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Crystal Structures of Compounds Obtained from Lead(II) Iodide-Hexamethylenetetramine System, $[C_6H_{13}N_4]_2[Pb_3I_8(C_6H_{12}N_4)_2]$ and $[C_6H_{13}N_4][PbI_3]$

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Formamide solution of lead(II) iodide (PbI_2) with hexamethylenetetramine (hmta) gave $[C_6H_{13}N_4]_2[Pb_3I_8(C_6H_{12}N_4)_2]$, while reaction of PbI_2 with hmta through intervention of water produced $[C_6H_{13}N_4][PbI_3]$. From characterization of the crystals by X-ray diffraction, hmta appears to tend to be protonated cations, but one of hmta is coordinated to Pb atom in the former compound.

Lead(II) iodide (PbI_2) forms adducts with Lewis bases.$^{1)}$ Hexamethylenetetramine (hmta) is known as a weak monoacidic base in water solution and produces some adducts with $AgNO_3$$^{2)}$ and $HgX_2$$^{3)}$ (X = Cl, Br, or I). For the purpose of yielding adduct of PbI_2 with hmta, they were mixed in water, ethanol, or formamide. However, we could have characterized at the present time two ionic compounds containing monoprotonated $[\text{hmtaH}]^+$ ($[C_6H_{13}N_4]^+$) cation, one of which includes hmta molecules coordinating to Pb atom. Here we report the preparation and crystal structure of the title compounds.

Preparation of $[\text{hmtaH}]_2[Pb_3I_8(\text{hmta})_2]$$^{4)}$ (1) was as follows: 1 mmol of PbI_2 and 1.2 mmol of hmta were dissolved in 10 cm^3 of formamide. Undissolved precipitant was filtered off and the filtrate was allowed to stand at room temperature. After a month, crystals were obtained from the solution. Found: Pb 28.2; I 45.2%. Calcd for $[C_6H_{13}N_4]_2[Pb_3I_8(C_6H_{12}N_4)_2]$: Pb 28.3; I 46.2%.

For $[\text{hmtaH}][PbI_3]$$^{5)}$ (2); 2.5 mmol of PbI_2 fine powder was placed at the bottom of a branched glass tube and then a solution of 1.4 mmol of hmta in 25 cm^3 of 0.5 mol dm^{-3} of acetic acid was poured into the tube. The end of the branch containing the PbI_2 was kept at 333 K in a water bath and the other kept at ambient temperature(ca. 292-294 K). After a few days, crystals grew in the lower-temperature region. Found: Pb 28.5; I 52.3; C 7.69; H 1.66; N 9.90%. Calcd for $[C_6H_{13}N_4][PbI_3]$: Pb 28.4; I 52.2; C 7.68; H 1.80; N 9.88%.

Colorless transparent crystal of 1 with dimension ca. 0.17 x 0.26 x 0.10 mm^3 was used for X-ray measurement. Crystal data are: $[C_6H_{13}N_4]_2[Pb_3I_8(C_6H_{12}N_4)_2]$, $F.W.$ = 2199.0, monoclinic, $C2/c$, a = 24.652(4), b = 10.913(2), c = 18.020(3) Å, β = 95.24(2)°, U = 4877.7(14) $Å^3$, Z = 4, Dx = 3.026 g cm^{-3}, μ(Mo Kα) = 15.62 mm^{-1},

$F(000) = 3896$, $T = 298$ K. Intensities were collected on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and corrected for Lorentz and polarization effects and absorption.[6] 5739 reflections ($2 < 2\theta < 55°$) were measured, of which 3544 unique reflections with $|F_o| > 4\sigma(F_o)$ were considered as observed. The structure was solved by heavy-atom method[7] and refined by block-diagonal least-squares method.[8] The final residual values were $R = 0.081$ and $R_w = 0.088$.[9] Bond distances and angles around Pb atoms are given in Table 1(a).

For compound 2, colorless transparent crystal with dimension ca. 0.21 x 0.19 x 0.23 mm^3 was used. Crystal data are: $[C_6H_{13}N_4][PbI_3]$, $F.W. = 729.1$, monoclinic, $P2_1/m$ (1st setting), $a = 11.419(6)$, $b = 9.441(2)$, $c = 7.669(3)$ Å, $\gamma = 110.63(3)°$, $U = 776.7(6)$ $Å^3$, $Z = 2$, $D_x = 3.116$ g cm^{-3}, $\mu(Mo\ K\alpha) = 16.8$ mm^{-1}, $F(000) = 634$, $T = 300$ K. 2078 reflections ($2 < 2\theta < 55°$) were measured, of which 1117 unique reflections with $|F_o| > 3\sigma(F_o)$ were considered as observed. The structure was solved by ordinary heavy atom method and refined as above. The final residual values were $R = 0.055$ and $R_w = 0.058$.[9] Bond distances and angles around Pb atoms are summarized in Table 1(b).

