Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Oishi, S., Nagai, Y., Chiba, K. & Ishizawa, N. (1998). *Chem. Lett.* 439–440.
Ruddlesden, S. N. & Popper, P. (1957). *Acta Cryst.* **10**, 538–539.
Sakowski-Cowley, A. C., Lukaszewicz, K. & Megaw, H. D. (1969). *Acta Cryst.* B**25**, 851–865.
Sato, M., Kono, Y. & Jin, T. (1993). *J. Ceram. Soc. Jpn*, **101**, 980–984.

Acta Cryst. (1999). C**55**, 1044–1046

Pentabarium tetraantimonide, β-Ba_5Sb_4: a more symmetrical arrangement for the Ba_5Sb_4 compound

GAELLE DERRIEN, LAURE MONCONDUIT, MONIQUE TILLARD AND CLAUDE BELIN

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, ESA 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier CEDEX 5, France. E-mail: moncondu@univ-montp2.fr

(*Received 19 January 1999; accepted 10 March 1999*)

Abstract

Ba_5Sb_4 crystallizes in the orthorhombic space group *Cmca* and is isostructural with Eu_5As_4 reported in the *Ccmb* alternate setting. β-Ba_5Sb_4 is a new arrangement which is more symmetrical than α-Ba_5Sb_4 [Brechtel, Cordier & Schäfer (1981). *Z. Naturforsch. Teil B*, **36**, 1341–1342; *Pnma*, isostructural with Sm_5Ge_4]. The structure contains two anionic moieties, *i.e.* Sb_2^{4-} dumbbells [Sb—Sb 2.886 (3) Å] and Sb^{3-}. The Sb1 atom (Sb^{3-}) lies inside a monocapped distorted trigonal prism (6 × Ba1 and 1 × Ba2). The Sb2 atom, which forms the Sb_2^{4-} dumbbell, sits inside a tricapped trigonal prism (6 × Ba1, 2 × Ba2 and 1 × Sb2).

Comment

The structure of Ba_5Sb_4 has been determined in the centrosymmetric space group *Cmca* (No. 64) and is isostructural with Eu_5As_4 (Wang *et al.*, 1978). We designate this the β form with respect to the form reported by Brechtel *et al.* (1981) in the *Pnma* space group, which results from a distortion of the *Cmca* structure. The two space groups *Pnma* and *Cmca* frequently occur in the R_5P_4 family (R = rare earth; P = Si, Ge, Rh); Eu_5As_4 crystallizes in the *Cmca* space group, while Gd_5Si_4 (Iglesias & Steinfink, 1972), Sm_5Ge_4 (Smith *et al.*, 1967) and Pu_5Rh_4 (Cromer, 1977) crystallize in *Pnma*. It is obvious that the two structural forms are closely related. Atomic positions (X,Y,Z) in the *Cmca* cell can be obtained from those (x,y,z) in the *Pnma* structure by the transformation: $X = y - \frac{1}{4}$, $Y = -x - \frac{1}{4}$, $Z = z + \frac{1}{2}$.

The orthorhombic *Pnma* structure of α-Ba_5Sb_4 [a = 9.012 (3), b = 17.823 (6) and c = 9.041 (3) Å] contains atoms Ba(1), Ba(2) and Sb(1) at 8*d* special positions, and Ba(3), Sb(2) and Sb(3) at 4*c* special positions.

Owing to the presence of supplementary twofold axes in the *Cmca* space group, the transformation of atomic positions from *Pnma* into *Cmca* evidently results in some extremely short interatomic distances (in the order of 0.4 Å). The number of independent atoms is then reduced by one third (four in *Cmca* instead of six in *Pnma*). Merging the two 8*d* positions [Ba(1) and Ba(2)], and the two 4*c* positions [Sb(2) and Sb(3)] of the *Pnma* structure gives 16*g* and 8*f* atomic positions, respectively, for Ba1 and Sb2 in the *Cmca* structure; Ba(3) (4*c*) and Sb(1) (8*d*) are transformed into Ba2 (4*a*) and Sb1 (8*d*). Then, in the *Cmca* structure, there are two independent Sb (Sb1 and Sb2) and two independent Ba (Ba1 and Ba2) atoms.

