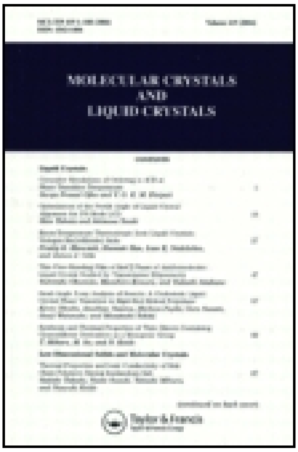

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UTILIZATION AND MODIFICATION OF PEROVSKITE-TYPE LAYERED STRUCTURES AS INORGANIC-ORGANIC HYBRID MATERIALS

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Abstract The aromatic ammonium-based layered halide compounds were obtained of bis(4-nitroanilinium)tetrachlorocadmate and bis(2-methyl-4-nitroanilinium) tetrachlorocadmate, aiming at a new type of inorganic-organic hybrid layered material. X-ray diffraction analyses of the single crystals revealed that both of the crystals take an alternate layered structure of the organic bilayer and the inorganic sheet. Cadmium ion and chloride anions form six-coordinated octahedra whose corner anions are shared with the neighboring octahedra for the crystal of bis(4-nitroanilinium)tetrachlorocadmate. In the case of bis(2-methyl-4-nitroanilinium) tetrachlorocadmate crystal the inorganic portion takes distorted four-coordinated tetrahedra. The structure of the inorganic portion for the latter crystal can be considered to be caused by the distortion of a perovskite-type octahedron due to the introduction of a bulky organic molecule.

INTRODUCTION

Organic-ammonium-based layered halide compounds (general formula: $(RNH_3)_2MX_4$) have been investigated extensively because of the unique properties such as third-order harmonic generation,[1] photoluminescence,[2,3] electroluminescence,[4] and electric conductivity.[5] Most of these compounds take perovskite-type structures in which halogen anions form corner-sharing octahedra centered by divalent metal atoms. Organic portion takes "tail-to-tail" bilayer sandwiched with inorganic sheets. This characteristic structure shows a new strategy to arrange organic molecules in such a manner as is not easily realized by other techniques, although the organic molecules employed so far have been limited to simple molecules such as alkylammonium,[6,7] alkyldiammonium,[8] and phenethylammonium.[4,9] The modification of the inorganic layer structure is also an interesting subject since the function of the hybrid system is mainly associated with the inorganic portion.[5,9]

In this paper we report on the extension of the perovskite-type layered structure aiming at the utilization of the inorganic layer as a host for arranging a cation of push-pull type molecule. Further we demonstrate the modification of the structure of inorganic portion by changing the size of an organic cation.

EXPERIMENTAL SECTION

Materials

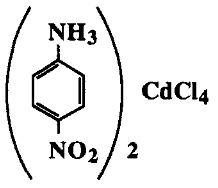
Pale yellow single crystals were obtained by slow evaporation of the 2/1 mixture of 4-nitroaniline or 2-methyl-4-nitroaniline and cadmium chloride ($CdCl_2$) in a mixed solvent of HCl aq. and ethanol.

Elemental Analysis for bis(4-nitroanilinium)tetrachlorocadmate **1** (% Obs.(Calc.)) : C 27.17(27.05), H 2.39(2.63), N 10.21(10.52), O 10.55(12.02), Cl 26.08(26.67).

Elemental Analysis for bis(2-methyl-4-nitroanilinium)tetrachlorocadmate **2** (% Obs.(Calc.)) : C 30.10(30.00), H 3.21(3.24), N 9.89(10.00), O 10.54(11.41), Cl 23.09(25.30).

