Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of the mixed-metal trisulfide $BaCu_{1/3}Ta_{2/3}S_3$

Kejun Bu,[a] Jianqiao He,[a] Dong Wang,[b] Chong Zheng[c]* and Fuqiang Huang[a]*

[a]State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China, [b]School of Materials Science and Engineering, Shanghai University, Shangda Road, No. 99, Shanghai 200444, People's Republic of China, and [c]Department of Chemistry and Biochemistry, Northern Illinois University, USA. *Correspondence e-mail: czheng@niu.edu, huangfq@mail.sic.ac.cn

Received 17 January 2017
Accepted 6 April 2017

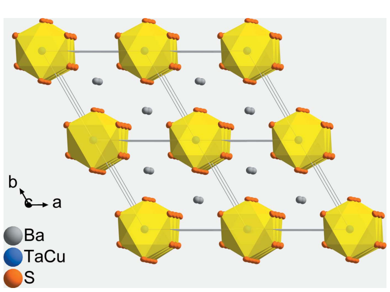
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; quasi-one-dimensional structure; mixed-metal trisulfide.

CCDC reference: 1542709

Supporting information: this article has supporting information at journals.iucr.org/e

The mixed-metal title compound, $BaCu_{1/3}Ta_{2/3}S_3$ [barium copper(II) tantalum(V) trisulfide], was prepared through solid-state reactions. The crystal structure adopts the $BaTaS_3$ structure type and consists of face-sharing [MS_6] (M = Ta,Cu) octahedra (point-group symmetry $\overline{3}m$.) that are condensed into infinite chains along [001]. Adjacent chains are linked through the barium cations (site symmetry $\overline{6}m2$), which exhibit a coordination number of twelve. The M site is occupied by 2/3 of Ta^{V} and 1/3 of Cu^{II}, whereby the average M—S distances are slightly longer than those of ordered $BaTaS_3$. The classical charge balance of the title compound can be represented by [Ba^{2+}] [$(Ta/Cu)^{4+}$] [S^{2-}]$_3$.



1. Chemical context

Barium vanadium trisulfide, $BaVS_3$ (Takano *et al.*, 1977), with which $BaTaS_3$ (Gardner *et al.*, 1969) crystallizes isotypically in space group $P6_3/mmc$, has a chain structure. The observed conductivity was attributed to the formation of conduction bands *via* vanadium$\cdots$vanadium *d*-orbital overlap. It shows three phase transitions and exhibits a number of intriguing physical properties (Nakamura *et al.*, 1994). While both $BaVS_3$ and $BaTaS_3$ are composed of the same type of linear chains, $BaTaS_3$ shows metallic conductivity and a Curie–Weiss behaviour of the magnetic susceptibility (Gardner *et al.*, 1969). To explore the physical properties of $BaTaS_3$ and related

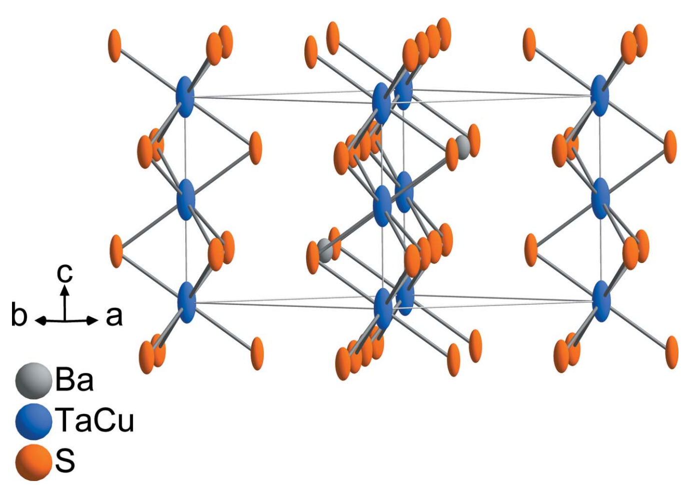


Figure 1
Face-sharing of MS_6 (M = Cu, Ta) octahedra in the structure of $BaCu_{1/3}Ta_{2/3}S_3$. Displacement ellipsoids are drawn at the 50% probability level.

