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SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENCE OF $(HGCL_3)_N(C_6NO_2H_6)_N(C_6NO_2H_5)_N\cdot NH_2O$

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ABSTRACT. A new isonicotinic acid compound with infinite mercury halide anionic chains, $(HgCl_3)_n(C_6NO_2H_6)_n(C_6NO_2H_5)_n\cdot nH_2O$ (**1**), was obtained from the hydrothermal reaction and structurally characterized by X-ray single diffraction. The title compound is characteristic of a one-dimensional structure, based on one-dimensional $(HgCl_3)^-$ anionic chains, protonated isonicotinic acid, neutral isonicotinic acid molecules and lattice water molecules. The protonated isonicotinic acid, neutral isonicotinic acid molecules and lattice water molecules are interconnected via hydrogen bonds to form a three-dimensional supramolecular framework. The $(HgCl_3)^-$ anionic chains are anchored in the voids of the supramolecular framework via hydrogen bonds. Photoluminescent investigation reveals that the title compound displays a strong emission in blue region. The emission band is identified as the π-π^* transitions of the isonicotinic acid moieties.

KEY WORDS: Crystal, Isonicotinic, Halide, Mercury, Photoluminescence

INTRODUCTION

The growing interest in the field of the crystal engineering of inorganic-organic hybrid materials is justified by the potential applications of these materials as catalysts, zeolite-like materials, biological materials, magnetic functional materials [1-5]. To our knowledge, transition metal compounds containing group 12 elements are particularly attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the d^{10} configuration of the group 12 metal, semiconductive properties, photoluminescent properties, and so on. Furthermore, isonicotinic acid has gained increasing attention in recent years due to its common character–delocalized π-electrons of the pyridyl rings, which makes it an excellent candidate in preparing light emitting compounds whose 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 become interested in the crystal engineering of group 12-based materials with isonicotinic acid. In this paper, we report the synthesis, crystal structure and photoluminescent property of $(HgCl_3)_n(C_6NO_2H_6)_n(C_6NO_2H_5)_n\cdot nH_2O$ (**1**), which displays fluorescent activities in the blue range.

EXPERIMENTAL

Synthesis of $(HgCl_3)_n(C_6NO_2H_6)_n(C_6NO_2H_5)_n\cdot nH_2O$ *(1).* All reactants of A.R. grade were obtained commercially and used without further purification. The title compound was prepared by mixing $HgCl_2$ (1 mmol, 0.272 g), isonicotinic acid (2 mmol, 0.246 g), 1 mL concentrated hydrochloric acid and 10 mL distilled water in a 23 mL Teflon-lined stainless steel autoclave and heated at 200 °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 71%. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

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X-ray structure determination. X-ray single diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromatic Mo-$K\alpha$ radiation (λ = 0.71073 Å) using an ω scanning technique. CrystalClear software was used for data reduction and empirical absorption correction [6]. The structure was solved by the direct methods using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software [7]. The difference 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. Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center No. 728421 for **1**. Copies of this information can be obtained without 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).

Table 1. Summary of crystallographic data and structure analysis for **1.**

Empirical formula	$C_{12}H_{13}Cl_3HgN_2O_5$
Formula weight	572.19
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 15.766(2) Å b = 15.355(2) Å c = 7.3068(7) Å β = 101.397(1)°
Z	2
V	1734.1(3) Å^3
D_x	2.192 Mg/m^3
Absorption coefficient	9.361 mm^{-1}
Crystal size	0.15 × 0.06 × 0.05 mm^3
No. of reflections collected/unique	10285/3021 [$R_{(int)}$ = 0.0325]
Refinement	Full matrix least squares on F^2
Goodness-of-fit on F^2	1.010
Data/restraints/parameters	1907 / 24 / 208
Final R indices	R_1 = 0.0396, wR_2 = 0.0987
R indices (all data)	R_1 = 0.0563, wR_2 = 0.1006
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-8 \le l \le 8$

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

Bond lengths (Å)		Bond angles (°)	
Hg(1)-Cl(1)	2.357(1)	Cl(1)-Hg(1)-Cl(2)	105.23(4)
Hg(1)-Cl(2)	2.626(1)	Cl(1)-Hg(1)-Cl(2)#1	93.44(3)
Hg(1)-Cl(2)#1	2.8100(9)	Cl(1)-Hg(1)-Cl(3)	146.06(4)
Hg(1)-Cl(3)	2.350(1)	Cl(2)-Hg(1)-Cl(2)#1	84.74(3)
O(1)-C(1)	1.297(4)	Cl(2)-Hg(1)-Cl(3)	106.44(4)
O(2)-C(1)	1.189(4)	Cl(2)-Hg(1)-Cl(3)#1	101.28(3)
O(3)-C(7)	1.252(4)	Hg(1)-Cl(2)-Hg(1)#2	94.91(3)
O(4)-C(7)	1.237(4)		

