Crystal structure of 2-aminoethylammonium *tris*-(1,2-ethanediamine) zinc(II)tetraselenoantimonate(V), $(C_2H_9N_2)[Zn(C_2H_8N_2)_3][SbSe_4]$, $C_8H_{33}N_8SbSe_4Zn$

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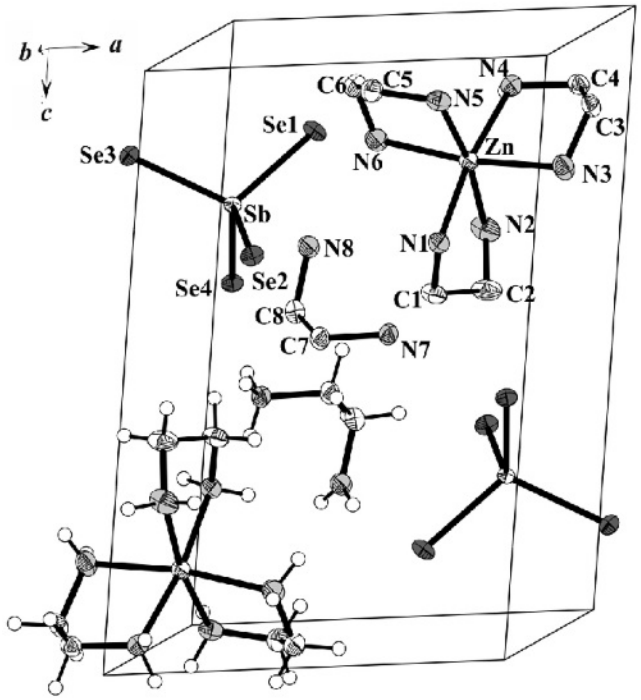

Abstract

$C_8H_{33}N_8SbSe_4Zn$, triclinic, $P\bar{1}$ (no. 2), a = 8.8100(2) Å, b = 9.6324(2) Å, c = 14.2606(4) Å, α = 104.963(2)°, β = 92.574(2)°, γ = 109.713(3)°, V = 1089.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.0274, $wR_{ref}(F^2)$ = 0.0711, T = 150 K.

Table 1. Data collection and handling.

Crystal:	yellow needles, size 0.3×0.3×0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	90.34 cm^{-1}
Diffractometer, scan mode:	Oxford-Diffraction Xcalibur3, φ and ω
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18868, 6339
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5069
$N(param)_{refined}$:	197
Programs:	SHELX [13]

Source of material

Single crystals of $(C_2H_9N_2)[Zn(C_2H_8N_2)_3][SbSe_4]$ were prepared solvothermally from a mixture of 64 mg (Alfa Aesar, 99.9%) Zn, 61 mg (Alfa Aesar, 99.5%) Sb and 240 mg (Alfa Aesar, 99.999%) Se. The filling of all starting materials were carried out under inert gas conditions (glove box, Ar; $H_2O/O_2 \leq 0.1$ ppm). Five millilitres of ethylenediamine ($C_2H_8N_2$, dried over Na/CaH_2, freshly distilled and degassed) were added to the reaction mixture which was then loaded into a Teflon-lined autoclave with an inner volume of 20 mL (filling degree approx. 30%). The sealed autoclave was heated at 443 K for 7 days before cooling down to room temperature. Air sensitive yellow needles of the target compound were isolated from the crystalline product, which also contained the unreacted selenium. The chemical composition of (Zn:Sb:Se = 1:1:4) was confirmed by EDXS measurements.

Experimental details

The positions of all protons attached to C and N atoms were located from the difference Fourier map. The protons of monoprotonated $[C_2H_9N_2]^+$ and $Zn(C_2H_8N_2)_3]^{2+}$ were refined using a riding model with d(C–H) = 0.95 Å (CH_2); d(N–H) = 0.89 Å (NH_3^+), 0.90 Å, and 0.86 Å (NH_2) with U_{iso}(H) = 1.2 U_{eq} (C or N).

