Crystal structure of ammonium triiodidomercurate(II) monohydrate, $NH_4HgI_3 \cdot H_2O$

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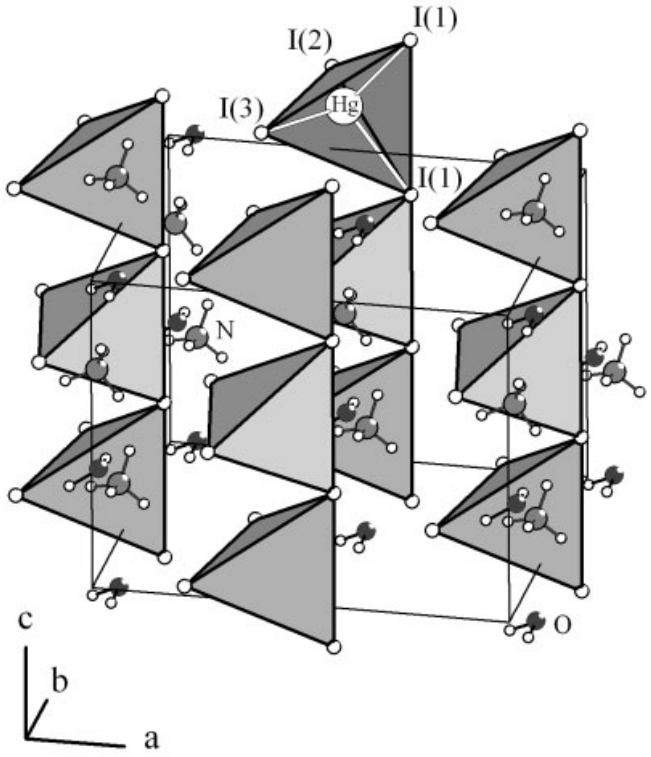

Abstract

H_6HgI_3NO, monoclinic, *C*1*c*1 (No. 9), $a = 11.1235(9)$ Å, $b = 9.8046(8)$ Å, $c = 8.7430(8)$ Å, $\beta = 90.185(7)°$, $V = 953.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.072$, $T = 299$ K.

Source of material

The crystals used for X-ray data collection were grown at room temperature by slow evaporation from water-ethanol hot solutions of NH_4I and HgI_2 with the molar ratio of 2:1. The needle crystals were transparent with increasingly yellow tints for higher HgI_2 content. They were washed in toluene and then dried over silica gel in a desiccator. They are decomposed slowly by light, but seem to be fairly stable if kept in the dark [1,2].

Discussion

The title compound belongs to the large ABX_3 family (A = alkali metal; B = metal; X = halogen). Most of the compounds of this family exhibit interesting structural and physical properties [3-6]. The crystal structure of $NH_4HgI_3 \cdot H_2O$ at room temperature has been studied by single crystal X-ray diffraction. In this structure, each mercury atom is tetrahedrally coordinated by four iodine atoms, the coordination polyhedron being somewhat distorted. The tetrahedra are linked through common corners to form chains running parallel to the *c* axis. The bond distances of Hg—I in HgI_4 tetrahedra range from 2.723(1) Å to 2.89(1) Å, with an average value of 2.808 Å and the bond angles I—Hg—I range from 99.07(3)° to 120.31(4)°. The ammonium ions are each surrounded by two water molecules at 2.892 Å and 2.902 Å and five iodine atoms I(1), two I(2) and two I(3) of the HgI_4 tetrahedra; the values of N—I bonds range from 3.740 Å to 3.937 Å. The crystalline building stability is ensured by hydrogen bonding contacts: N–H···I, O–H···I and N–H···O provide a linkage between ammonium groups, water molecules and $[HgI_4]^{2-}$ tetrahedra. A comparison between the arrangement of the two salts $NH_4HgI_3 \cdot H_2O$ and $KHgI_3 \cdot H_2O$ [1] shows that they are isostructural. However, we observe that the substitution of K^+ by NH_4^+ leads to an increase of the unit cell volume and a decrease of the symmetry from orthorhombic to monoclinic.

Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.03 × 0.04 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	257.76 cm^{-1}
Diffractometer, scan mode:	Xcalibur CCD, ω
$2\theta_{max}$:	59.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3379, 1744
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1413
$N(param)_{refined}$:	74
Programs:	SHELXL-97 [7], DIAMOND [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	4*a*	1.039(5)	0.043(2)	0.296(9)	0.071
H(4)	4*a*	1.096(3)	0.157(7)	0.210(4)	0.071
H(5)	4*a*	1.059(4)	0.176(7)	0.369(4)	0.071
H(6)	4*a*	0.968(2)	0.161(5)	0.249(5)	0.071
H(1)	4*a*	1.041(5)	–0.029(2)	0.44(3)	0.115
H(2)	4*a*	0.97(1)	–0.15(1)	0.40(2)	0.115

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	4*a*	0.9157(2)	0.53404(5)	0.1241(3)	0.0530(3)	0.0501(3)	0.0523(3)	–0.0004(3)	–0.0018(2)	–0.0002(3)
I(1)	4*a*	1.0806(2)	0.50344(9)	0.3723(3)	0.0375(4)	0.0502(4)	0.0284(3)	0.0002(3)	–0.0002(3)	0.0001(3)
I(2)	4*a*	0.8365(2)	0.79677(9)	0.1193(3)	0.0515(5)	0.0528(6)	0.0560(5)	0.0155(4)	–0.0008(4)	0.0007(5)
I(3)	4*a*	0.7558(2)	0.3237(1)	0.1184(3)	0.0502(5)	0.0652(7)	0.0587(5)	–0.0165(5)	0.0015(4)	–0.0020(5)
N	4*a*	1.0407(9)	0.134(1)	0.280(1)	0.10(1)	0.040(6)	0.043(6)	0.006(6)	0.009(6)	0.000(5)
O	4*a*	1.042(1)	–0.121(2)	0.450(1)	0.13(1)	0.10(1)	0.059(8)	–0.024(9)	–0.006(8)	0.007(7)

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