X-ray diffraction analyses

The diffraction data were collected on a Rigaku AFC5S Diffractometer, using MoKα ($\lambda = 0.71069$ Å). The program system used for the analyses was TEXSAN (MSC). The details were described elsewhere.[10,11]



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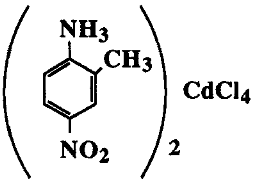

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RESULTS AND DISCUSSION

X-ray diffraction analysis of the single crystal of **1** revealed that the crystal takes an alternate layered structure of the organic bilayer and the inorganic sheet (Figure 1). Cadmium ions and chloride anions form six-coordinated octahedra whose equatorial corner anions are shared with the neighboring octahedra. The organic bilayer takes a "tail-to-tail" structure in which the nitro groups of the molecules are positioned in the central portion of the organic layer. Figure 2 shows the projection along the **a**-axis, i. e., along the direction parallel to the layer normal. The NH_3 group of 4-nitroanilinium is juxtaposed between the axial vertices of the chloride octahedra. The molecular axis of 4-nitroanilinium is tilted by ca. 20° with respect to the layer normal. These features are similar to those for *n*-alkylammonium compounds ($(C_nH_{2n+1}NH_3)_2MCl_4$) reported so far.[6,7]

TABLE I Crystal Data.

	1	2
Empirical Formula	$C_{12}H_{14}N_4O_4CdCl_4$	$C_{14}H_{18}N_4O_4CdCl_4$
Formula Weight	532.49	560.54
Crystal Color	pale yellow	pale yellow
Crystal Dimensions	spherical (0.2 mm in diameter)	block 0.23 × 0.2 × 0.07 mm^3
Crystal System	orthorhombic	orthorhombic
Space Group	Pbca (No. 61)	Pnma (No. 62)
Lattice parameters	a = 33.131(3) Å b = 7.792(1) Å c = 7.256(1) Å U = 1873.2(3) $Å^3$	a = 8.266(2) Å b = 30.465(5) Å c = 8.334(1) Å U = 2098.7(7) $Å^3$
Z value	4	4
D_{calc}	1.888 g cm^{-1}	1.774 g cm^{-1}
F_{000}	1048.00	1112.00
$\mu(MoK\alpha)$	17.62 cm^{-1}	15.77 cm^{-1}
No. of Reflections	2741*	3527
Program System	TEXSAN(MSC)	TEXSAN(MSC)
Structure Solutions	Direct method (MULTAN78)	Patterson method
No. of Observations ($I>3\sigma(I)$)	2120	1298
No. of Variables	143	127
Residuals: R; Rw	0.028; 0.034	0.043; 0.042

*The reflections (0kl) with k = odd, (h0l) with l = odd and (hk0) with h = odd were omitted based on our preliminary measurement and analysis.

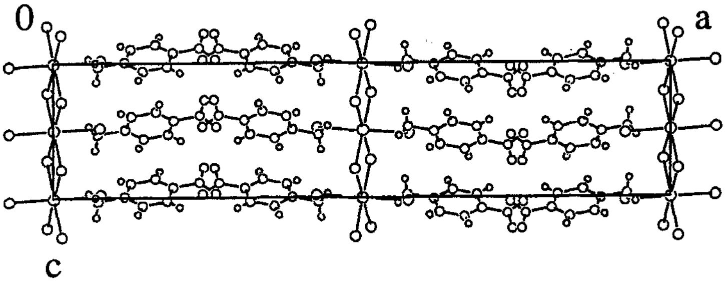

FIGURE 1 Molecular packing of 1 viewed from the [010] axis.

The above results demonstrate the versatility of the perovskite-type layered structure for arranging organic functional molecules. The molecular arrangement of 4-nitroaniline in the present crystal is unique and is very different from the ones of 4-nitroaniline-HCl salt[12] or 4-nitroaniline itself,[13] where the occurrence of the "head-to-tail" molecular alignment indicates the dominant role of the intermolecular dipolar interaction of the push-pull type molecule in determining the molecular arrangement in