Discussion

The solvothermal reaction in amine has proven to be a versatile route for the syntheses of chalcogenometalates [1-4]. In recent years, an increasing interest in chalcogenide framework structures has been observed due to their promising combination of zeotype structures with novel properties [5]. Although, a large number of thioantiomonates (Sb_xS_y) exhibiting a variety of polymeric complex anions have been well explored, the chemistry of higher chalcogenoantimonates (Sb_xSe_y or Sb_xTe_y) is less developed [4]. Our recent investigation on the selenoantimonate system using transition metals in ethylenediamine led to a new $(C_2H_9N_2)[Zn(C_2H_8N_2)_3][SbSe_4]$, which is the first selenoantimonate containing $[Zn(C_2H_8N_2)_3]^{2+}$ cations. The crystal structure of the title compound is an isotype of $[C_2H_9N_2][M(C_2H_8N_2)_3][SbSe_4]$ (M = Mn, Fe, Co, Ni) [6-9] and consists of a packing of tetrahedral $[SbSe_4]^{3-}$ anions and $[Zn(C_2H_8N_2)_3]^{2+}$ cations. The monoprotanated $[C_2H_9N_2]^+$ solvent molecules complete the overall crystal structure and charge balance the $[SbSe_4]^{3-}$ anions. The transition metal Zn^{2+} cations are in distorted octahedral coordination geometry coordinated by three bidentate ligands of ethylenediamine. The Zn–N bond legths and the three axial N–Zn–N angles range from 2.160(2) Å to 2.204(3) Å and 171.01(11)° to 171.57(10)°, respectively. The bond legths and angles of $[Zn(C_2H_8N_2)_3]^{2+}$ are in accordance with the trend observed for other compounds containing $[Zn(C_2H_8N_2)_3]^{2+}$ cations [10]. The $[SbSe_4]^{3-}$ anion shows tetrahedral arrangement and the Sb–Se distances vary from 2.4706(4) Å to 2.4795(4) Å which agree well with those of the related Sb^V compounds such as $[Ba(C_2H_8N_2)_3]_2[Ba(C_2H_8N_2)_4][SbSe_4]_2$ (2.438(9) Å -

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2.497(10) Å) and K_3SbSe_4 (2.473(4) Å and 2.475(2) Å) [11]. Sb^{III}–Se bond lengths are generally longer such as in $Ba(C_2H_8N_2)_4[SbSe_2]_2$ (2.457(3) Å - 2.624(3) Å) [12]. All terminal Se atoms of the $[SbSe_4]^{3-}$ unit are involved in intermolecular N–H···Se hydrogen bonding with adjacent $[Zn(C_2H_8N_2)_3]^{2+}$ and $[C_2H_9N_2]^+$. The N–H···Se distances and angles vary from 3.289(1) Å to 3.737(1) Å and 149.33(1)° to 169.98(1)°, respectivley, which are consistent with the values reported in the literature [6-9].

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7A)	2*i*	0.2453	0.7183	0.5475	0.028
H(7B)	2*i*	0.2559	0.6737	0.6368	0.028
H(7C)	2*i*	0.2132	0.5579	0.5417	0.028
H(8A)	2*i*	0.4853	0.8631	0.7371	0.029
H(8B)	2*i*	0.5972	1.0156	0.7320	0.029
H(7D)	2*i*	0.4627	0.6355	0.5036	0.027
H(7E)	2*i*	0.4850	0.6300	0.6122	0.027
H(8C)	2*i*	0.6645	0.8648	0.5943	0.029
H(8D)	2*i*	0.5141	0.9030	0.5621	0.029
H(1A)	2*i*	0.8501	1.0813	0.3151	0.025
H(1B)	2*i*	0.6732	1.0150	0.2888	0.025
H(2A)	2*i*	0.7270	0.6469	0.3074	0.040
H(2B)	2*i*	0.9002	0.6863	0.2983	0.040
H(5A)	2*i*	0.7666	1.0232	0.0967	0.028
H(5B)	2*i*	0.7586	0.8880	0.0181	0.028
H(6A)	2*i*	0.5022	0.5898	0.1472	0.031
H(6B)	2*i*	0.4746	0.7279	0.2016	0.031
H(1C)	2*i*	0.6362	0.8764	0.3909	0.033
H(1D)	2*i*	0.7767	1.0307	0.4503	0.033
H(2C)	2*i*	0.9725	0.9230	0.4022	0.039
H(2D)	2*i*	0.8488	0.8167	0.4533	0.039
H(5C)	2*i*	0.5077	0.8776	–0.0063	0.033
H(5D)	2*i*	0.5067	0.9377	0.1070	0.033
H(6C)	2*i*	0.3477	0.6790	0.0541	0.035
H(6D)	2*i*	0.4903	0.6389	0.0061	0.035
H(3A)	2*i*	1.0712	1.0371	0.2004	0.034
H(3B)	2*i*	1.1035	0.9238	0.2415	0.034
H(4A)	2*i*	0.8064	0.5513	0.0907	0.025
H(4B)	2*i*	0.7897	0.6256	0.0158	0.025
H(3C)	2*i*	1.2081	0.8976	0.0994	0.027
H(3D)	2*i*	1.0479	0.8952	0.0446	0.027
H(4C)	2*i*	1.0407	0.6437	0.0102	0.027
H(4D)	2*i*	1.0693	0.6599	0.1226	0.027