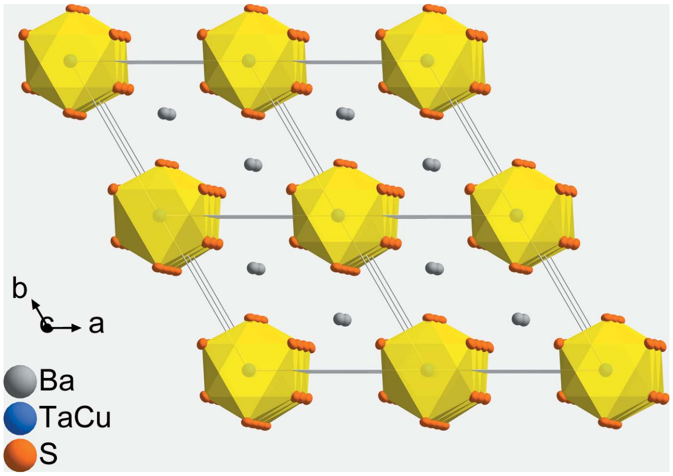


Figure 2
The crystal structure of $BaCu_{1/3}Ta_{2/3}S_3$, viewed down [001].

compounds, we have introduced copper and studied mixed-metal phases $Ba(Ta/Cu)S_3$. Here we report on the synthesis and structural characterization of the mixed-metal trisulfide with composition $BaCu_{1/3}Ta_{2/3}S_3$.

2. Structural commentary

$BaCu_{1/3}Ta_{2/3}S_3$ adopts the $BaTaS_3$ structure type in space group $P6_3/mmc$. A detailed description of this structure type has been given previously (Gardner *et al.*, 1969). The asymmetric unit of $BaCu_{1/3}Ta_{2/3}S_3$ contains one Ba site (Wyckoff position 2c), one mixed-occupied (Cu/Ta) site (2a) and one S site (6h). The structure contains face-sharing octahedral [MS_6] (M = Cu, Ta) units, which construct infinite chains along [001] (Fig. 1). In the crystal structure, these chains are linked through Ba cations (coordination number 12) to adjacent chains (Fig. 2).

The M site is occupationally disordered and contains 1/3 Cu and 2/3 Ta. It is surrounded by six S atoms with an M—S bond length of 2.475 (4) Å, which is slightly longer than that of ordered $BaTaS_3$ (2.461 Å; Gardner *et al.*, 1969). This trend is in agreement with the different ionic radii of Ta (0.64 Å for Ta^{V} with coordination number of six) and Cu^{II} (0.73 Å) using the data provided by Shannon (1976).

The (Cu,Ta)···(Cu,Ta) distance within a chain is 2.9159 (3) Å, which is much shorter than the interchain (Cu,Ta)···(Cu,Ta) distance of 6.8437 (18) Å. The Ba—S interactions between adjacent metal sulfide chains are reflected by one shorter [3.422 (6) Å] and one longer distance [3.523 (3) Å], in good agreement with those found in other barium tantalum sulfides (Onoda & Saeki, 1989).

The classical charge balance of the title compound can be represented by the formula $[Ba^{2+}]$ $[(Ta/Cu)^{4+}]$ $[S^{2-}]_3$.

3. Synthesis and crystallization

The title compound was prepared using solid-state reactions between the elements Cu, Ta, S and BaS. Ta powder (99.999%, Alfa Aesar Puratronic), Cu powder (99.999%, Alfa Aesar Puratronic), S powder (99.999%, Alfa Aesar Puratronic), and BaS powder (99.999%, Alfa Aesar Puratronic) were mixed in a fused-silica tube in an Ta:Cu:S:BaS molar ratio of 0.67:0.33:2:1. The tube was evacuated to 0.1 Pa, sealed and heated gradually (60 K h^{-1}) to 973 K, where it was kept for 2 d. The tube was then cooled to 673 K at a rate of 3 K h^{-1} and then quenched to room temperature. The crystals are stable in air and alcohol.