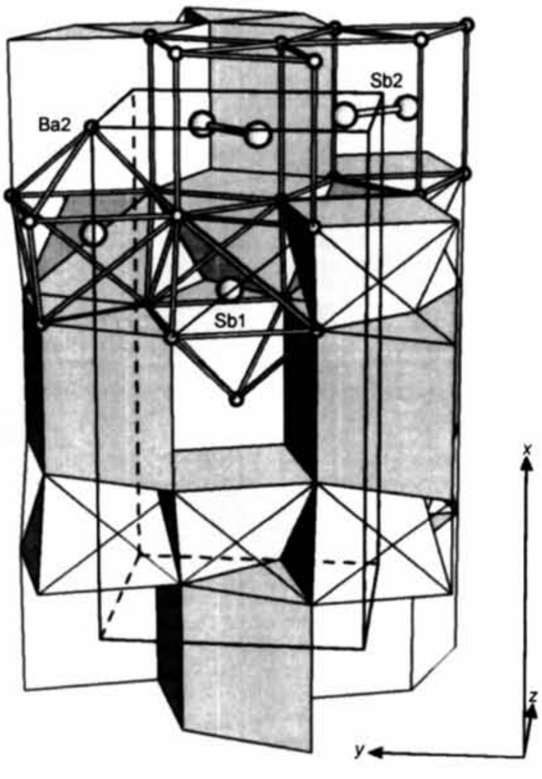

Fig. 1. Representation of the unit cell of β-Ba_5Sb_4. The Sb^{3-} and Sb_2^{4-} anionic moieties are shown inside their barium coordination prisms. The Ba atoms lie at the corners of the polyhedra.

The occurrence of two forms for Ba_5Sb_4 probably arises from the different experimental conditions of synthesis and crystal growth. The *Pnma* phase was obtained from stoichiometric quantities of Ba and Sb heated for 2 h at 1623 K and then quenched. Both structures contain two anionic moieties, *i.e.* Sb_2^{4-} dumbbells and Sb^{3-}. In the *Cmca* structure, Sb1 (Sb^{3-}) is coordinated by seven Ba atoms (6 × Ba1 and 1 × Ba2) forming a distorted monocapped (on a rectangular face) trigonal prism. The Sb2 atom forms dumbbells and sits inside a trigonal prism of Ba1 atoms; its coordination is completed by one Sb2 and two Ba2 atoms capping rectangular faces of the prism.

Experimental

With the aim of obtaining a quaternary Ba_3TaSb_3O phase, an analogue of the recently discovered Ba_3NbAs_3O phase (Monconduit *et al.*, 1999), BaO, Sb, Ta and Ba (ratio 1:3:1:2) were inserted in a tantalum reactor weld-sealed under argon. The tantalum reactor was protected in a quartz ampoule sealed under vacuum. Single crystals of β-Ba_5Sb_4 were obtained serendipitously by heating to 1473 K (50 K h^{-1}) for 120 h and then cooling the mixture at a rate of 150 K h^{-1}. The non-homogeneous product contained a large amount of Ba_5Sb_4. Elemental analyses (SEM) of the flat crystals confirmed the presence of barium and antimony in the ratio 5:4, and the absence of tantalum.

Crystal data

Ba_5Sb_4
M_r = 1173.70
Orthorhombic
Cmca
a = 17.749 (3) Å
b = 9.021 (3) Å
c = 9.059 (2) Å
V = 1450.4 (6) Å^3
Z = 4
D_x = 5.375 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.2–19.3°
μ = 20.609 mm^{-1}
T = 293 (2) K
Wedge
0.080 × 0.080 × 0.028 mm
Dark grey

Data collection

Nonius CAD-4 diffractometer
ω–$\frac{1}{3}\theta$ scans
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)
T_{min} = 0.223, T_{max} = 0.563
2305 measured reflections
1083 independent reflections

632 reflections with $I > 2\sigma(I)$
R_{int} = 0.087
θ_{max} = 29.96°
h = −9 → 24
k = −12 → 11
l = −12 → 12
3 standard reflections every 100 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 0.926
1083 reflections
26 parameters

$\Delta\rho_{max}$ = 2.223 e Å^{-3}
$\Delta\rho_{min}$ = −3.099 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 4 (2) × 10^{-5}

$w = 1/[\sigma^2(F_o^2) + (0.0150P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.14613 (4)	0.17003 (10)	0.66594 (9)	0.0160 (2)
Ba2	0	1/2	1/2	0.0159 (4)
Sb1	0.30151 (7)	0	1/2	0.0146 (3)
Sb2	0	0.11275 (15)	0.38701 (14)	0.0151 (3)