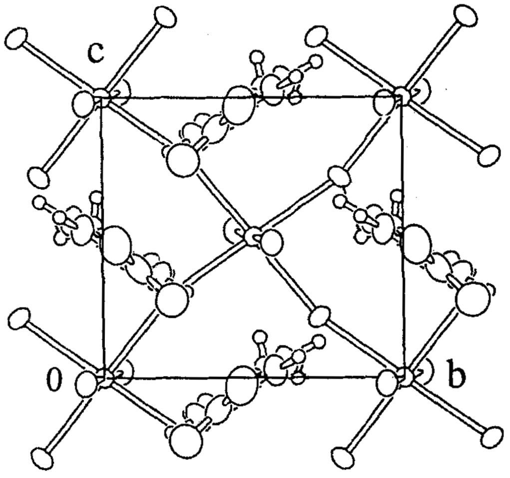

FIGURE 2 Projection along the [100] axis of **1**.

the crystals. The tail-to-tail structure of 4-nitroaniline moiety in the crystal of **1** shows that the molecular arrangement is mainly determined by the inorganic layer structure which acts as a host for the organic molecule.

X-ray diffraction analysis of **2** revealed that the crystal also takes a layered structure (Figure 3). 2-methyl-4-nitroanilinium molecules form a "tail-to-tail" bilayer with the nitro groups positioned in the central portion of the organic layer. $CdCl_4$ portion, on the other hand, takes a distorted four-coordinated tetrahedra, which is quite different from the case of **1**. This structure is formed by the substitution of methyl group to benzene ring, which makes the organic component bulkier. Figure 4 shows the projection along the **b**-axis, i. e., along the layer normal. The lattice constants of the layer plane are 8.26 × 8.33 Å^2, which are larger than the ones for **1** (7.79 × 7.26 Å^2) or bis(*n*-octylammonium)tetrachlorocadmate in a room-temperature phase (7.35 × 7.55 Å^2).[6] The Cd-Cl distances in a tetrahedra unit are 2.46 Å, 2.47 Å, and 2.57 Å while the distance between Cd and the nearest Cl anion of the neighboring unit is 3.40 Å.

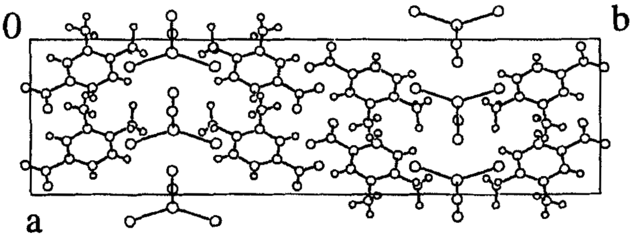

FIGURE 3 Molecular packing of **2** viewed from the [001] axis.

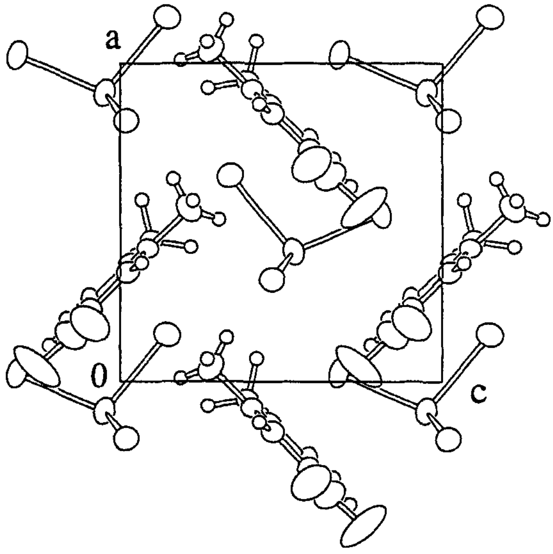

FIGURE 4 Projection along the [010] axis of **2**.

The structure of **2** is considered to form through the distortion of a perovskite-type layered structure and is called a distorted perovskite-type layered structure. This is because the tetrahedron in the structure of **2** is distorted in such a manner that we like to assume that this distorted tetrahedron is an intermediate between the standard tetrahedron and octahedron as is shown in the following:

i) two of the Cd-Cl bonds in a $CdCl_4$ unit lie in the **a-c** plane.

ii) the Cl-Cd-Cl angle lying in the **a-b** plane is 135.8°, significantly larger than the standard angle of a tetrahedron.