Scanning electron microscopy (SEM) images of selected crystals were taken on a Hitachi S-4800 microscope equipped with an electron microprobe analyzer for a semiquantitative elemental analysis in the energy dispersive X-ray spectroscopy (EDX) mode. The presence of both copper and tantalum was confirmed (Fig. 3).

Table 1
Experimental details.

Crystal data	
Chemical formula	$BaCu_{1/3}Ta_{2/3}S_3$
M_r	375.14
Crystal system, space group	Hexagonal, $P6_3/mmc$
Temperature (K)	297
a, c (Å)	6.8350 (6), 5.8318 (5)
V (Å^3)	235.94 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	26.34
Crystal size (mm)	0.04 × 0.03 × 0.01
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.44, 0.86
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4312, 125, 106
R_{int}	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.645
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.113, 1.25
No. of reflections	125
No. of parameters	11
No. of restraints	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.50, −1.50

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2007) and *publCIF* (Westrip, 2010).

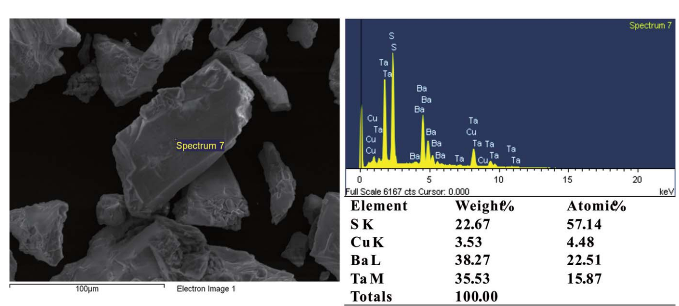


Figure 3
SEM image and EDX spectrum of $BaCu_{1/3}Ta_{2/3}S_3$.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The refinement of the model with occupational disorder on the *M* site resulted in a significant decrease of the reliability factors in comparison with a fully occupied Ta site ($R1$ = 0.73, wR = 0.197). No evidence, *e.g.* in the form of superstructure reflections, was found for an ordering of this site and thus a statistically disordered model was considered. In the final model, atoms of the disordered site were restrained to have the same displacement parameters, with a fixed Cu:Ta ratio of 1/3:2/3 required for charge neutrality and in good agreement with the EDX measurement. The remaining maximum and minimum electron densities are located 1.06 Å from the (Cu,Ta)1 site and 1.96 Å from the S1, respectively.

Funding information

Funding for this research was provided by: State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China. (award No. XDB04040200); CAS Center for Excellence in Superconducting Electronics, National key research and development program (award No. 2016YFB0901600); NSF of China (award Nos. 11404358, 51402341); Science and Technology Commission of Shanghai (award Nos. 13JC1405700, 14520722000).

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supporting information

Acta Cryst. (2017). E**73**, 713-715 [https://doi.org/10.1107/S2056989017005266]

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Barium copper(II) tantalum(V) trisulfide

Crystal data

$BaCu_{0.33}Ta_{0.67}S_3$
M_r = 375.14
Hexagonal, $P6_3/mmc$
a = 6.8350 (6) Å
c = 5.8318 (5) Å
V = 235.94 (5) Å^3
Z = 2
F(000) = 325
D_x = 5.280 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1738 reflections
θ = 3.4–25.9°
μ = 26.34 mm^{-1}
T = 297 K
Plate, black
0.04 × 0.03 × 0.01 mm

