Collection des données

Diffractomètre CAD-4
Balayage $\omega/2\theta$
Correction d'absorption: empirique par balayage ψ (North *et al.*, 1968)
$T_{\rm min} = 0,69$, $T_{\rm max} = 0,99$
1095 réflexions mesurées
1003 réflexions indépendantes
951 réflexions avec $I > 2\sigma(I)$
$R_{\rm int} = 0,030$
$\theta_{\rm max} = 31,09°$
$h = -28 \rightarrow 28$
$k = -7 \rightarrow 0$
$l = 0 \rightarrow 7$
1 réflexion de référence
fréquence: 120 min
variation d'intensité: 0,0%

Affinement

Affinement à partir des F^2
$R[F^2 > 2\sigma(F^2)] = 0,043$
$wR(F^2) = 0,129$
$S = 1,265$
1003 réflexions
59 paramètres
$w = 1/[\sigma^2(F_o^2) + (0,0620P)^2 + 8,3643P]$
où $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0,001$
$\Delta\rho_{\rm max} = 1,805$ e Å^3 (prés de Cs)
$\Delta\rho_{\rm min} = -1,977$ e Å^{-3}
Correction d'extinction: *SHELXL*93 (Sheldrick, 1993)
Coefficient d'extinction: 0,077 (5)
Facteurs de diffusion des *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	$U_{\rm éq}$
Ag	0,18055 (4)	0	0,8113 (2)	0,0416 (3)
Cs	0,09010 (3)	1/2	0,2686 (1)	0,0315 (3)
N1	0,0393 (4)	0	0,7576 (13)	0,024 (1)
N2	0,2411 (4)	0	1,3217 (15)	0,028 (1)
O1	−0,0219 (4)	0	0,7449 (13)	0,032 (1)
O2	0,0715 (3)	−0,1929 (11)	0,7686 (9)	0,039 (1)
O3	0,2642 (4)	0	1,5329 (14)	0,034 (1)
O4	0,1805 (4)	0	1,2764 (16)	0,038 (2)
O5	0,2778 (5)	0	1,1476 (18)	0,054 (2)

Tableau 2. *Paramètres géométriques (Å)*

Ag—O3$^{\rm i}$	2,317 (8)	Cs—O2$^{\rm vii}$	3,157 (5)
Ag—O4	2,460 (8)	Cs—O2$^{\rm viii}$	3,194 (5)
Ag—O2	2,474 (7)	Cs—O2$^{\rm ii}$	3,194 (5)
Ag—O2$^{\rm ii}$	2,474 (7)	Cs—O4$^{\rm vi}$	3,349 (4)
Ag—O5	2,590 (11)	Cs—O4$^{\rm i}$	3,349 (4)
Cs—O3$^{\rm iii}$	3,100 (7)	Cs—O5$^{\rm ix}$	3,578 (9)
Cs—O1$^{\rm iv}$	3,123 (4)	Cs—O2$^{\rm x}$	3,716 (7)
Cs—O1$^{\rm v}$	3,123 (4)	Cs—O2$^{\rm v}$	3,716 (7)
Cs—O2$^{\rm vi}$	3,157 (5)	O3—Ag$^{\rm xi}$	2,318 (8)

Codes de symétrie: (i) $x, y, z-1$; (ii) $x, -y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$; (iv) $-x, 1-y, 1-z$; (v) $-x, -y, 1-z$; (vi) $x, 1+y, z-1$; (vii) $x, -y, z-1$; (viii) $x, 1+y, z$; (ix) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (x) $-x, 1+y, 1-z$; (xi) $x, y, 1+z$.

La collecte a été effectuée avec la largeur de balayage (0,87 + 1,5tgθ)°. Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par la méthode de l'atome lourd (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíçek & Yordanov, 1992; Enraf-Nonius, 1994)). Affinement des paramètres de la maille: *CAD*-4 *EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

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Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: GS1014). Les processus d'accès à ces archives sont donné au dos de la couverture.

