$V = 1235,4$ (9) Å^3
$Z = 4$
$D_x = 1,81$ Mg m^{-3}
$D_m = 1,80$ (2) Mg m^{-3}
D_m measurée par flottaison

0,35 × 0,28 × 0,22 mm
Jaune

Collection des données

Diffractomètre Syntex $P2_1$
Balayage θ–2θ
Pas de correction d'absorption
3027 réflexions mesurées
3027 réflexions indépendantes
1046 réflexions observées $[I \geq 4\sigma(I)]$

$\theta_{\max} = 27,5°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 17$
3 réflexions de référence fréquence: 120 min variation d'intensité: <0,1%

Affinement

Affinement basé sur les F
$R = 0,049$
$wR = 0,046$
$S = 1,78$
1046 réflexions
128 paramètres
Les paramètres des atomes d'hydrogène n'ont pas été affinés
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0,0028$
$\Delta\rho_{\max} = 0,54$ e Å^{-3}
$\Delta\rho_{\min} = -0,54$ e Å^{-3}
Correction d'extinction: aucune
Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974, Tome IV)

Tableau 1. *Coordonnées atomiques et facteurs d'agitation thermique isotrope équivalents* (Å^2)

$$U_{\acute{e}q} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\acute{e}q}$
Cu	0,2530 (1)	0,0589 (2)	0,2856 (1)	0,0315 (9)
Cl(1)	0,3813 (2)	−0,0812 (4)	0,2183 (2)	0,041 (2)
Cl(2)	0,1343 (2)	−0,0219 (4)	0,3747 (2)	0,041 (2)
Cl(3)	0,4056 (3)	0,1845 (4)	0,4036 (2)	0,034 (2)
Cl(4)	0,1014 (3)	0,1417 (4)	0,1526 (2)	0,040 (2)
N(1)	0,1490 (7)	0,127 (1)	0,5980 (6)	0,032 (6)
N(2)	0,3397 (7)	0,024 (1)	0,5890 (6)	0,041 (7)
N(3)	0,3152 (7)	0,050 (1)	0,7369 (6)	0,031 (6)
N(4)	0,1388 (7)	−0,049 (1)	0,7715 (6)	0,032 (6)
N(5)	0,3000 (7)	0,073 (1)	0,8882 (6)	0,029 (6)
C(1)	0,265 (1)	0,070 (2)	0,6390 (8)	0,034 (8)
C(2)	0,248 (1)	0,027 (1)	0,8018 (8)	0,027 (8)
C(51)	0,238 (1)	0,035 (2)	0,9601 (7)	0,045 (8)
C(52)	0,406 (1)	0,187 (2)	0,9162 (8)	0,043 (8)

Tableau 2. *Paramètres géométriques* (Å, °)

Cu—Cl(1)	2,266 (3)	C(1)—N(3)	1,39 (1)
Cu—Cl(2)	2,226 (3)	C(2)—N(3)	1,40 (1)
Cu—Cl(3)	2,250 (3)	C(2)—N(4)	1,31 (1)
Cu—Cl(4)	2,250 (3)	C(2)—N(5)	1,28 (1)
C(1)—N(1)	1,32 (1)	N(5)—C(51)	1,46 (1)
C(1)—N(2)	1,32 (1)	N(5)—C(52)	1,44 (1)
Cl(2)—Cu—Cl(3)	96,6 (1)	N(2)—C(1)—N(3)	115,3 (9)
Cl(2)—Cu—Cl(4)	100,2 (1)	N(3)—C(2)—N(5)	118 (1)
Cl(3)—Cu—Cl(1)	97,3 (1)	N(3)—C(2)—N(4)	118 (1)
Cl(4)—Cu—Cl(1)	99,5 (1)	N(4)—C(2)—N(5)	124,0 (9)
Cl(2)—Cu—Cl(1)	133,4 (1)	C(52)—N(5)—C(51)	116,8 (9)
Cl(3)—Cu—Cl(4)	136,5 (1)	C(2)—N(5)—C(52)	123 (1)
N(1)—C(1)—N(2)	122 (1)	C(2)—N(5)—C(51)	119,6 (9)
N(1)—C(1)—N(3)	122 (1)	C(1)—N(3)—C(2)	126,8 (9)

Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue à l'aide des méthodes directes (*MULTAN*88; Debaerdemaeker *et al.*, 1988). L'affinement des paramètres x, y, z, β_{ij} pour les atomes non-hydrogènes et $B_{\rm iso}$ pour les atomes d'hydrogène, basé sur les F, a été effectué à l'aide du programme *ORXFLS* (Busing, 1971). Les dessins de la structure ont été obtenus à l'aide du programme *ORTEP*II (Johnson, 1976). Les angles dièdres ont été calculés à l'aide du programme *BEST PLANES* (Ito & Sugawara, 1983).