Data collection

Bruker D8 QUEST diffractometer
Detector resolution: 10.4167 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
T_{min} = 0.44, T_{max} = 0.86
4312 measured reflections
125 independent reflections
106 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.3°, θ_{min} = 3.4°
h = −8→8
k = −8→8
l = −7→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.113
S = 1.25
125 reflections
11 parameters
2 restraints
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 4.8137P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.50 e Å^{-3}
$\Delta\rho_{min}$ = −1.50 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ba	0.6667	0.3333	0.75	0.0341 (7)	
Ta	0	0	0.5	0.0707 (12)	0.6666 (8)
Cu	0	0	0.5	0.0707 (12)	0.3334 (18)
S	0.1689 (4)	0.3378 (8)	0.75	0.0449 (15)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.0246 (7)	0.0246 (7)	0.0529 (13)	0.0123 (4)	0	0
Ta	0.0306 (8)	0.0306 (8)	0.151 (3)	0.0153 (4)	0	0
Cu	0.0306 (8)	0.0306 (8)	0.151 (3)	0.0153 (4)	0	0
S	0.0217 (18)	0.015 (2)	0.096 (4)	0.0074 (10)	0	0

Geometric parameters (Å, º)

Ba—S^{i}	3.4176 (3)	Ta—S	2.475 (4)
Ba—S^{ii}	3.4176 (3)	Ta—S^{xiii}	2.475 (4)
Ba—S^{iii}	3.4176 (3)	Ta—S^{vii}	2.475 (4)
Ba—S^{iv}	3.4176 (3)	Ta—S^{xiv}	2.475 (4)
Ba—S	3.4176 (3)	Ta—Ta^{xv}	2.9159 (3)
Ba—S^{v}	3.4176 (3)	Ta—Cu^{xvi}	2.9159 (3)
Ba—S^{vi}	3.506 (3)	Ta—Cu^{xv}	2.9159 (3)
Ba—S^{vii}	3.506 (3)	Ta—Ta^{xvi}	2.9159 (3)
Ba—S^{viii}	3.506 (3)	S—Cu^{xv}	2.475 (4)
Ba—S^{ix}	3.506 (3)	S—Ta^{xv}	2.475 (4)
Ba—S^{x}	3.506 (3)	S—Ba^{xvii}	3.4176 (3)
Ba—S^{xi}	3.506 (3)	S—Ba^{vi}	3.506 (3)
Ta—S^{xii}	2.475 (4)	S—Ba^{ix}	3.506 (3)
Ta—S^{iii}	2.475 (4)		
S^{i}—Ba—S^{ii}	60.89 (16)	S^{xii}—Ta—S^{iii}	180.0
S^{i}—Ba—S^{iii}	120.0010 (10)	S^{xii}—Ta—S	91.18 (10)
S^{ii}—Ba—S^{iii}	59.11 (17)	S^{iii}—Ta—S	88.82 (10)
S^{i}—Ba—S^{iv}	59.11 (17)	S^{xii}—Ta—S^{xiii}	88.82 (10)
S^{ii}—Ba—S^{iv}	120.0010 (10)	S^{iii}—Ta—S^{xiii}	91.18 (10)
S^{iii}—Ba—S^{iv}	179.11 (16)	S—Ta—S^{xiii}	180.0
S^{i}—Ba—S	179.11 (17)	S^{xii}—Ta—S^{vii}	88.82 (10)
S^{ii}—Ba—S	120.0000 (10)	S^{iii}—Ta—S^{vii}	91.18 (10)
S^{iii}—Ba—S	60.89 (17)	S—Ta—S^{vii}	91.18 (10)

