Crystal structures of α- and β-antimony dimercury tetrachloroaluminate, $SbHg_2AlCl_4$

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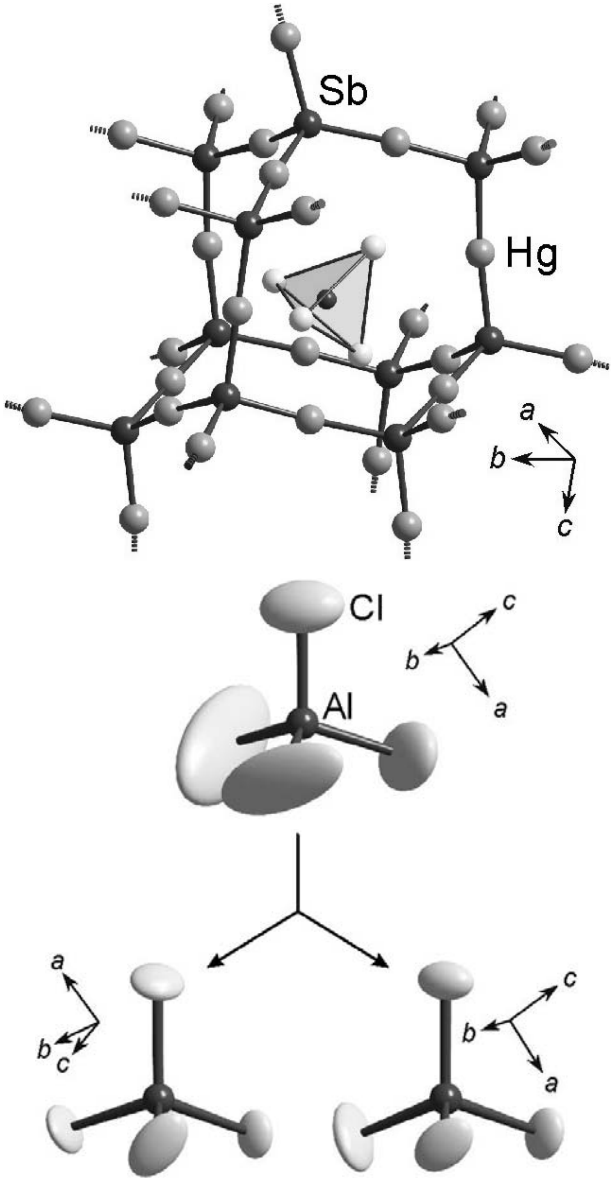

Abstract

$AlCl_4SbHg_2$, orthorhombic, *Pbcn* (no. 60), a = 11.9771(5) Å, b = 8.7826(4) Å, c = 17.5237(7) Å, V = 1843.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.098, T = 293 K.

$AlCl_4SbHg_2$, orthorhombic, $P2_1cn$ (no. 33), a = 11.9529(7) Å, b = 8.7536(3) Å, c = 17.4532(7) Å, V = 1826.1 Å^3, Z = 8, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.101, T = 173 K.

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Source of material

α-$[SbHg_2]AlCl_4$ was obtained by annealing a mixture of $HgCl_2$ (> 99.5 %, Acros), Sb (Shot, 1-3 mm, 99.999%, HERAEUS) and Al (pieces: 2.5 – 3.9 mm, 99.999 %, Chempur) in the ratio 2:1:1 at 493 K for seven days. The dark red crystalline product is highly air sensitive and does not show any contamination phases in standard X-ray powder diagrams. Single crystals for X-ray studies were isolated under dry argon and transferred into sealed capillaries.

Discussion

α-$[SbHg_2]AlCl_4$ the high-temperature modification of this compound crystallizes isotypic to α-$[SbHg_2]GaCl_4$ [1]. The crystal structure is of the Millons base type [2,3] and thus characterized by a cationic $[SbHg_2]^+$ network, topologically related to cristobalite, with tetrahedral anionic $[AlCl_4]^-$ groups located in the cavities (figure, top). Interatomic distances d(Sb—Hg) and corresponding angles of the cationic network are similar to those ones for $[SbHg_2]GaCl_4$, whereas the distances d(Al—Cl) are by about 0.03 Å to 0.05 Å shorter. Similar to the $GaCl_4$ groups in α-$[SbHg_2]GaCl_4$ a pronounced librational disorder is observed for the $AlCl_4$ groups (figure, bottom; 95 % probability for the thermal ellipsoids of Cl). This disorder is drastically reduced upon the formation of the low-temperature modification β-$[SbHg_2]AlCl_4$ (higher-order phase transition investigated in detail for $[SbHg_2]GaCl_4$ [1]). The cationic $[SbHg_2]^+$ network of the low-temperature modification, β-$[SbHg_2]AlCl_4$, is very similar to that one of α-$[SbHg_2]AlCl_4$. In accordance with β-$[SbHg_2]GaCl_4$ there are, however, significant differences in the spatial orientation of the $AlCl_4$ groups. Whereas in the α-modification only one crystallographic type of tetrahedra is present, the β-modification shows two of them, represented by two sets of corresponding crystallographic parameters. The non-standard setting chosen for β-$[SbHg_2]AlCl_4$ (space group $P2_1cn$ instead of $Pna2_1$) enables a better comparability between the structural parameters of the two modifications.

1. α-Antimony dimercury tetrachloroaluminate, $SbHg_2AlCl_4$

Table 1. Data collection and handling.