Crystal structure of the compound 1 is depicted in Fig.1. There are two chemically different hmta molecules: One coordinates to a Pb atom through its one of N atoms [N(1)] and the other is mono-protonated cation. $N(7)...N(2^{iii})$ [symmetry operation: iii) x, -y, 1/2 + z] interatomic distance of 2.90(3) Å suggests a hydrogen bond formation between the atoms. In this connection, the average bond length around the N(7) atom of 1.52(4) Å is longer than that of the other N-C bonds of the cation of 1.47(4) Å. The fact is consistent with that bond lengths around the protonated N atoms are longer than the distances around the unprotonated N atoms by about 0.06-0.07 Å in [hmtaH]Br[10] and [hmtaH]Cl.[11] Such differences are also observed in the distances around the N(1) atom. In the

Table 1. Bond distances (Å) and angles (°) around the heavy atoms

(a) $[hmtaH]_2[Pb_3I_8(hmta)_2]$ (1)[a)]

Pb(1)-I(2)	3.266(2)	I(2)-Pb(1)-I(3)	84.23(5)	I(1)-Pb(2)-I(2)	89.81(6)
-I(3)	3.160(2)	-I(4)	85.31(6)	-I(3)	92.75(6)
-I(4)	3.296(2)	$-I(2^{ii})$	95.13(7)	-I(4)	168.07(6)
Pb(2)-I(1)	2.976(2)	$-I(3^{ii})$	177.83(5)	$-I(4^{i})$	100.43(7)
-I(2)	3.189(2)	$-I(4^{ii})$	96.79(6)	-N(1)	85.2(5)
-I(3)	3.266(2)	I(3)-Pb(1)-I(4)	85.23(6)	I(2)-Pb(2)-I(3)	83.78(6)
-I(4)	3.625(2)	$-I(3^{ii})$	96.49(7)	-I(4)	81.18(6)
$-I(4^{i})$	3.335(2)	$-I(4^{ii})$	92.70(6)	$-I(4^{i})$	169.71(7)
-N(1)	2.70(2)	$I(4)-Pb(1)-I(4^{ii})$	176.90(8)	-N(1)	91.5(5)
		I(3)-Pb(2)-I(4)	78.57(6)	$I(4)-Pb(2)-I(4^{i})$	88.53(6)
		$-I(4^{i})$	94.62(6)	-N(1)	102.7(5)
		-N(1)	174.9(5)	$N(1)-Pb(2)-I(4^{i})$	90.4(5)

a) Symmetry operations: i) -x, -y, -z; ii) -x, y, 1/2-z.

(b) $[hmtaH][PbI_3]$ (2)[a)]

Pb-I(1)	3.203(2)	I(1)-Pb-I(2)	88.81(5)	I(2)-Pb-I(3)	87.68(5)
-I(2)	3.212(2)	-I(3)	88.51(5)	$-I(3^{i})$	92.32(5)
-I(3)	3.275(2)	$-I(2^{i})$	91.19(5)	$Pb-I(1)-Pb^{ii}$	73.53(5)
		$-I(3^{i})$	91.44(5)	-I(2)-	73.30(5)
$Pb...Pb^{ii}$	3.835(1)			-I(3)-	71.67(6)

a) Symmetry operations: i) -x, -y, -z; ii) -x, -y, 1/2+z.

similar way, bond lengths around N(3) atom on the mirror plane in 2 [1.50(4) Å] is slightly longer than the other ones [1.44(4) Å], suggesting that the N(3) atom might be protonated.

Three chemically distinct I atoms exist in the crystal of the compound 1. One is a terminal [I(1)], the seconds [I(2) and I(3)] are bridging between Pb(1) and Pb(2), and the other one [I(4)] is three coordination, connecting $[Pb_3I_8(hmta)_2]_n^{2n-}$ moieties to form an infinite chain structure. Consequently, the Pb(2)-I(1) bond is the shortest Pb-I bond in the crystal, while the Pb(2)-I(4) bond is the longest.

The Pb(1) on the 2-fold symmetry is in a slightly elongated I_6 octahedron along the $Pb(2^{iii})$...Pb(1)...Pb(2). Coordination octahedron around the Pb(2) atom is a largely distorted one in which two of the bond angles, $I(1)-Pb(2)-I(4^{i})$ and I(4)-Pb(2)-N(1), are extremely expanded from 90°, while the bond angle of I(3)-Pb(2)-I(4) is quite smaller than 90°. The longest Pb-I bond of Pb(2)-I(4) is behind the shortest one of Pb(2)-I(1). These are suggesting that the inert $6s^2$ pair electrons of Pb(2) atom accumulate around the Pb(2)-I(4) bond, avoiding the electrostatic repulsion from I(1) atom. The inert pair of Pb(1) exhibit no such accumulation. The Pb(2)-N(1) bond distance of 2.70(2) Å is slightly longer than those observed in the other systems.12)