Références

Dean, C., Hambley, T. W. & Snow, M. R. (1985). *Acta Cryst.* **C40**, 1512–1515.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Enraf-Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, Les Pays-Bas.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, Les Pays-Bas.
Flor, G. & Sinistri, C. (1968). *Ric. Sci.* **38**, 227–230.
Gioia Lobbia, G. & Cingolani, A. (1975). *Ann. Chim.* **65**, 361–367.
Hellali, D., Zamali, H., Sebaoun, A. & Jemal, M. (1999). *J. Therm. Anal. Calorim.* Accepté.
Khutsistova, F. M., Berdyukova, V. A., Popova, T. B., Trufanov, V. N. & Kolomin, L. G. (1988). *Zh. Neorg. Khim.* **33**, 1024–1027.
Macíçek, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
Meyer, P. & Capponi, J.-J. (1982). *Acta Cryst.* **B38**, 2543–2546.
Meyer, P., Rimsky, A. & Chevalier, R. (1978). *Acta Cryst.* **B34**, 1457–1462.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Pohl, D. & Gross, T. (1993). *Acta Cryst.* **C49**, 316–318.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Université de Göttingen, Allemagne.

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$Cs_6Sn_2Te_6$, a new telluridodistannate(III)

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Abstract

The new compound hexacaesium hexatelluridodistannate(III), $Cs_6Sn_2Te_6$, has been prepared by reacting a stoichiometric ratio of the elements at 923 K in an evacuated silica-glass tube. The title compound crystallizes as black columns of the $K_6Ge_2Te_6$ type. The structure is composed of isolated distorted Te_6 octahedra, with Sn–Sn dumbbells at the centres. The caesium cations are arranged between the isolated Sn_2Te_6 octahedra.

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Comment

Compounds containing anions of the formula $[(Si/Ge/Sn)_2(S/Se/Te)_6]^{6-}$ have been reported in the literature between 1978 and 1988 with a variety of counter-cations, such as Na^+, K^+ (Eisenmann *et al.*, 1981, 1984, 1985; Dittmar, 1978*a*,*b*), Mn^{2+} (Ouvrad *et al.*, 1988) and Cr^{3+} (Vincent *et al.*, 1986). The common feature of their crystal structures is an $M_2^{III}X_6$ building unit, in which an M^{III}–M^{III} dumbbell is surrounded octahedrally by six chalcogen atoms. The title compound is the first in which caesium acts as the counter-cation of an $M_2^{III}X_6$ unit.

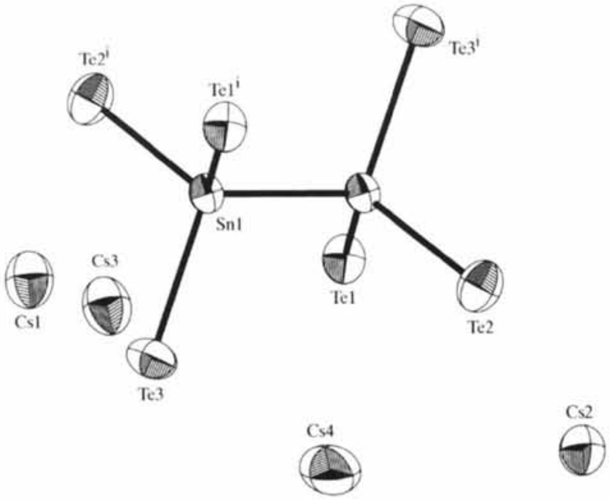

Fig. 1. A view of the staggered conformation of the anion of $Cs_6Sn_2Te_6$ and the unique cations. Displacement ellipsoids are shown at the 90% probability level. [Symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $2-z$.]

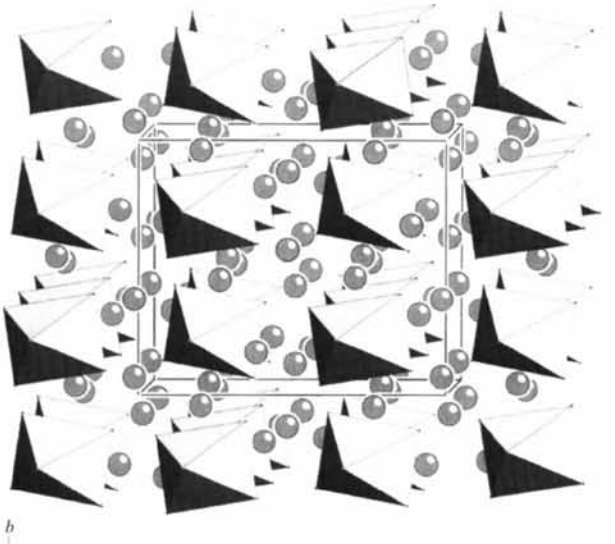

Fig. 2. View of the crystal structure of $Cs_6Sn_2Te_6$. The Sn_2Te_6 building units have been designed as polyhedra.