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des distances des atomes d'hydrogène, des plans moyens et des angles de torsion ont été déposées au dépôt d'archives de l'UICr (Référence: PA1093). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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A Novel Antimony Sulfide Templated by Ethylenediammonium

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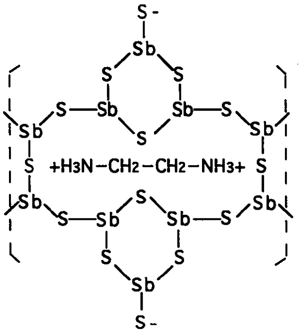
Abstract

The structure of ethylenediammonium antimony sulfide, $C_2H_{10}N_2^{2+}.Sb_8S_{13}^{2-}$, is characterized by double chains of corner-linked SbS_3 pyramids. These chains

contain openings formed by 16-membered rings, consisting of alternating Sb and S atoms, and interlock to form sheets in (001).

Comment

Hydrothermal treatment of Sb_2S_3 in the presence of ethylenediamine and hydrogen sulfide at 473 K produces a novel open structure, $C_2H_{10}N_2^{2+}.Sb_8S_{13}^{2-}$, (I). This work is part of an ongoing program to explore the synthesis, properties and structures of open-framework sulfides (Bedard, Wilson, Vail, Bennett & Flanigen, 1989; Parise, 1990, 1991; Parise & Ko, 1992).



(I)

Like other antimony sulfides in this series (Dittmar & Schäfer, 1977; Volk & Schäfer, 1979; Parise, 1990; Parise & Ko, 1992), the primary building unit in the structure of the title compound is an SbS_3 pyramid with three Sb—S bond lengths in the range 2.40–2.50 Å (Table 2). Three of these units corner-link, as shown in Fig. 1, to form secondary building units, designated 'semicubes' (Parise, 1990). These are linked by individual SbS_3 pyramids to form double chains with openings formed by 16-membered rings consisting of alternating Sb and S atoms as shown in Fig. 2. Sheets in the (001) plane are generated by packing of the double chains in a 'zipper' arrangement. S(5) is bonded to only one Sb and fits into a pocket of a second chain, allowing weak interactions with Sb(1), Sb(2) and Sb(4) (Fig. 2). The distances between the sheets, stacked along [001], are typified by Sb(1)···S(4) [3.239 (3) Å] and Sb(3)···S(5) [3.457 (2) Å], which suggest weak bonding interactions. Fig. 3 is an *ORTEP* (Johnson, 1965) stereoview of the structure.

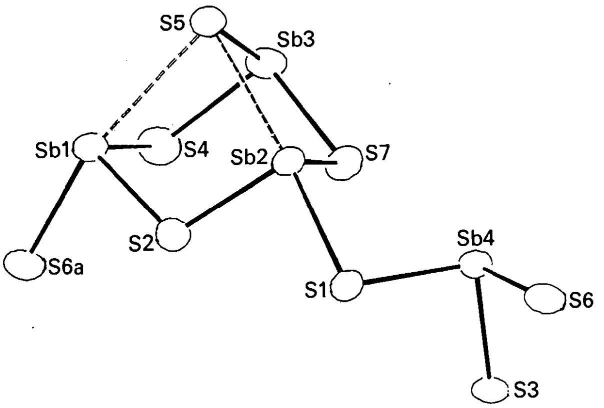


Fig. 1. *ORTEP* drawing of semicube secondary building unit and an individual pyramid. Probability ellipsoids are drawn at 74%.

