Crystal structure of tetrakis(4-bromoanilinium) hexachlorotin(IV) dichloride, $(BrC_6H_4NH_3)_4[SnCl_6]Cl_2$

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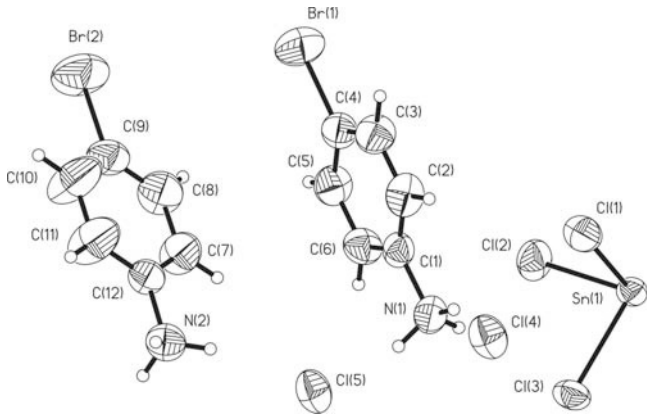

Abstract

$C_{24}H_{28}Br_4Cl_8N_4Sn$, monoclinic, *C*12/*c*1 (no. 15), $a = 28.1444(4)$ Å, $b = 8.0409(1)$ Å, $c = 20.8965(3)$ Å, $\beta = 126.825(1)°$, $V = 3785.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.037$, $wR_{ref}(F^2) = 0.114$, $T = 293$ K.

Source of material

Crystals of the title compound were prepared by slow-cooling method similar to [1], with all synthetic processes being operated in dry nitrogen atmosphere or in vacuum. First, the solution of 4-bromoanilinium chloride was prepared by the dropwise addition of excess of concentrated aqueous hydrogen chloride (37.0 %, 15 ml) to a solution of *p*-bromoaniline (1.73 g, 0.01 mol) in 10 ml of anhydrous ethanol under following nitrogen at 60 °C. Then the solution of $SnCl_4 \cdot 5H_2O$ (1.76 g, 5.0 mmol) in concentrated aqueous hydrogen chloride (37.0 %, 10.0 ml) was added to the 4-bromoanilinium chloride solution gradually with stirring. The resulting solution was allowed to stand at 60 °C for 5 hours and then slowly cooled to room temperature without stirring. The precipitate was filtered off. After drying in vacuum, colorless prism-like crystals (1.58 g, 28.8 %) suitable for X-ray single crystal structure determination were obtained.

Discussion

In order to study the influent of cations on crystal structures of organic ammonium hexachlorostannate(IV) hybrids, several crystals of this type were prepared and their structures were determined [2-5]. The general structure displays an alternation of the hydrocarbon layers, made up of ammonium cations, and inorganic layers, made up of discrete $SnCl_6$ octahedra. The interface between inorganic and organic layer contains Cl^- and $-NH_3^+$ ions, in which charge-assisted hydrogen bonds connect two kinds of layers. Similiar to tetrakis(anilinium) hexacholotin(IV) dichloride [4], the title compound, is also a double salt of 4-bromoanilinium chloride and bis(4-bromoanilinium) hexachlorotin(IV).

The asymmetric unit of the title crystal structure consists of two 4-bromoanilinium cations on general positions, two choloride anions on 2-fold rotation axis, one Sn atom on a center of inversion at (½,0,½) and three Cl atoms in general positions. The Sn—Cl bond lengths are 2.400(1), 2.442(1), and 2.446(1) Å, the *cis* Cl–Sn–Cl bond angles range from 89.04(4)° to 90.96(4)°, indicating small distortions from ideal octahedral geometry. A similar configuration of the $[SnCl_6]^{2-}$ anion was also found for $[HPPh_3]_2[SnCl_6]$ [6] and $[WCl(CO)(t\text{BuC–CH})(NCMe)(PPh_3)_2]_2[SnCl_6] \cdot 4CH_3CN$ [7]. The cations pack in an interdigitated fashion within the organic layers, whose thickness is about two 4-bromoanilinium lengths along the long molecular axis. The C—C bond lengths in the phenyl ring range from 1.328(8) Å to 1.389(9) Å with the mean value of 1.365(8) Å, while mean C—N and C—Br bond lengths are 1.466(5) Å and 1.898(5) Å, respectively. C–C–C angles in phenyl ring are between 118.5(4)° and 121.8(4)°. Bond angles C–C–N and C–C–Br are similar to those of C–C–C. The average values of C–C–N and C–C–Br bond angles are 119.5(4)° and 119.4(4)°. The hydrogen-bonding interactions linking the organic layer and the inorganic layer involve the two hydrogen atoms on the ammonium group. There are one simple and one bifurcated hydrogen bonds between a cation and three different Cl atoms.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.14 × 0.14 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	54.85 cm^{-1}
Diffractometer, scan mode:	Bruker APEX2 CCD, φ/ω
$2\theta_{max}$:	55.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17394, 4352
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2944
$N(param)_{refined}$:	191
Programs:	SHELXL-97, SHELXTL [8], SIR97 [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	8*f*	0.3698	0.2524	0.2129	0.071
H(3)	8*f*	0.2715	0.3162	0.1550	0.074
H(5)	8*f*	0.3243	0.6781	0.3153	0.070
H(6)	8*f*	0.4225	0.6136	0.3737	0.068