The structure is composed of isolated Sn_2Te_6 units in which each Sn atom is surrounded tetrahedrally by three Te atoms and another Sn atom. These units can be described as distorted octahedra with Sn–Sn dumbbells at the centres. Along the *c* direction, the isolated octahedra are arranged to form chains. Neighbouring chains are shifted by half of the diameter of the octahedra along the *c* direction. This results in a sequence of cavities that are occupied by Cs atoms. The bond lengths are in good agreement with similar compounds reported previously (Dittmar, 1978*b*). The Cs—Te contact distances vary significantly between 3.7 and 4.1 Å.

Experimental

Hexacaesium hexatelluridodistannate(III) was prepared by a standard method (Dittmar, 1978*a*) in which a stoichiometric ratio of the elements was reacted in an evacuated silica-glass tube at 923 K. The elements were placed in a 20 cm silica-glass tube under dry argon. To compensate for the reaction of the alkali metal with the glass surface, an excess of 10% in weight of caesium was used. The glass tube was sealed *in vacuo* at 10^{-3} mbar (1 bar = 10^5 Pa) and heated to 923 K over a period of 5 h. It was held at this temperature for 1 h and then allowed to cool to room temperature overnight by switching off the furnace. The title compound was isolated as black columns grown from the solidified melt. The crystals were prepared under perfluorether oil for subsequent analysis (Kottke & Stalke, 1993).

Crystal data

$Cs_6Sn_2Te_6$
$M_r = 1800.44$
Monoclinic
C_2/c
$a = 17.460\,(4)$ Å
$b = 14.330\,(3)$ Å
$c = 10.250\,(2)$ Å
$\beta = 96.73\,(3)°$
$V = 2546.9\,(9)$ Å^3
$Z = 4$
$D_x = 4.695$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.5$–$24.9°$
$\mu = 17.128$ mm^{-1}
$T = 223\,(2)$ K
Column
$0.20 \times 0.10 \times 0.05$ mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
Variable $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.51$, $T_{max} = 1.00$
5472 measured reflections
2245 independent reflections

1957 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25°$
$h = -20 \rightarrow 20$
$k = -17 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.199$
2245 reflections
66 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 9.9534P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.345$ e Å^{-3} (0.76 Å from Cs4)
$\Delta\rho_{min} = -0.943$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997*a*)
Extinction coefficient: 0.00095 (3)
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}
Sn1	0.32367 (3)	0.24149 (3)	0.95419 (5)	0.01064 (14)
Te1	0.18711 (3)	0.23262 (4)	1.31347 (5)	0.01534 (14)
Te2	0.07858 (3)	0.12969 (4)	0.92296 (5)	0.01782 (14)
Te3	0.38101 (3)	0.06713 (3)	1.02176 (5)	0.01704 (14)
Cs1	1/2	0.10687 (5)	3/4	0.02079 (17)
Cs2	0	−0.08656 (5)	3/4	0.01895 (17)
Cs3	0.40693 (3)	0.18995 (4)	1.36699 (5)	0.02165 (15)
Cs4	0.21559 (3)	−0.02746 (4)	1.18407 (6)	0.03128 (16)