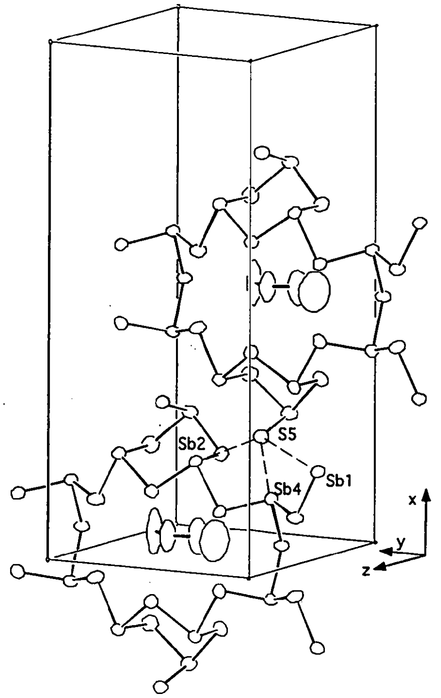


Fig. 2. *ORTEP* drawing of the zipper-like spatial configuration of the two double chains related by the *C* center. Probability ellipsods are drawn at 74%.

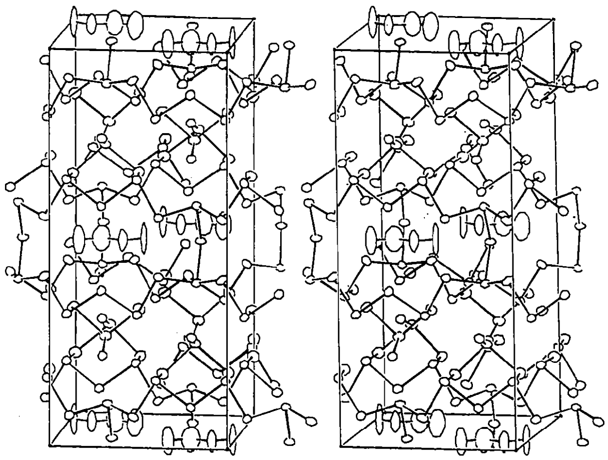


Fig. 3. *ORTEP* stereoview of the title compound. The origin of the cell unit is in the back bottom right-hand corner, with *x* vertical and *y* to the left. Only those Sb—S bonds <2.5 Å are shown. Probability ellipsoids are drawn at 64%.

Bond-strength (Brown & Wu, 1976) calculations suggest formal oxidation states of 3+ and 2− for Sb and S, respectively. This implies a charge of 2− on the Sb_8S_{13} framework and 2+ on ethylenediamine. The diprotonated template (ethylenediammonium) lies on the mirror plane within the opening of the double chains, as shown in Figs. 2 and 3. The closest approach between the cation and the surrounding framework atoms is S(3)···N(1) [3.244 (21) Å], implying hydrogen bonding within the framework. The elongation of the displacement ellipsoids for atoms in the ethylenediammonium cation may indicate some degree of disorder about the mirror plane perpendicular to [100]. This is to be expected for a cation loosely bound to the framework.

The residual electron densities could be reduced to $\Delta\rho_{max} = 2.5$ e Å^{-3} and $\Delta\rho_{min} = -3.1$ e Å^{-3} when only those reflections with $I > 3\sigma(I)$ were used in the refinement. In this case, four major peaks from a final difference Fourier map were located 0.835–0.898 Å from the four Sb atoms. They are situated close to the position expected to be occupied by the $5s^2$ lone-pair electrons of Sb^{3+}, opposite the base of the SbS_3 pyramid (Fig. 1).

Experimental

The title compound was prepared by hydrothermal treatment of Sb_2S_3 at 473 K, in the presence of hydrogen sulfide and ethylenediamine in the ratio 0.5-ethylenediamine:0.15-H_2S:30-H_2O, then recrystallized from Sb_2S_3.