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

RESULTS AND DISCUSSION

X-ray single diffraction analysis revealed that the structure of the title compound consists of 1-D $(HgCl_3)^-$ anionic chains, protonated isonicotinic acid, neutral isonicotinic acid molecules and lattice water molecules. The mercury atom is coordinated by four chlorine atoms to yield a $HgCl_4^{2-}$ tetrahedron, with the bond lengths of Hg-Cl ranging from 2.350(1) to 2.8100(9) Å and the average value being 2.536(1) Å, which is similar to those reported [8, 9]. Each $HgCl_4^{2-}$ tetrahedron interconnects to two neighboring ones via corner-sharing to form a 1-D $(HgCl_3)^-$ anionic chain (Figure 1). Result of the bond valence calculation indicates that the mercury is in +2 oxidation state (Hg1: 2.096) [10, 11]. Due to the oxidation states of the chloride and the mercury ion are –1 and +2, part of the isonicotinic acid should be neutral and others should be +1 to keep the charge balance of the compound, as is the case in other isonicotinic acid containing compounds [12-14]. For C(1)-containing carboxyl group, the bond length of O(1)-C(1) is 1.297(4) Å, obviously longer than that of O(2)-C(1) being 1.189(4) Å, indicating that O(1)-C(1) is a single bond and O(1) bonds to a hydrogen atom. However, for C(7)-containing carboxyl group, the bond lengths of O(3)-C(7) and O(4)-C(7) are very close with the values being of 1.252(4) and 1.237(4) Å, respectively, suggesting the de-localization of COO^-.

In **1**, no $\pi \ldots \pi$ stacking interactions were established between the adjacent isonicotinic acid ligands, because the minimum distance (5.041 Å) between the centriods of py rings is longer than 3.6 Å. As shown in Figure 2, the protonated isonicotinic acid, neutral isonicotinic acid molecules and lattice water molecules are linked together through hydrogen bonds to give a 3-D supramolecular framework. The $(HgCl_3)^-$ anionic chains are anchored in the voids of the 3-D framework via hydrogen bonds. It should be pointed out that it is possible to exist an electrostatic interaction between anionic chains and cationic moieties. This electrostatic interaction will strengthen the 3-D supramolecular framework.

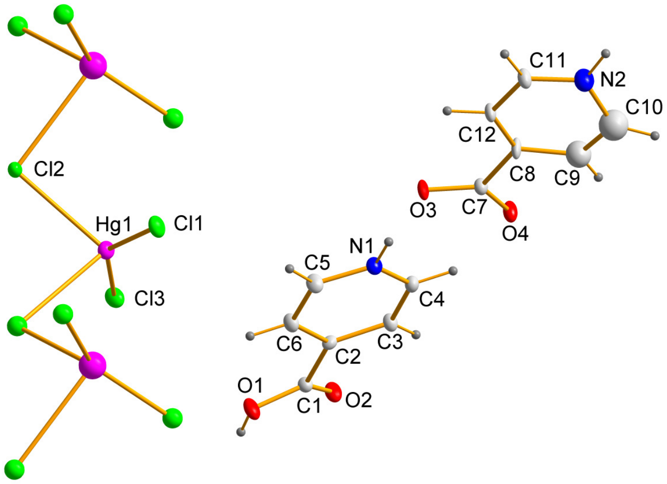

Figure 1. Molecular structure of **1** with 10% thermal ellipsoids. Hydrogen atoms were represented as small spheres. Lattice water molecules were omitted for clarity.

