Crystal structure of ammonium tetrachloromercurate(II) monohydrate, $(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$

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Abstract

$\text{Cl}_4\text{H}_{10}\text{HgN}_2\text{O}$, orthorhombic, *Pbam* (No. 55), $a = 8.473(3)$ Å, $b = 11.929(3)$ Å, $c = 9.197(3)$ Å, $V = 929.6$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.048$, $wR_{\text{ref}}(F^2) = 0.101$, $T = 299$ K.

Source of material

$(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ is prepared by slow evaporation from a solution of water and acetone containing a mixture of NH_4Cl and HgCl_2 with the molar ratio of 2:1. Colourless needles were grown after vaporizing for approximately 12 days in air [1–3].

Discussion

The crystal structure of the title compound is characterized by parallel centro-symmetric tetrahedral $[\text{Hg}_2\text{Cl}_6]^{2-}$ dimers. The mercury atoms are located on a two-fold axis and the long dimension of the dimers is oriented parallel to $[001]$. Each Hg atom is surrounded by four Cl atoms forming a distorted tetrahedron with distances 2.360(2) Å and 2.822(2) Å. The two shortest distances

correspond to covalent bonds Hg—Cl1 with an angle of 168.1(1)°. The other distances correspond to the coordination bonds Hg—Cl2 with an angle of 86.69(8)°. Two tetrahedra share Cl2—Cl2 edges to form $[\text{Hg}_2\text{Cl}_6]^{2-}$ dimers. A fifth contact is Hg—Cl3 with a distance of 3.395 Å, greater than the sum of van der Waals radii. Therefore, the chlorine ions Cl3[−] are considered to be isolated in this structure. They are located in the (a,b) plane at $z = 1/2$. The structure is completed by a water molecule and two non-equivalent ammonium groups in between the dimers. The environment of the N atoms is as following. Environment of N(1): four Cl atoms belonging to the $[\text{Hg}_2\text{Cl}_6]^{2-}$ dimers and three Cl isolated atoms; the values of N—Cl bonds range from 3.181 Å to 3.393 Å. Environment of N(2): seven Cl atoms belonging to the $[\text{Hg}_2\text{Cl}_6]^{2-}$ dimers and two water molecules. The N—Cl distances range from 3.325 Å to 3.475 Å, while the N—O distances are 2.973 Å. The cohesion of the atomic arrangement is ensured by hydrogen bonding contacts: N—H...Cl and N—H...O provide a linkage between NH_4^+ cationic entities, water molecules and $[\text{Hg}_2\text{Cl}_6]^{2-}$ dimers. In comparison with $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ [4], we state that the substitution of K^+ by NH_4^+ leads to a change from a one-dimensional chain structure of edge-sharing octahedra to isolated bitetrahedral $[\text{Hg}_2\text{Cl}_6]^{2-}$ units sharing one edge and Cl[−] anions.

Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.04 × 0.08 × 0.24 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	176.38 cm ^{−1}
Diffraction, scan mode:	Oxford Diffraction Xcalibur CCD, ω/ϕ
$2\theta_{\text{max}}$:	62.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5226, 1476
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 872
$N(\text{param})_{\text{refined}}$:	61
Programs:	SHELXS-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	8i	0.08(1)	0.517(9)	0.200(9)	0.061
H(1A)	8i	0.041(1)	0.301(2)	0.07972(6)	0.040
H(1B)	4g	0.169(4)	0.245(3)	0	0.040
H(1C)	4g	0.159(5)	0.367(2)	0	0.040
H(2A)	8i	0.100(3)	0.383(1)	0.42028(6)	0.041
H(2B)	4h	−0.026(2)	0.325(4)	1/2	0.041
H(2C)	4h	0.135(5)	0.280(3)	1/2	0.041

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Hg	4 <i>e</i>	1/2	1/2	0.27684(7)	0.0467(3)	0.0293(3)	0.0922(5)	−0.0095(3)	0	0
Cl(1)	8 <i>i</i>	0.6164(2)	0.6786(2)	0.2502(2)	0.0353(9)	0.0291(9)	0.036(1)	−0.0047(8)	0.0030(9)	0.0016(8)
Cl(2)	4 <i>h</i>	0.2982(3)	0.5763(2)	1/2	0.021(1)	0.031(2)	0.044(2)	−0.001(1)	0	0
Cl(3)	4 <i>g</i>	0.2483(4)	0.5590(3)	0	0.042(2)	0.026(2)	0.067(2)	−0.007(1)	0	0
O(1)	4 <i>f</i>	0	1/2	0.2593(9)	0.048(5)	0.066(6)	0.039(5)	−0.004(6)	0	0
N(1)	4 <i>g</i>	0.102(1)	0.3037(7)	0	0.030(5)	0.025(5)	0.046(6)	0.001(4)	0	0
N(2)	4 <i>h</i>	0.077(1)	0.3429(7)	1/2	0.035(5)	0.034(6)	0.033(5)	0.001(4)	0	0

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