Crystal data

$(C_2H_{10}N_2)[Sb_8S_{13}]$
$M_r = 1452.90$
Orthorhombic
$Cmc2_1$
$a = 22.874\ (4)$ Å
$b = 10.058\ (3)$ Å
$c = 11.338\ (4)$ Å
$V = 2609\ (2)$ Å^3
$Z = 4$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 12 reflections
$\theta = 12$–$15°$
$\mu = 9.19$ mm^{-1}
$T = 294$ K
Plate
0.256 × 0.167 × 0.157 mm
Dark red

Data collection

Picker diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{min} = 0.232$, $T_{max} = 0.303$
5529 measured reflections
3665 independent reflections
3665 observed reflections

$R_{int} = 0.0157$
$\theta_{max} = 33.57°$
$h = 0 \rightarrow 34$
$k = 0 \rightarrow 15$
$l = -17 \rightarrow 14$
1 standard reflection monitored every 30 reflections
intensity variation: 1.34%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.052$
$S = 1.75$
3634 reflections
121 parameters
H atoms not located
$w = [\sigma^2(I) + 0.0009I^2]^{-1/2}$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 3.9$ e Å^{-3}
$\Delta\rho_{min} = -5.6$ e Å^{-3}

Extinction correction: isotropic secondary
Extinction coefficient: 0.38 (2) × 10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sb(1)	0.17016 (2)	0.98442 (5)	0.47407 (1)	1.7 (1)
Sb(2)	0.16905 (2)	0.59510 (5)	0.48883 (7)	1.6 (1)
Sb(3)	0.24296 (2)	0.77693 (6)	0.24315 (7)	2.0 (1)
Sb(4)	0.09758 (2)	0.30248 (5)	0.34209 (7)	1.7 (1)
S(1)	0.0759 (1)	0.4672 (2)	0.4928 (2)	2.1 (1)
S(2)	0.1064 (1)	0.7934 (2)	0.5201 (2)	2.0 (1)
S(3)	0	0.3109 (3)	0.2418 (3)	1.8 (1)
S(4)	0.1727 (1)	0.9656 (3)	0.2563 (2)	2.3 (1)
S(5)	0.2745 (1)	0.7884 (2)	0.4453 (2)	1.7 (1)
S(6)	0.0752 (1)	0.1054 (2)	0.4583 (3)	2.5 (1)
S(7)	0.1687 (1)	0.6006 (2)	0.2712 (2)	2.1 (1)
N(1)	0	0.6313 (19)	0.2746 (26)	10.6 (12)
N(2)	0	0.9832 (13)	0.1988 (19)	8.6 (9)
C(1)	0	0.7506 (29)	0.2176 (20)	7.0 (10)
C(2)	0	0.8749 (15)	0.2626 (20)	5.3 (6)

Table 2. *Selected geometric parameters* (Å, °)

Sb(1)—S(2)	2.467 (2)	Sb(3)—S(4)	2.491 (2)
Sb(1)—S(4)	2.477 (3)	Sb(3)—S(5)	2.406 (2)
Sb(1)—S(6^i)	2.496 (2)	Sb(3)—S(7)	2.477 (2)
Sb(2)—S(1)	2.489 (2)	Sb(4)—S(1)	2.431 (2)
Sb(2)—S(2)	2.481 (2)	Sb(4)—S(3)	2.506 (2)
Sb(2)—S(7)	2.468 (3)	Sb(4)—S(6)	2.435 (2)
S(2)—Sb(1)—S(4)	99.50 (9)	S(1)—Sb(4)—S(3)	96.57 (9)
S(2)—Sb(1)—S(6^i)	83.15 (8)	S(1)—Sb(4)—S(6)	97.5 (1)
S(4)—Sb(1)—S(6^i)	89.21 (9)	S(3)—Sb(4)—S(6)	94.9 (1)
S(1)—Sb(2)—S(2)	85.35 (7)	Sb(2)—S(1)—Sb(4)	99.49 (8)
S(1)—Sb(2)—S(7)	91.54 (8)	Sb(1)—S(2)—Sb(2)	104.76 (9)
S(2)—Sb(2)—S(7)	97.04 (9)	Sb(4)—S(3)—Sb(4^{ii})	125.9 (1)
S(4)—Sb(3)—S(5)	95.74 (8)	Sb(1)—S(4)—Sb(3)	97.65 (8)
S(4)—Sb(3)—S(7)	95.44 (9)	Sb(1^{iii})—S(6)—Sb(4)	104.65 (8)
S(5)—Sb(3)—S(7)	96.77 (7)	Sb(2)—S(7)—Sb(3)	98.17 (8)
Sb(1)···S(5)	3.113 (2)	Sb(2)···S(5^{vi})	3.380 (2)
Sb(2)···S(5)	3.137 (2)	Sb(3)···S(5^{vii})	3.457 (2)
S(3)···N(1)	3.244 (21)	Sb(4)···S(5^{vi})	3.156 (2)
Sb(1)···S(4^{iv})	3.239 (3)	S(2)···S(6^i)	3.296 (3)
Sb(1)···S(5^v)	3.324 (2)		

Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, y, z$; (iii) $x, y-1, z$ (iv) $x, 2-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (vi) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (vii) $-x, 1-y, \frac{1}{2}+z$.