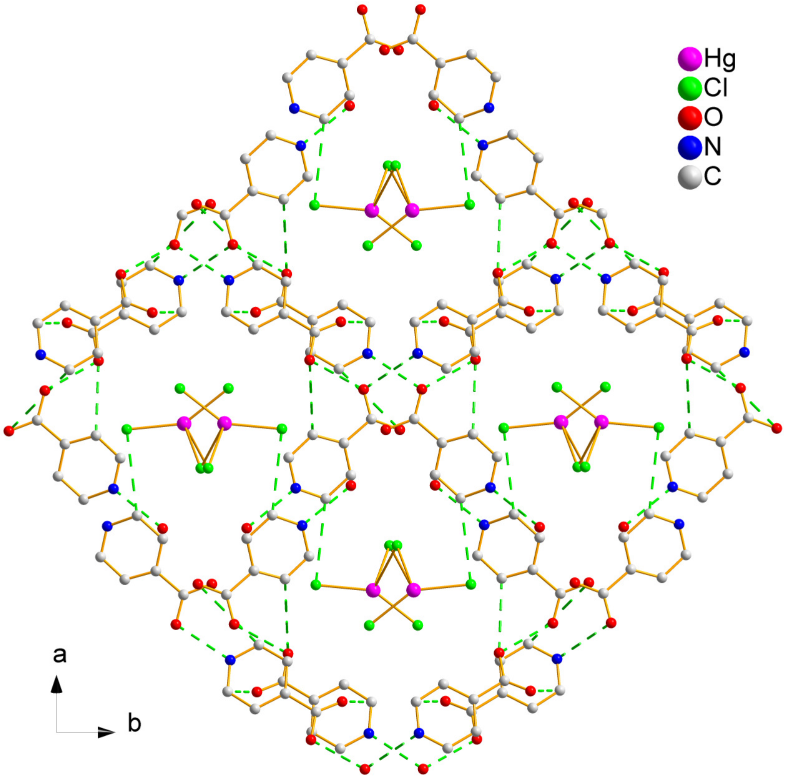

Figure 2. Crystal packing diagram of **1** with the dashed lines representing the hydrogen bonds. Distances of the hydrogen bonds in **1** (Å)**:** O(1)-H(1A)···O(3) 2.555(3), N(1)-H(1B)···O(3) 2.712(4), N(2)-H(2A)···O(1W) 2.632(6), C(4)-H(4A)···O(4) 3.183(4), C(9)-H(9A)···O(4) 2.727(7), C(12)-H(12A)···O(1) 3.261(4), C(5)-H(5A)···O(2) 3.054(4), and C(10)-H(10A)···Cl(3) 3.560(8).

The solid-state luminescence of **1** was investigated at room temperature (Figure 3). The solid-state excitation spectrum of the title compound shows that the effective energy absorption mainly takes place in the ultraviolet region of the range 300-400 nm. The excitation band of compound **1** under the emission of 451 nm possesses one main peak of 372 nm. We further measured the corresponding emission spectrum. The emission spectrum shown in Figure 3 was collected by exciting at 372 nm. Compound **1** shows a strong but broad band at 451 nm. To understand the nature of the luminescence of **1**, the luminescent spectrum of pure isonicotinic acid was also measured under the same condition. For pure isonicotinic acid, the emission spectrum shows one intense emission band in blue region with the maximum wavelength of 455 nm upon photo-excitation at 397 nm (inner plot of Figure 3). The similarity of the luminescent spectra of **1** and pure isonicotinic acid suggests that the emission spectrum of **1** should be assigned as an intraligand π-π* transition of isonicotinic acid moieties.

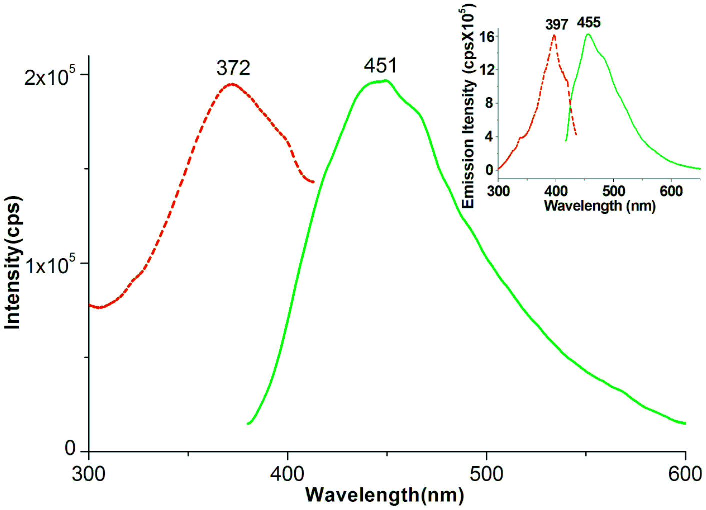

Figure 3. Solid-state photoluminescent spectra of **1** and pure isonicotinic acid (inset) at room temperature (Red: excitation spectra; green: emission spectra).

In conclusion, a novel group 12-isonicotinic acid compound was successfully prepared via hydrothermal reaction techniques. The crystal structure of the title compound is characterized by a 1-D structure based on one-dimensional $(HgCl_3)^-$ anionic chains, protonated isonicotinic acid, neutral isonicotinic acid molecules and lattice water molecules. The title compound exhibits intense luminescence at 451 nm. Thus, this compound may be a candidate for blue-light luminescent materials.

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