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}
Sb(1)	2*i*	0.11915(2)	0.42612(2)	0.27180(1)	0.0152(1)	0.0114(1)	0.0122(1)	0.00468(8)	0.00269(7)	0.00429(7)
Se(1)	2*i*	0.29026(4)	0.32188(4)	0.16285(2)	0.0274(2)	0.0230(2)	0.0193(2)	0.0128(2)	0.0108(1)	0.0065(1)
Se(2)	2*i*	0.23735(4)	0.71110(4)	0.33562(2)	0.0241(2)	0.0121(2)	0.0205(2)	0.0033(1)	0.0004(1)	0.0043(1)
Se(4)	2*i*	0.10858(4)	0.31539(4)	0.41060(2)	0.0231(2)	0.0166(2)	0.0153(2)	0.0067(1)	0.0022(1)	0.0077(1)
Se(3)	2*i*	–0.16576(4)	0.33789(4)	0.19091(2)	0.0173(2)	0.0168(2)	0.0194(2)	0.0040(1)	–0.0009(1)	0.0057(1)
Zn(1)	2*i*	0.78488(5)	0.81613(4)	0.18410(3)	0.0193(2)	0.0192(2)	0.0178(2)	0.0077(2)	0.0037(1)	0.0053(2)
N(7)	2*i*	0.2731(3)	0.6551(3)	0.5745(2)	0.018(1)	0.023(2)	0.023(1)	0.008(1)	0.001(1)	–0.000(1)
N(8)	2*i*	0.5438(4)	0.9192(3)	0.7043(2)	0.021(2)	0.021(2)	0.025(2)	0.004(1)	0.004(1)	0.003(1)
C(7)	2*i*	0.4487(4)	0.6809(4)	0.5702(3)	0.021(2)	0.023(2)	0.027(2)	0.013(1)	0.002(1)	0.003(1)
C(8)	2*i*	0.5523(3)	0.8513(3)	0.6027(2)	0.021(2)	0.026(2)	0.027(2)	0.009(1)	0.005(1)	0.008(2)
N(1)	2*i*	0.7620(3)	0.9944(3)	0.3041(2)	0.022(1)	0.019(2)	0.021(1)	0.008(1)	0.004(1)	0.006(1)
N(2)	2*i*	0.8189(5)	0.7234(4)	0.3054(2)	0.050(2)	0.035(2)	0.031(2)	0.029(2)	0.013(2)	0.015(2)
N(5)	2*i*	0.7214(4)	0.9197(3)	0.0744(2)	0.031(2)	0.017(1)	0.021(1)	0.008(1)	0.006(1)	0.005(1)
N(6)	2*i*	0.5240(4)	0.6900(3)	0.1528(2)	0.024(2)	0.021(2)	0.027(2)	0.005(1)	0.006(1)	0.003(1)
C(1)	2*i*	0.7477(5)	0.9425(4)	0.3924(3)	0.037(2)	0.031(2)	0.018(2)	0.017(2)	0.008(2)	0.008(2)
C(2)	2*i*	0.8603(5)	0.8550(5)	0.3964(3)	0.051(3)	0.039(2)	0.019(2)	0.028(2)	0.005(2)	0.013(2)
C(5)	2*i*	0.5420(5)	0.8702(5)	0.0573(3)	0.030(2)	0.035(2)	0.026(2)	0.021(2)	0.003(2)	0.009(2)
C(6)	2*i*	0.4651(4)	0.7076(4)	0.0607(3)	0.021(2)	0.031(2)	0.028(2)	0.006(2)	0.001(1)	0.001(2)
N(3)	2*i*	1.0478(4)	0.9358(4)	0.1916(2)	0.023(2)	0.023(2)	0.034(2)	0.007(1)	0.007(1)	0.002(1)
N(4)	2*i*	0.8414(3)	0.6409(3)	0.0756(2)	0.022(1)	0.020(1)	0.021(1)	0.007(1)	0.002(1)	0.007(1)
C(3)	2*i*	1.0906(4)	0.8639(4)	0.0962(3)	0.018(2)	0.023(2)	0.026(2)	0.006(1)	0.009(1)	0.008(1)
C(4)	2*i*	1.0190(4)	0.6916(4)	0.0742(3)	0.025(2)	0.025(2)	0.021(2)	0.014(2)	0.005(1)	0.007(1)

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