Table 2. *Selected bond lengths (Å)*

Ba1—Sb1^{i}	3.4618 (13)	Ba2—Ba1^{x}	4.2246 (12)
Ba1—Sb1	3.4954 (13)	Ba2—Ba1^{xi}	4.2246 (12)
Ba1—Sb1^{ii}	3.5178 (10)	Ba2—Ba1^{viii}	4.2246 (12)
Ba1—Sb2	3.6576 (13)	Ba2—Ba1^{xii}	4.2706 (9)
Ba1—Sb2^{iii}	3.6693 (15)	Ba2—Ba1^{xiii}	4.2706 (9)
Ba1—Sb2^{iv}	3.8181 (13)	Sb1—Ba1^{xiv}	3.4618 (13)
Ba1—Ba1^{ii}	3.989 (2)	Sb1—Ba1^{i}	3.4618 (13)
Ba1—Ba2	4.2246 (12)	Sb1—Ba1^{v}	3.4954 (13)
Ba1—Ba2^{iv}	4.2706 (9)	Sb1—Ba1^{ii}	3.5178 (10)
Ba1—Ba1^{v}	4.295 (2)	Sb1—Ba1^{xv}	3.5178 (10)
Ba1—Ba1^{iv}	4.7537 (10)	Sb1—Ba2^{xvi}	3.5230 (13)
Ba1—Ba1^{vi}	4.7537 (10)	Sb2—Sb2^{iii}	2.886 (3)
Ba2—Sb1^{vii}	3.5230 (13)	Sb2—Ba2^{vi}	3.6504 (14)
Ba2—Sb1^{i}	3.5230 (13)	Sb2—Ba1^{xi}	3.6576 (13)
Ba2—Sb2^{viii}	3.640 (2)	Sb2—Ba1^{iii}	3.6693 (15)
Ba2—Sb2	3.640 (2)	Sb2—Ba1^{v}	3.6693 (15)
Ba2—Sb2^{ix}	3.6504 (14)	Sb2—Ba1^{vi}	3.8181 (13)
Ba2—Sb2^{iv}	3.6504 (14)	Sb2—Ba1^{xiii}	3.8181 (13)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} - x, y, \frac{3}{2} - z$; (iii) $-x, -y, 1 - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $x, -y, 1 - z$; (vi) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (viii) $-x, 1 - y, 1 - z$; (ix) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (x) $x, 1 - y, 1 - z$; (xi) $-x, y, z$; (xii) $x, \frac{1}{2} + y, \frac{3}{2} - z$; (xiii) $-x, \frac{1}{2} - y, z - \frac{1}{2}$; (xiv) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (xv) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (xvi) $\frac{1}{2} + x, y - \frac{1}{2}, z$.

The atomic parameters and the crystallographic space group were initially determined by oscillation and Weissenberg techniques. The best diffracting crystal was used for accurate determination of the cell parameters and data collection. The space group was found to be *Cmca* (No. 64) (reflection conditions: hkl for $h + k = 2n$, $h0l$ for $l = 2n$ and $hk0$ for $h = 2n$).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1235). Services for accessing these data are described at the back of the journal.

References

Brechtel, E., Cordier, G. & Schäfer, H. (1981). *Z. Naturforsch. Teil B*, **36**, 1341–1342.
Cromer, D. T. (1977). *Acta Cryst.* B**33**, 1993–1995.
Dowty, E. (1993). *ATOMS. A Computer Program for Displaying Atomic Structures*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Iglesias, J. E. & Steinfink, H. (1972). *J. Less Common Met.* **26**, 45–52.

Monconduit, L., Tillard, M., Favier, F. & Belin, C. (1999). *J. Alloys Compd*, **284**, 124–127.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Smith, G. S., Johnson, Q. & Tharp, A. G. (1967). *Acta Cryst.* **22**, 269–272.
Wang, Y., Calvert, L. D., Gabe, E. J. & Taylor, J. B. (1978). *Acta Cryst.* B**34**, 1962–1965.

Acta Cryst. (1999). C**55**, 1046–1047

K_2TeS_3

Christian Rumpf, Christian Näther and Wolfgang Bensch

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany. E-mail: wbensch@ac.uni-kiel.de

(*Received 16 September 1998; accepted 22 December 1998*)

Abstract

The reaction of K_2S_3, tellurium and sulfur yields light-yellow single crystals of dipotassium tellurium trisulfide, K_2TeS_3. The structure consists of isolated TeS_3^{2-} anions, and K^+ cations coordinated by six S atoms from five different TeS_3^{2-} anions within distorted octahedra.

