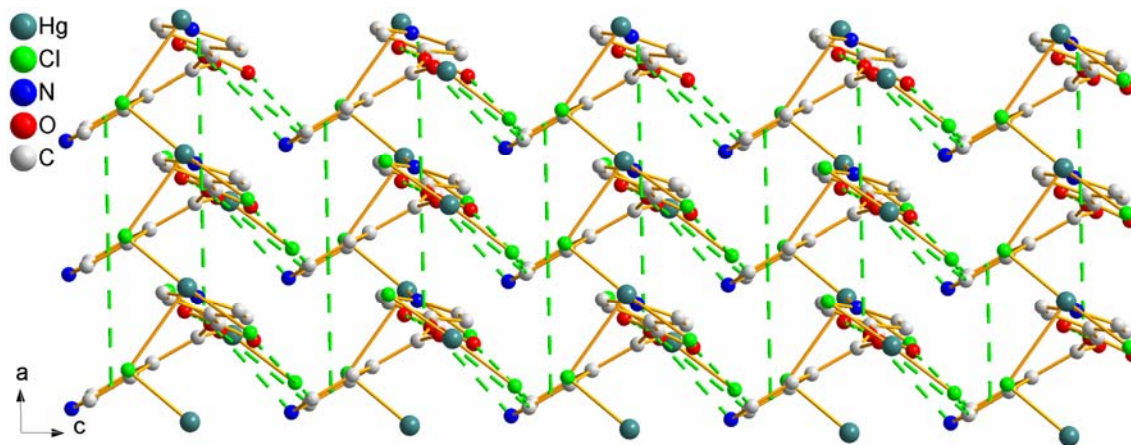


Fig. 2. Two-dimensional supramolecular layer of **1** with the dashed lines representing the hydrogen bonds and π - π interactions. Distances of the hydrogen bonds in **1** (Å): O(1)-H(1B)...O(3) 2.625(4), N(2)-H(2B)...O(3) 2.647(4), C(7)-H(7A)...Cl(3) 3.498(4), C(7)-H(7A)...O(4) 3.231(5), C(11)-H(11A)...O(2) 3.299(6), C(11)-H(11A)...O(2) 2.52.