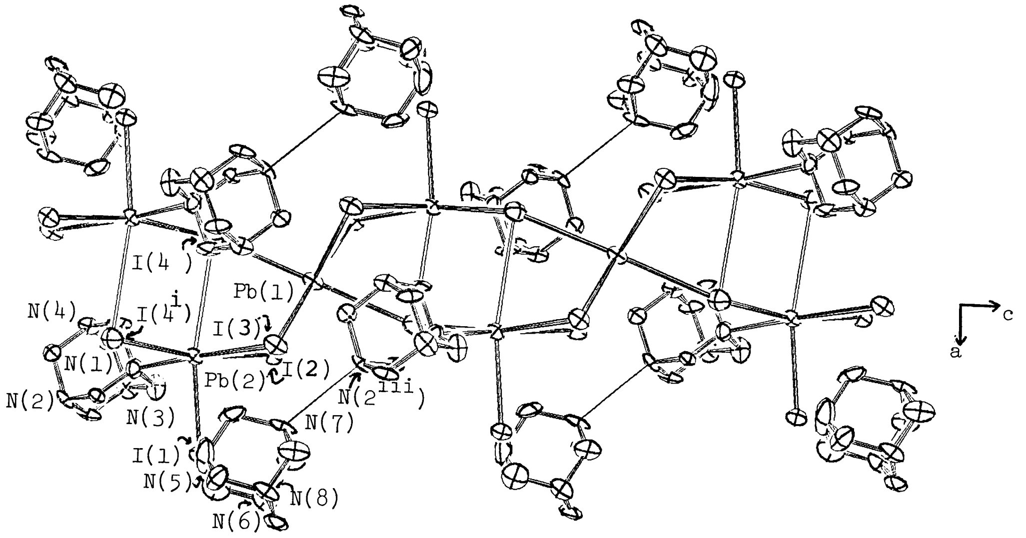

Fig. 1. A part of infinite chain structure of the compound 1 along - *b* with atom numbering.

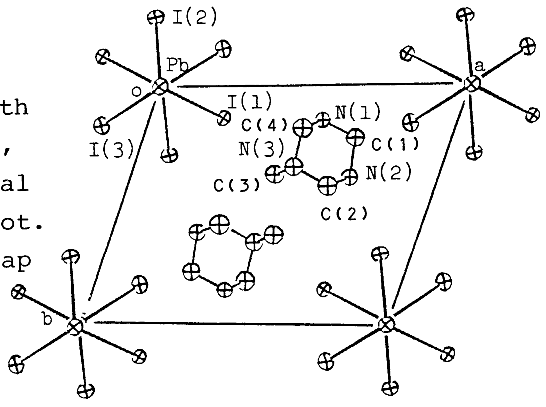

Fig. 2. Packing diagram of the compound 2 with atom numbering, viewed along *c*. N(1), N(2), C(1), and C(3) are on the mirror plane normal to c axis, while N(3), C(2), and C(4) are not. Therefore, one N atom and two C atoms overlap N(3), C(2), and C(4), respectively.

Structure of **2** is illustrated in Fig.2. The crystal is composed of infinite $[PbI_3]_n^{n-}$ anion and isolated mono-protonated hmtaH$^+$ cation. The $[PbI_3]_n^{n-}$ chain is formed by face-sharing PbI_6 octahedra. The chain extended along the c axis has no significant iteractions with organic cation which occupies channels between the chains.

Infinite $[PbI_3]_n^{n-}$ anion chain has been observed in $APbI_3.nH_2O$ (A = Li, Na, K, NH_3, Rb, or Cs; n = 0, 2, or 4).[13] However, the structure of the $[PbI_3]_n^{n-}$ anion is composed of edge-sharing PbI_6 octahedra. On the other hand, the A$^+$ cation is "coordinated" by surrounding I atoms and/or water molecules. The difference of the structure between the two types of $[PbI_3]_n^{n-}$ chains might be a result of the size of positively charged particle in the system.

The PbI_6 octahedron is elongated along the chain. However, the Pb...Pb distance within the chain of 3.855(2) Å is much shorter than that in PbI_2 of 4.556 Å ,[13] $KPbI_3.2H_2O$ of 4.557 Å, and $RbPbI_3$ of 4.773 Å.[14] In this connection, the I-Pb-I bond angles along the chain is contracted to 72.83(5)° in average. On the contrary, bond distances between Pb and I atoms are almost equivalent with that in PbI_2 of 3.215 Å.[15]

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5) Hexaminium catena-Tri-μ-iodoplumbite(II).
6) Absorption correction was performed by calculation using UNICS-III program system.
7) Using SHELXS-86 program system (reference manual, G.Sheldrick, 1986).
8) All the calculations were carried out with the UNICS-III program system on a FACOM M-360 computer at the Computer Center of Josai University.
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14) R.W.G.Wyckoff, "Crystal Structures," John Wiley & Sons, New York (1963), Vol. I, pp. 267-269 : Pb...Pb shortest distance is 4.239(1) Å in the compound **1**.
15) Estimated value from the data of Ref. 14.

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