The assumed distortion from the standard octahedron is schematically shown in Figure 5. The $CdCl_4$ unit in the observed structure of **2** depicted in the right side of Figure 5 is considered to form through the distortion by the displacement of the atoms in the direction as is shown by the arrows in the left side of Figure 5. This means that two of the four Cl atoms in each $CdCl_4$ unit share the **a-c** plane with the Cd atoms, suggesting a weak network structure which connects the neighboring $CdCl_4$ units in this plane, although the distance between Cd and the nearest Cl anion of the neighboring unit 3.40 Å is too long for the coordination of a metal and a halide.

The displacement of atoms shown in Figure 5 is understandable if we assume that the crystal structure is determined by a compromise between the preference of a

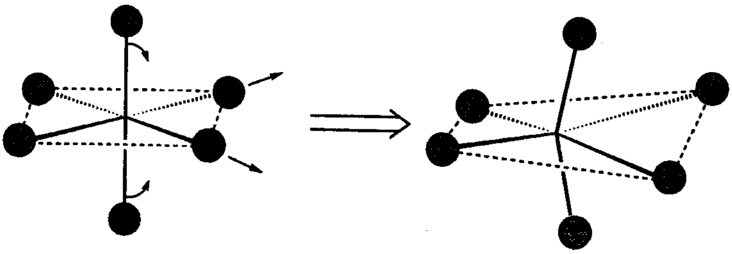

FIGURE 5 Schematic drawing of the displacement of atoms in the inorganic portion from the standard octahedron to the distorted tetrahedron in **2**.

TABLE II Structure of the inorganic portion.

compound	area per divalent metal in the layer plane (Å^2)	structure of MCl_4 unit	source
$(C_{10}H_{21}NH_3)_2CdCl_4$	27.7	octahedron	ref. 6
1	28.3	octahedron	this work
2	34.4	distorted tetrahedron	this work
$(C_{13}H_{27}NH_3)_2ZnCl_4$	38.9	tetrahedron	ref. 14

perovskite-type layered structure and the bulkiness of the organic cation. Table 2 summarizes the area per divalent metal in the layer plane for the present two crystals and two reference crystals. The $CdCl_4$ unit in the crystal of $(C_{10}H_{21}NH_3)_2CdCl_4$ is an octahedron[6] while that in the crystal of $(C_{13}H_{27}NH_3)_2ZnCl_4$ is a tetrahedron and each tetrahedron is completely isolated from the neighbors.[14] The $CdCl_4$ unit of **1**, showing an area per divalent metal similar to $(C_{10}H_{21}NH_3)_2CdCl_4$ crystal, is also an octahedron. The area of **2** is located between those of the two reference crystals and it seems that the crystal structure of **2** is also an intermediate between the two: the $CdCl_4$ unit of **2** is a tetrahedron, though distorted, like $(C_{13}H_{27}NH_3)_2ZnCl_4$ crystal, but a network structure of Cd and Cl atoms exists as in $(C_{10}H_{21}NH_3)_2CdCl_4$ crystal. In other words, the bulkiness of the organic cation in **2** increases the distance between the neighboring $CdCl_4$ units, but is not sufficiently large to completely isolate each $CdCl_4$ unit.

CONCLUSIONS

In this paper we have demonstrated two examples of organic cation-based layered halide compounds.

(1) We have shown a new strategy to arrange functional molecules in two dimensional arrays using the layered structure of these compounds as a host for organic molecules. The resulting molecular arrangement is reminiscent of the one obtainable by the Langmuir-Blodgett (LB) technique, which has widely been used to construct molecular assemblies.[15] This strategy has advantage over the LB technique in that it can be readily applied to non-amphiphilic molecules, which points out the unnecessity of the chemical modification to make the molecules amphiphilic.

(2) We have shown further that the structure of the inorganic portion can be modified by changing the size of the organic molecule. It is realized due to a compromise between the preference of the characteristic inorganic-organic layered structure and the bulkiness of the organic cation. Modifying the structure of the inorganic portion will result in the control of the physical properties and the functions of the materials.

These strategies will be further utilized for the fabrication of inorganic-organic hybrid materials with novel structures and functions.

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