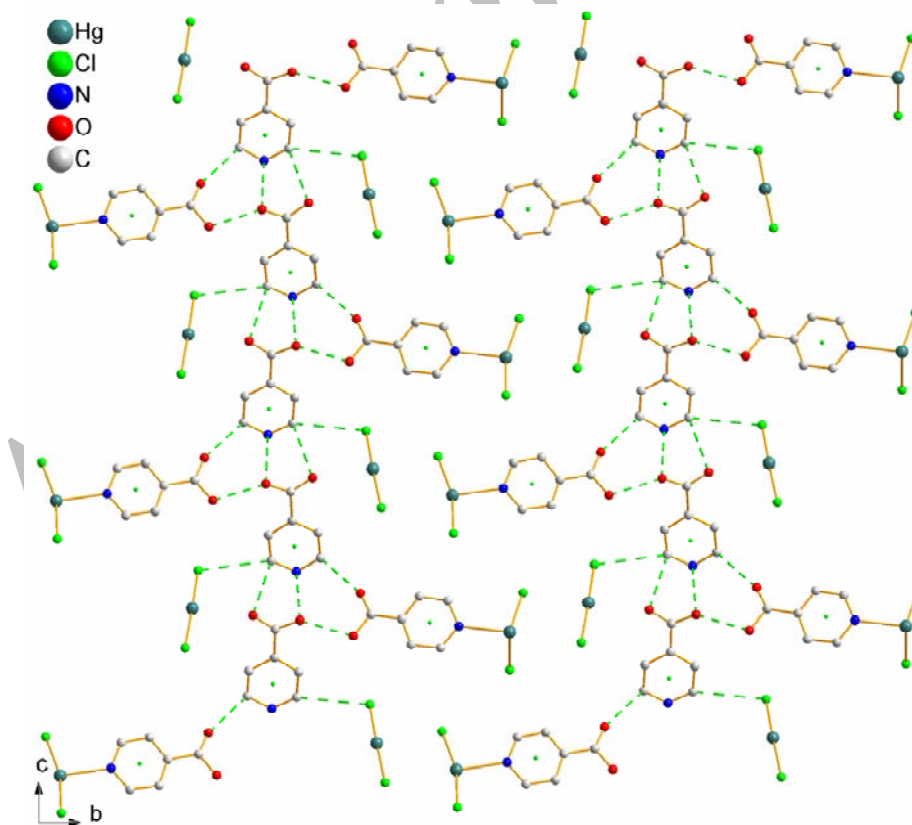


Fig. 3. Crystal packing diagram of **1** with the dashed lines representing the hydrogen bonds and π - π interactions.

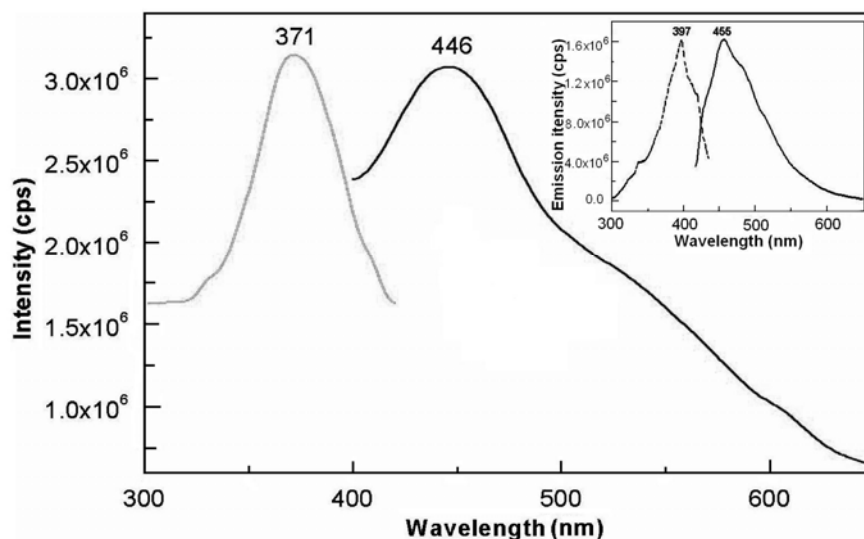


Fig. 4. Solid-state emission spectra of **1** at room temperature (Inset: the luminescent spectra of pure isonicotinic acid).

noteworthy that compound **1** is the first example of isonicotinic acid compounds with infinite mercury halide chains, although hundreds of isonicotinic acid compounds have been documented thus far.

The solid-state luminescence of **1** was investigated at room temperature (Fig. 4). The solid-state excitation spectra of the title compound show that the effective energy absorption mainly takes place in the ultraviolet region of the range 350-400 nm. The excitation band of compound **1** under the emission of 446 nm possesses one main peak of 371 nm. We further measured the corresponding emission spectra by using the excitation wavelength of 371 nm for the title compound, and obtained the emission spectra as shown in Fig. 4. For compound **1**, the emission spectra show one strong and broad emission band with the maximum emission wavelength locating at 446 nm. To understand the nature of the luminescence of **1**, the luminescent spectra of pure isonicotinic acid were also measured under the same conditions. For pure isonicotinic acid, the emission spectra show one intense emission band in blue region with the maximum wavelength of 455 nm upon photo-excitation at 397 nm (inner plot of Fig. 4). The similarity between the luminescent spectra of **1** and pure isonicotinic acid suggests that the emission spectra of **1** should be assigned to an intraligand π - π^* transition of isonicotinic acid moieties.

In conclusion, we have successfully prepared a novel group 12-isonicotinic acid compound via hydrothermal reaction. The crystal structure of the title compound was characterized by a 1-D structure based on infinite 1-D $[\text{HgCl}_2(\text{C}_6\text{NO}_2\text{H}_5)]_n$ chains, $[\text{HgCl}_2]$ moieties and isolated isonicotinic acid molecules. The title compound is the first example of isonicotinic acid compounds with infinite mercury halide chains. The title compound exhibits intense luminescence at 446 nm. Thus, this compound may be a candidate for blue-light luminescent materials.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center No. 734397 for **1**. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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