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7)	8*f*	0.3801	0.8203	0.1981	0.085
H(8)	8*f*	0.2872	0.8711	0.1668	0.094
H(10)	8*f*	0.2316	1.0498	–0.0427	0.136
H(11)	8*f*	0.3246	1.0045	–0.0122	0.123
H(1A)	8*f*	0.4683	0.2967	0.3113	0.086
H(1B)	8*f*	0.4847	0.3604	0.3872	0.086
H(1C)	8*f*	0.4846	0.4706	0.3319	0.086
H(2A)	8*f*	0.4424	0.9768	0.1425	0.091
H(2B)	8*f*	0.4178	0.8693	0.0734	0.091
H(2C)	8*f*	0.4377	0.7988	0.1498	0.091

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}
Br(1)	8*f*	0.20917(2)	0.55606(9)	0.18342(4)	0.0559(3)	0.1028(5)	0.0944(4)	0.0054(3)	0.0450(3)	–0.0012(3)
Br(2)	8*f*	0.17555(3)	1.0039(1)	0.03345(5)	0.0679(4)	0.1340(7)	0.1367(7)	0.0079(4)	0.0714(4)	–0.0058(5)
C(1)	8*f*	0.4043(2)	0.4265(6)	0.2982(2)	0.049(2)	0.047(2)	0.048(2)	0.004(2)	0.032(2)	0.009(2)
C(2)	8*f*	0.3603(2)	0.3380(6)	0.2334(3)	0.074(3)	0.054(3)	0.051(2)	0.006(2)	0.039(2)	–0.007(2)
C(3)	8*f*	0.3020(2)	0.3762(6)	0.1987(3)	0.060(3)	0.060(3)	0.050(2)	–0.003(2)	0.026(2)	–0.010(2)
C(4)	8*f*	0.2895(2)	0.5049(6)	0.2299(3)	0.053(2)	0.054(3)	0.060(2)	0.003(2)	0.039(2)	0.006(2)
C(5)	8*f*	0.3336(2)	0.5925(6)	0.2947(3)	0.065(3)	0.052(3)	0.063(3)	0.003(2)	0.041(2)	–0.007(2)
C(6)	8*f*	0.3920(2)	0.5542(6)	0.3297(3)	0.057(3)	0.052(3)	0.055(2)	–0.009(2)	0.031(2)	–0.011(2)
C(7)	8*f*	0.3504(2)	0.8682(7)	0.1493(3)	0.067(3)	0.092(4)	0.065(3)	0.011(3)	0.046(3)	0.020(3)
C(8)	8*f*	0.2948(2)	0.8972(8)	0.1303(4)	0.077(4)	0.096(5)	0.095(4)	0.009(3)	0.069(3)	0.017(4)
C(9)	8*f*	0.2516(2)	0.9634(7)	0.0587(3)	0.054(3)	0.071(4)	0.078(3)	–0.003(2)	0.048(3)	–0.006(3)
C(10)	8*f*	0.2617(3)	1.004(1)	0.0063(4)	0.066(4)	0.193(9)	0.084(4)	0.039(4)	0.047(3)	0.059(5)
C(11)	8*f*	0.3174(3)	0.9769(9)	0.0245(4)	0.073(4)	0.173(7)	0.078(4)	0.030(4)	0.055(3)	0.054(4)
C(12)	8*f*	0.3611(2)	0.9100(6)	0.0965(2)	0.052(2)	0.055(3)	0.053(2)	–0.001(2)	0.037(2)	0.000(2)
Cl(1)	8*f*	0.43893(5)	–0.0159(2)	0.35678(6)	0.0578(6)	0.0657(8)	0.0399(5)	–0.0128(5)	0.0250(5)	0.0018(5)
Cl(2)	8*f*	0.44827(5)	0.2528(2)	0.49188(7)	0.0650(7)	0.0546(7)	0.0793(7)	0.0161(6)	0.0524(6)	0.0122(6)
Cl(3)	8*f*	0.57032(4)	0.1724(1)	0.49751(6)	0.0426(5)	0.0582(7)	0.0554(5)	–0.0109(5)	0.0328(5)	0.0006(5)
Cl(4)	4*e*	½	0.1452(2)	¼	0.084(1)	0.055(1)	0.080(1)	0	0.062(1)	0
Cl(5)	4*e*	½	0.6233(2)	¼	0.082(1)	0.0445(9)	0.078(1)	0	0.057(1)	0
N(1)	8*f*	0.4666(2)	0.3844(5)	0.3359(2)	0.055(2)	0.054(2)	0.065(2)	0.009(2)	0.036(2)	0.014(2)
N(2)	8*f*	0.4206(2)	0.8864(5)	0.1176(2)	0.059(2)	0.066(3)	0.070(2)	0.000(2)	0.045(2)	0.003(2)
Sn(1)	4*b*	½	0	½	0.0353(2)	0.0418(2)	0.0392(2)	–0.0016(2)	0.0252(2)	0.0023(2)

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