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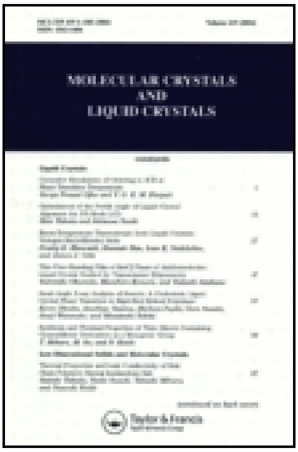

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A New Organic-Inorganic Hybrid Crystal Prepared from 1-Methyl-4-Carbamoylpyridinium Iodide and Cadmium Iodide

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A New Organic-Inorganic Hybrid Crystal Prepared from 1-Methyl-4-Carbamoylpyridinium Iodide and Cadmium Iodide

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Although 4-substituted pyridinium derivatives studied so far form the 2:1 complexes with cadmium iodide, an exceptional 1:1 complex was found for 1-methyl-4-carbamoylpyridinium iodide. Its X-ray crystallographic analysis revealed that its inorganic portion has a unique structure with corner-sharing one-dimensional tetrahedral chains of $(CdI_3^-)_n$.

Keywords Pyridinium; Triiodocadmate; Second-order nonlinear optics

INTRODUCTION

Organic-inorganic hybrid materials have been attracted attention for their properties expected by combining superior parts of both organic and inorganic portions. Among such hybrid materials, layered perovskites have been widely investigated due to their interesting optical and electronic properties originated from the dimension and structure of the inorganic layers [1]. Their fabrication techniques for thin films [2] or fine particles [3] have also been studied. Recently, a variety of organic chromophores to functinalize organic layers have been introduced [4].

In our previous study, we aimed at introduction of pyridinium derivatives possessing large second-order optical nonlinearity and relatively short cutoff wavelength [5] into the layered perovskite system. However, when **1** or **2** in FIGURE 1 is combined with CdI_2, inorganic portion did not form the octahedral structure but formed a tetrahedral

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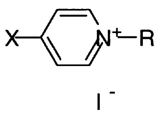

1 : X=N(CH_3)$_2$, R=CH_3
2 : X=CN, R=CH_3
3 : X=NH_2, R=CH_3
4 : X=N(CH_3)$_2$, R=C_2H_5
5 : X=$CONH_2$, R=CH_3

FIGURE 1 Chemical structures of pyridinium derivatives.

divalent anion structure which could described as CdI_4^{2-} [6]. Pyridinium derivatives **3** and **4** with CdI_2 were also found to give 2:1 complexes with tetraiodocadmate. However, when **5** and CdI_2 were combined, we found that it exceptionally formed a 1:1 complex. In this article, we report the structure of this unique complex.

EXPERIMENTAL

Acetone solution of the 1:1 mixture of **5** and CdI_2 was slowly evaporated to give crystals of the 1:1 complex (CP/CdI_3), which were confirmed by elemental analysis. Although acetone solution of the 2:1 mixture gave the 2:1 complex for **1-4** with CdI_2, **5** gave only CP/CdI_3. Its X-ray crystallographic analysis was performed using a Mac Science MXC3 four-circle diffractometer [7].

RESULTS AND DISCUSSION

The structure of an asymmetrical unit obtained for the CP/CdI_3 crystal actually contained a pyridinium cation with nearly plane structure and a triangular-pyramidal CdI_3^- anion. The CP/CdI_3 crystal belongs to the orthorhombic space group Fdd2 which is noncetrosymmetric structure with the unique *c*-axis. FIGURE 2 shows the crystal structure of the CP/CdI_3 viewed along [101] direction. For organic portion, cation does not show a different structure compared with its salts of 4-substituted-benzenesulfonate anion studied previously [5]. The orientation of the nearest two cations is shown in FIGURE 3 (a). The dihedral angle between two cation planes is about 80°. Since the distance between the

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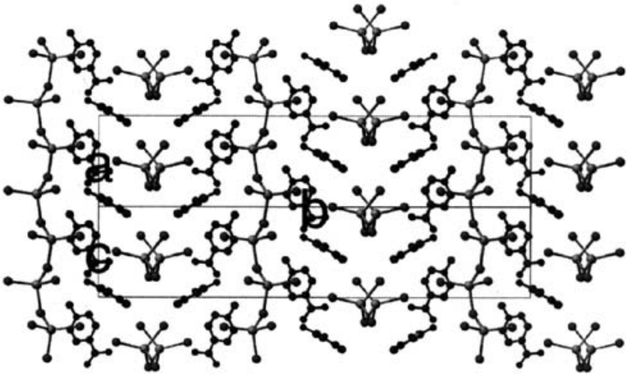

FIGURE 2 Crystal structure of the CP/CdI_3 viewed along the [101] direction. Hydrogen atoms are omitted.

nitrogen atom of one cation and the oxygen atom of the other cation is 3.108 Å, hydrogen bonding between these two cations is not strong.

The structure of inorganic portion of the CP/CdI_3 crystal is unique. An asymmetric unit of CdI_3^- is connected to the adjacent CdI_3^- resulting in the corner-sharing one-dimensional (1D) chain of tetrahedral structures. Such a 1D structure of $(CdI_3^-)_n$ has been scarcely reported, and examples were hydrated CdI_3^- salts of alkaline metals [8]. Although all 1D columns are in the same direction in the inorganic salts, the 1D columns of the hybrid salt extend along two directions, i.e., the [101] and [$10\bar{1}$] directions. The columns extending the same direction exist on a plane parallel to the (010) plane. A part of the 1D column structure in the

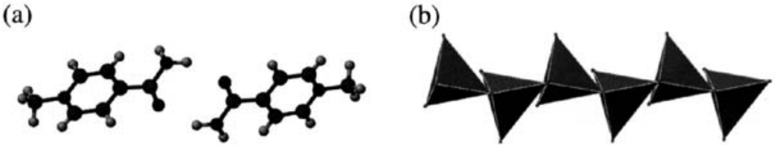

FIGURE 3 The orientation of the nearest two cations in crystalline CP/CdI_3 (a) and a part of the $(CdI_3^-)_n$ 1D column structure (b), where the $(CdI_3^-)_n$ structure is represented by the sequence of tetrahedra in which cadmium and iodide occupy its center and apexes, respectively.

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CP/CdI_3 crystal is displayed in FIGURE 3 (b). Its angle between two tetrahedral sides along the 1D direction is 163.5°, while that for the inorganic salts is almost straight. This may be due to lower symmetry of the organic cation compared with metal cations.

Interestingly, these crystals possessing the 1D $(CdI_3^-)_n$ structure belong to polar space groups. Thus, introduction of the $(CdI_3^-)_n$ structure may be a good motif to generate noncentrosymmetric structure in the crystals. According to the same procedure based on the oriented-gas model reported previously [6], the d_{31} value was calculated to be 2 pm/V using the calculated β of the cation by MOPAC PM3 and the same local field factors as *N*-(4-nitrophenyl)-L-prolinol (NPP). This *d* value was estimated to be about one twelfth of the largest off-diagonal *d* of NPP.

In conclusion, we have found that the hybrid crystal from **5** and CdI_2 is the 1:1 complex with a polar structure. The inorganic portion has the unique 1D structure of the corner-sharing tetrahedral chain.

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