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

$Sn1—Te2^{i}$	2.7206 (9)	$Te2—Cs4^{v}$	3.9034 (11)
Sn1—Te3	2.7500 (8)	$Te2—Cs3^{vi}$	3.9482 (9)
$Sn1—Te1^{i}$	2.7530 (9)	$Te2—Cs3^{i}$	3.9689 (9)
$Sn1—Sn1^{i}$	2.8506 (11)	Te2—Cs4	4.0566 (12)
$Te1—Cs4^{ii}$	3.8336 (10)	Te3—Cs1	3.7089 (11)
Te1—Cs3	3.8616 (10)	Te3—Cs4	3.7514 (11)
$Te1—Cs2^{iii}$	3.8703 (9)	$Te3—Cs1^{vii}$	3.8558 (11)
$Te1—Cs1^{i}$	3.9861 (9)	Te3—Cs3	3.9306 (10)
$Te1—Cs3^{iv}$	3.9894 (11)	$Te3—Cs3^{v}$	4.0572 (10)
Te1—Cs4	4.0064 (11)	$Te3—Cs3^{viii}$	4.1373 (11)
Te2—Cs2	3.7495 (10)	$Te3—Cs4^{v}$	4.2782 (16)
$Te2—Cs2^{iii}$	3.8184 (10)		
$Te2^{i}—Sn1—Te3$	108.05 (3)	$Te2^{i}—Sn1—Sn1^{i}$	109.32 (3)
$Te2^{i}—Sn1—Te1^{i}$	109.62 (3)	$Te3—Sn1—Sn1^{i}$	108.11 (3)
$Te3—Sn1—Te1^{i}$	110.72 (2)	$Te1^{i}—Sn1—Sn1^{i}$	110.96 (4)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$; (iii) $-x, -y, 2 - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 3 - z$; (v) $x, -y, z - \frac{1}{2}$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $1 - x, -y, 2 - z$; (viii) $1 - x, y, \frac{5}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CELDIM* in *CAD*-4 *Software*. Data reduction: *CADSHEL* in *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *DIAMOND* (Crystal Impact, 1998). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1072). Services for accessing these data are described at the back of the journal.

References

Crystal Impact (1998). *DIAMOND. Visual Crystal Structure Information System*. Crystal Impact, Bonn, Germany.
Dittmar, G. (1978*a*). *Z. Anorg. Allg. Chem.* **453**, 68–78.
Dittmar, G. (1978*b*). *Acta Cryst.* **B34**, 2390–2393.
Eisenmann, B., Hansa, J. & Schäfer, H. (1985). *Z. Naturforsch. Teil B*, **40**, 450–457.
Eisenmann, B., Kieselbach, E., Schäfer, H. & Schrod, H. (1984). *Z. Anorg. Allg. Chem.* **516**, 49–54.
Eisenmann, B., Schwerer, H. & Schäfer, H. (1981). *Z. Naturforsch. Teil B*, **36**, 1538–1541.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Ouvrad, G., Sandre, E. & Brec, R. (1988). *J. Solid State Chem.* **73**, 27–32.
Sheldrick, G. M. (1997*a*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Vincent, H., Leroux, D. & Bijaoui, B. (1986). *J. Solid State Chem.* **63**, 349–352.

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$K_4Ni_7(AsO_4)_6$

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Abstract

The title compound, tetrapotassium heptanickel hexaarsenate, has a three-dimensional open anionic framework built up from AsO_4 tetrahedra and NiO_6 octahedra sharing corners and edges. They delimit parallel tunnels, running along the *a* direction, where the K^+ ions reside. This centrosymmetric framework appears to be similar to that of $Na_4Ni_7(PO_4)_6$ which is claimed to be non-centrosymmetric.

Commentaire

Lors de l'étude du système $K_2O–NiO–As_2O_5–WO_3$, nous avons isolé une phase constituée de cristaux marrons en forme de parallélépipède. Son étude par diffraction des rayons X sur monocristal a révélé la formule $K_4Ni_7(AsO_4)_6$. Cet orthoarseniate est caracterisé par une charpente anionique tridimensionnelle, formée d'un assemblage d'octaèdres NiO_6 et de tétraèdres AsO_4 connectés par des arêtes et des sommets oxygène. Ils laissent libre des tunnels parallèles à la direction [100] au sein desquels logent les cations K^+ (Fig. 1). Ces tunnels communiquent entre eux selon la direction [010], par des fenêtres en forme de quadrilatère délimité par quatre arêtes appartenant respectivement à deux tétraèdres AsO_4 et deux octaèdres NiO_6.