S^{iv}—Ba—S	119.9990 (10)	S^{xiii}—Ta—S^{vii}	88.82 (10)
S^{i}—Ba—S^{v}	120.0000 (10)	S^{xii}—Ta—S^{xiv}	91.18 (10)
S^{ii}—Ba—S^{v}	179.11 (17)	S^{iii}—Ta—S^{xiv}	88.82 (10)
S^{iii}—Ba—S^{v}	119.9990 (10)	S—Ta—S^{xiv}	88.82 (10)
S^{iv}—Ba—S^{v}	60.89 (17)	S^{xiii}—Ta—S^{xiv}	91.18 (10)
S—Ba—S^{v}	59.11 (17)	S^{vii}—Ta—S^{xiv}	180.0
S^{i}—Ba—S^{vi}	89.75 (5)	S^{xii}—Ta—Ta^{xv}	126.10 (7)
S^{ii}—Ba—S^{vi}	118.88 (3)	S^{iii}—Ta—Ta^{xv}	53.90 (7)
S^{iii}—Ba—S^{vi}	118.88 (3)	S—Ta—Ta^{xv}	53.90 (7)
S^{iv}—Ba—S^{vi}	61.40 (8)	S^{xiii}—Ta—Ta^{xv}	126.10 (7)
S—Ba—S^{vi}	89.75 (5)	S^{vii}—Ta—Ta^{xv}	126.10 (7)
S^{v}—Ba—S^{vi}	61.40 (8)	S^{xiv}—Ta—Ta^{xv}	53.90 (7)
S^{i}—Ba—S^{vii}	118.88 (3)	S^{xii}—Ta—Cu^{xvi}	53.90 (7)
S^{ii}—Ba—S^{vii}	89.75 (5)	S^{iii}—Ta—Cu^{xvi}	126.10 (7)
S^{iii}—Ba—S^{vii}	61.40 (8)	S—Ta—Cu^{xvi}	126.10 (7)
S^{iv}—Ba—S^{vii}	118.88 (3)	S^{xiii}—Ta—Cu^{xvi}	53.90 (7)
S—Ba—S^{vii}	61.40 (8)	S^{vii}—Ta—Cu^{xvi}	53.90 (7)
S^{v}—Ba—S^{vii}	89.75 (5)	S^{xiv}—Ta—Cu^{xvi}	126.10 (7)
S^{vi}—Ba—S^{vii}	147.76 (6)	Ta^{xv}—Ta—Cu^{xvi}	180.0
S^{i}—Ba—S^{viii}	118.88 (3)	S^{xii}—Ta—Cu^{xv}	126.10 (7)
S^{ii}—Ba—S^{viii}	89.75 (5)	S^{iii}—Ta—Cu^{xv}	53.90 (7)
S^{iii}—Ba—S^{viii}	61.40 (8)	S—Ta—Cu^{xv}	53.90 (7)
S^{iv}—Ba—S^{viii}	118.88 (3)	S^{xiii}—Ta—Cu^{xv}	126.10 (7)
S—Ba—S^{viii}	61.40 (8)	S^{vii}—Ta—Cu^{xv}	126.10 (7)
S^{v}—Ba—S^{viii}	89.75 (5)	S^{xiv}—Ta—Cu^{xv}	53.90 (7)
S^{vi}—Ba—S^{viii}	57.48 (11)	Ta^{xv}—Ta—Cu^{xv}	0
S^{vii}—Ba—S^{viii}	112.55 (14)	Cu^{xvi}—Ta—Cu^{xv}	180.0
S^{i}—Ba—S^{ix}	89.75 (5)	S^{xii}—Ta—Ta^{xvi}	53.90 (7)
S^{ii}—Ba—S^{ix}	118.88 (3)	S^{iii}—Ta—Ta^{xvi}	126.10 (7)
S^{iii}—Ba—S^{ix}	118.88 (3)	S—Ta—Ta^{xvi}	126.10 (7)
S^{iv}—Ba—S^{ix}	61.40 (8)	S^{xiii}—Ta—Ta^{xvi}	53.90 (7)
S—Ba—S^{ix}	89.75 (5)	S^{vii}—Ta—Ta^{xvi}	53.90 (7)
S^{v}—Ba—S^{ix}	61.40 (8)	S^{xiv}—Ta—Ta^{xvi}	126.10 (7)
S^{vi}—Ba—S^{ix}	112.55 (14)	Ta^{xv}—Ta—Ta^{xvi}	180.0
S^{vii}—Ba—S^{ix}	57.48 (11)	Cu^{xvi}—Ta—Ta^{xvi}	0
S^{viii}—Ba—S^{ix}	147.76 (6)	Cu^{xv}—Ta—Ta^{xvi}	180.0
S^{i}—Ba—S^{x}	61.40 (8)	Ta—S—Cu^{xv}	72.2
S^{ii}—Ba—S^{x}	61.40 (8)	Ta—S—Ta^{xv}	72.19 (13)
S^{iii}—Ba—S^{x}	89.75 (5)	Cu^{xv}—S—Ta^{xv}	0
S^{iv}—Ba—S^{x}	89.75 (5)	Ta—S—Ba	89.64 (7)
S—Ba—S^{x}	118.88 (3)	Cu^{xv}—S—Ba	89.64 (7)
S^{v}—Ba—S^{x}	118.88 (3)	Ta^{xv}—S—Ba	89.64 (7)
S^{vi}—Ba—S^{x}	57.48 (11)	Ta—S—Ba^{xvii}	89.64 (7)
S^{vii}—Ba—S^{x}	147.76 (6)	Cu^{xv}—S—Ba^{xvii}	89.64 (7)
S^{viii}—Ba—S^{x}	57.48 (11)	Ta^{xv}—S—Ba^{xvii}	89.64 (7)
S^{ix}—Ba—S^{x}	147.76 (6)	Ba—S—Ba^{xvii}	179.11 (16)
S^{i}—Ba—S^{xi}	61.40 (8)	Ta—S—Ba^{vi}	159.82 (13)
S^{ii}—Ba—S^{xi}	61.40 (8)	Cu^{xv}—S—Ba^{vi}	87.629 (7)