Data collection, cell refinement and data reduction were performed using a local implementation of software written by L. W. Finger, Geophysical Laboratory, Carnegie Institute of Washington, USA. Structure resolution and refinement, molecular graphics, and preparation of material for publication were acheived with a package of programs written and maintained by J. C. Calabrese, EI DuPont.

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Lists of structure factors, anisotropic displacement parameters and complete geometry of the non-H atoms have been deposited with the IUCr (Reference: BK1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Bis(acetato-*O*)bis(4-methylpyridine-*N*)copper(II)

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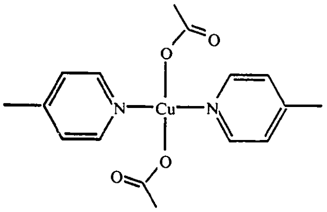
Abstract

The structure of *trans*-bis(acetato-*O*)bis(4-methylpyridine-*N*)copper(II), $[Cu(C_2H_3O_2)_2(C_6H_7N)_2]$, reported herein, represents a monomeric parent acetate complex with a distorted square-planar arrangement of acetate and 4-methylpyridine ligands around the Cu atom with the following distances and angles: Cu—N = 2.027 (4) and Cu—O1 = 1.950 (3) Å; O1—Cu—N = 89.1 (2) and O1—Cu—N′ = 90.9 (2)°. The Cu atom resides on a center of inversion. The most important dihedral angles are the angle between the 4-methylpyridine plane and the acetate plane (O1, O2, C21 and C22), 78.2°, and the angle between the 4-methylpyridine ring and the coordination plane (Cu, N, O1), 31.6°.

Comment

The title compound, (I), was prepared by the reaction of gallium sulfide with copper(I) acetate in 4-methylpyridine solution. A solution of copper(I) acetate (0.31 g, 2.4 mmol) and gallium sulfide (0.37 g, 3.6 mmol) in 25 ml of 4-methylpyridine was stirred for 3 days at 293 K under argon. All manipulations were performed in a drybox or on a vacuum line under an inert atmosphere using standard Schlenk techniques. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexanes produced prismatic blue crystals of the title compound (I).



(I)

X-ray structures of the two following copper(II) acetate complexes have been determined: *trans*-bis[(chloroacetato)(α-picoline)]copper(II) and *trans*-bis[(dichloroacetato)(α-picoline)]copper(II) (Davey & Stephens, 1971*a*,*b*). The complex reported herein represents the unchlorinated compound. The Cu atom is surrounded by four ligands in a virtually square-planar arrangement with an O atom (O2) of the acetate group efficiently blocking the two remaining axial sides of the Cu atom above and below the coordination plane defined by atoms Cu, O1, O1′, N and N′. The Cu—O2 distance of 2.623 (4) Å is indicative of a weak interaction between the two atoms. The two 4-methylpyridine rings, as well as the two acetato groups, are forced to be coplanar by a center of symmetry residing on the Cu atom. The dihedral angle between the 4-methylpyridine plane and the acetate plane is 78.2°. Steric interactions force the 4-methylpyridine ring to be skewed at an angle of 31.6° with respect to the coordination plane. The C21—O2 distance of 1.227 (7) Å is shorter than the C21—O1 distance of 1.279 (6) Å, which suggests more double-bond character for the C21—O2 bond (Davey & Stephens, 1971*a*,*b*). The O1—C21—O2 angle of 122.7 (5)° is significantly smaller than the O—C—O angles of 126.6 and 128.0° in the dimeric copper(II) acetate complex $[Cu_2(C_2H_2ClO_2)_4(C_6H_7N)_2]$ (Davey & Stephens, 1970). All angles and bonds within the 4-methylpyridine rings are as expected.

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