Comment

This work is part of a project on the synthesis of new ternary and quaternary chalcogenides prepared in reactive alkali-metal polychalcogenide fluxes. The title compound was obtained as light-yellow air-sensitive crystals by the reaction of elemental iron and tellurium in a potassium polysulfide flux at 573 K. In an earlier communication, it was assumed that the compound crystallizes in the orthorhombic crystal system, with a = 9.06 (2), b = 13.13 (2) and c = 6.40 (2) Å (Eisenmann *et al.*, 1969). From the observed extinction rules, the two space groups $Pmn2_1$ and $Pmmn$ were proposed. Unfortunately, no further structural details were reported. Our investigations using single-crystal X-ray experiments demonstrate clearly that the title compound crystallizes in the monoclinic system, with angle β = 90.40 (2)°. The monoclinic symmetry is supported by the low internal R value. Averaging symmetry-related reflections assuming the Laue symmetry mmm leads to an internal R value of 32%. The observed extinction rules for the orthorhombic space group $Pmn2_1$ observed in the work of Eisenmann *et al.* (1969) are the same as in the space group $P2_1/n$.

In the crystal structure, the TeS_3^{2-} anions are arranged in layers parallel to the (101) plane, with the K^+ cations located between them. The Te atoms exhibit three intermolecular contacts to S atoms of 3.680 (2), 4.042 (2) and 4.063 (2) Å, which are too long to be treated as bonds. In the resulting strongly distorted TeS_6 octahedra, the Te atom is shifted from the center of the octahedra, effectively forming only three bonds to the S atom. Another way to describe the structure starts with a close-packed arrangement of S atoms. The K^+ cations occupy two-thirds and the Te atoms one-third of the octahedral sites. The K^+ cation is coordinated by six S atoms within a distorted octahedron, with typical K—S distances in the range 3.136 (2)–3.294 (2) Å for K1, and in the range 3.145 (2)–3.536 (2) Å for K2. The shortest K···Te contact amounts to 4.038 (1) Å. The TeS_3^{2-} anions form trigonal pyramids, with Te—S distances ranging from 2.341 (1) to 2.356 (1) Å (average 2.350 Å). The Te atoms are about 1.023 Å above the plane defined by the three S atoms. The S—Te—S angles [102.14 (3)–103.09 (3)°] deviate from ideal values due to the steric demands of the electron lone pair at the Te atom. The S···S distances within the TeS_3^{2-} anion range from 3.6534 to 3.6767 Å. The geometrical parameters of TeS_3^{2-} are comparable to those in other TeS_3^{2-}-containing compounds like $K_3(SH)TeS_3$ (Dittmar & Schäfer, 1978), $BaTeS_3$ (Jumas *et al.*, 1976) and $(NH_4)_2TeS_3$ (Gerl *et al.*, 1974). We note that the TeS_3^{2-} anion is also found in transition metal compounds like $Cs_6Cu_2(TeS_3)_2(S_6)_2$ (McCarthy *et al.*, 1993), $AMTeS_3$ (A = K, Rb, Cs; M = Cu, Ag; Zhang & Kanatzidis, 1994*a*), $A_2Mn(TeS_3)_2$ (A = Cs, Rb) (Zhang & Kanatzidis, 1994*b*) and $(CuI)_3Cu_2TeS_3$ (Pfitzner & Zimmerer, 1997). A tetraphenylphosphonium salt containing the TeS_3^{2-} anion has also been reported (Rubenheim *et al.*, 1994).

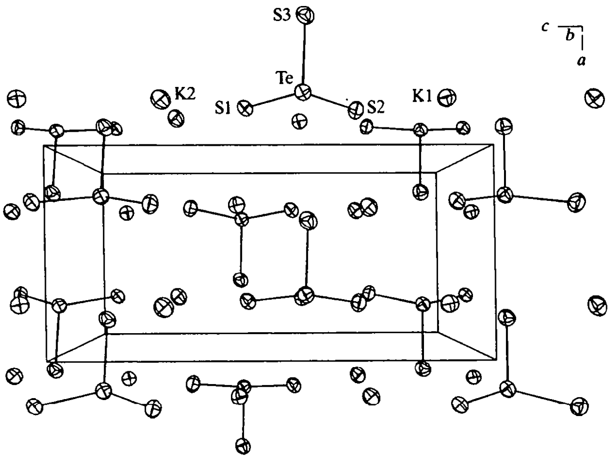

Fig. 1. The crystal structure of K_2TeS_3 viewed along the b axis. Displacement ellipsoids are drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999