S^{iii}—Ba—S^{xi}	89.75 (5)	Ta^{xv}—S—Ba^{vi}	87.629 (7)
S^{iv}—Ba—S^{xi}	89.75 (5)	Ba—S—Ba^{vi}	90.25 (5)
S—Ba—S^{xi}	118.88 (3)	Ba^{xvii}—S—Ba^{vi}	90.25 (5)
S^{v}—Ba—S^{xi}	118.88 (3)	Ta—S—Ba^{ix}	87.629 (7)
S^{vi}—Ba—S^{xi}	147.76 (6)	Cu^{xv}—S—Ba^{ix}	159.82 (13)
S^{vii}—Ba—S^{xi}	57.48 (11)	Ta^{xv}—S—Ba^{ix}	159.82 (13)
S^{viii}—Ba—S^{xi}	147.76 (6)	Ba—S—Ba^{ix}	90.25 (5)
S^{ix}—Ba—S^{xi}	57.48 (11)	Ba^{xvii}—S—Ba^{ix}	90.25 (5)
S^{x}—Ba—S^{xi}	112.55 (13)	Ba^{vi}—S—Ba^{ix}	112.55 (13)

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*y*+1, *x*−*y*, *z*; (iii) −*x*+*y*, −*x*, *z*; (iv) −*x*+*y*+1, −*x*+1, *z*; (v) −*y*+1, *x*−*y*+1, *z*; (vi) −*x*+1, −*y*+1, −*z*+2; (vii) *y*, −*x*+*y*, −*z*+1; (viii) *y*, −*x*+*y*, −*z*+2; (ix) −*x*+1, −*y*+1, −*z*+1; (x) *x*−*y*+1, *x*, −*z*+2; (xi) *x*−*y*+1, *x*, −*z*+1; (xii) *x*−*y*, *x*, −*z*+1; (xiii) −*x*, −*y*, −*z*+1; (xiv) −*y*, *x*−*y*, *z*; (xv) −*x*, −*y*, *z*+1/2; (xvi) −*x*, −*y*, *z*−1/2; (xvii) *x*−1, *y*, *z*.