Crystal:	transparent red cuboctahedron, size 0.1 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	373.07 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ
$2\theta_{max}$:	58.22°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18576, 2467
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2009
$N(param)_{refined}$:	76
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

Table 2. 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(1)	8*d*	0.26608(4)	0.17273(5)	0.12370(3)	0.0320(2)	0.0231(2)	0.0307(2)	–0.0045(2)	–0.0011(2)	–0.0018(2)
Hg(2)	4*c*	½	0.45360(8)	¼	0.0386(4)	0.0298(3)	0.0255(4)	0	–0.0122(3)	0
Hg(3)	4*a*	0	0	0	0.0287(3)	0.0333(3)	0.0266(4)	–0.0010(2)	–0.0014(3)	0.0009(3)
Sb(1)	8*d*	0.37587(6)	0.43800(8)	0.12381(4)	0.0261(3)	0.0186(3)	0.0199(3)	–0.0009(2)	–0.0037(3)	–0.0004(3)
Al(1)	8*d*	0.1095(3)	0.4180(4)	0.3719(2)	0.028(2)	0.034(2)	0.026(2)	–0.002(1)	–0.006(2)	0.001(2)
Cl(1)	8*d*	0.0362(3)	0.3478(5)	0.0677(3)	0.050(2)	0.067(3)	0.062(3)	0.026(2)	0.015(2)	0.025(2)
Cl(2)	8*d*	0.2485(4)	0.4138(8)	0.4460(3)	0.046(2)	0.140(5)	0.038(2)	–0.007(3)	–0.022(2)	–0.007(3)
Cl(3)	8*d*	0.1408(5)	0.262(1)	0.2831(4)	0.063(3)	0.226(9)	0.090(4)	–0.032(4)	0.017(3)	–0.119(6)
Cl(4)	8*d*	0.4174(7)	0.1376(9)	0.3331(8)	0.109(6)	0.092(5)	0.33(2)	–0.004(4)	0.034(8)	0.137(8)

2. β-Antimony dimercury tetrachloroaluminate, $SbHg_2AlCl_4$

Table 3. Data collection and handling.

Crystal:	transparent red cuboctahedron, size 0.1 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	376.58 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ
$2\theta_{max}$:	58.28°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14829, 4545
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4282
$N(param)_{refined}$:	147
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6]

Table 4. 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(1A)	4*a*	0.33184(5)	0.08286(7)	0.37536(3)	0.0199(4)	0.0081(3)	0.0165(3)	–0.0021(2)	–0.0001(2)	–0.0005(2)
Hg(1B)	4*a*	0.86598(5)	0.08182(7)	0.12211(3)	0.0192(4)	0.0087(3)	0.0163(3)	0.0041(2)	–0.0010(2)	0.0006(2)
Hg(2)	4*a*	0.59617(7)	0.29956(6)	0.24283(3)	0.0220(2)	0.0130(2)	0.0119(3)	–0.0001(3)	0.0052(2)	0.0004(2)
Hg(3)	4*a*	0.60184(7)	0.24365(7)	0.49258(3)	0.0175(2)	0.0138(2)	0.0115(2)	0.0005(2)	–0.0016(3)	0.0003(2)
Sb(1A)	4*a*	0.7226(1)	0.3168(1)	0.11771(5)	0.0160(5)	0.0050(4)	0.0091(4)	0.0003(3)	0.0006(3)	–0.0001(3)
Sb(1B)	4*a*	0.4740(1)	0.3159(1)	0.37069(5)	0.0145(5)	0.0063(5)	0.0081(4)	0.0012(3)	0.0012(3)	–0.0002(3)
Al(1A)	4*a*	0.9876(5)	0.3327(6)	0.3775(2)	0.017(3)	0.014(2)	0.006(2)	–0.005(2)	0.003(1)	0.004(2)
Al(1B)	4*a*	0.2089(5)	0.3374(6)	0.1341(2)	0.018(3)	0.009(2)	0.006(2)	–0.002(2)	0.004(2)	–0.003(2)
Cl(1A)	4*a*	0.1326(4)	0.4215(5)	0.4358(3)	0.030(2)	0.017(2)	0.040(3)	–0.013(1)	–0.006(2)	0.003(2)
Cl(1B)	4*a*	0.0584(4)	0.3820(6)	0.0715(3)	0.026(2)	0.031(2)	0.023(2)	0.010(2)	–0.006(2)	–0.010(2)
Cl(2A)	4*a*	0.8421(3)	0.3775(5)	0.4429(2)	0.028(2)	0.027(2)	0.016(2)	0.003(2)	0.010(1)	0.003(2)
Cl(2B)	4*a*	0.3429(4)	0.3069(5)	0.0545(2)	0.029(2)	0.035(2)	0.021(2)	–0.000(2)	0.011(2)	–0.009(2)
Cl(3A)	4*a*	0.9690(4)	0.4439(8)	0.2701(3)	0.035(2)	0.063(4)	0.025(2)	0.015(2)	0.006(2)	0.027(2)
Cl(3B)	4*a*	0.7475(4)	0.0276(6)	0.2942(3)	0.029(2)	0.033(3)	0.036(2)	–0.004(2)	–0.003(2)	0.026(2)
Cl(4A)	4*a*	0.0141(4)	0.0957(5)	0.3645(3)	0.038(2)	0.009(2)	0.047(3)	0.004(2)	–0.005(2)	–0.011(2)
Cl(4B)	4*a*	0.1924(5)	0.1382(6)	0.2017(4)	0.062(3)	0.027(2)	0.046(3)	0.009(2)	0.016(2)	0.026(2)

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