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$Na_7Au_5S_6$ — A novel thioaurate(I) based on a b.c.c. chalcogen packing*

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Abstract

Colourless transparent crystals of $Na_7Au_5S_6$ were prepared by reacting a stoichiometric mixture of Na_2S, gold and sulphur at 1070 K. The compound is orthorhombic, oP72, space group *Pbcn* (number 60) with $a = 10.424(6)$ Å, $b = 7.024(6)$ Å, $c = 22.27(1)$ Å and $Z = 4$. The compound crystallizes with a new structure type, which was determined from single-crystal diffractometer data (Mo Kα radiation). The structure was solved by direct methods and refined to a conventional R of 0.062 ($R_w = 0.059$) for 685F_0 with $F_0^2 > 4\sigma(F_0^2)$. The outstanding feature of $Na_7Au_5S_6$ — in a partial ionic description — is the coexistence of two very different anionic species — infinite ${}^1_\infty(AuS)^-$ chains and isolated $(AuS_2)^{3-}$ dumbbells — in its structure. In both anions gold is doubly coordinated by sulphur; Au–S distances are close to 2.30 Å; and S–Au–S bond angles vary from 170.3° to 180°. The Na^+ ions which separate the anions are in a distorted tetrahedral sulphur coordination. The crystal structure is based on a cubic body-centred packing of chalcogen atoms; the principles of this packing are discussed.

1. Introduction

The investigation of compounds of the coinage metals containing d^{10} ions is of considerable interest with respect to potential attractive d^{10}–d^{10} interactions whose origin is still a matter of controversy [1, 2]. Au(I) compounds merit particular attention in this context because of the importance of relativistic effects in these systems.

The majority of experimental data has been obtained on coordination compounds of Au(I) [3, 4], while structural information on "inorganic" Au(I) compounds is comparatively scarce.

The study of alkali thioaurates(I) — which can be readily obtained through melt reactions — may in this respect serve as a contribution to fill this gap.

Investigations in the Na–Au–S system have led to the detection of a novel thioaurate, $Na_7Au_5S_6$, whose structural features will be presented in this paper.

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*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

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2. Experimental details

Starting materials for the preparation of $Na_7Au_5S_6$ were gold flake (20 μm, 99.99%; from Degussa), elemental sulphur (99.99%; from Alfa Ventron) and X-ray pure Na_2S which was obtained by gently dehydrating doubly recrystallized $Na_2S \cdot 9H_2O$ under vacuum. Stoichiometric amounts of the intimately mixed components were sealed into an evacuated silica tube. The sample was gradually heated to 1070 K, kept at this temperature for 3 days and then allowed to cool to ambient temperature with a constant cooling rate of 2 K h^{-1}. Colourless tabular crystals of $Na_7Au_5S_6$ could be isolated from the crushed ingot. Since the compound is sensitive to moisture it has to be handled under inert conditions.

3. Structure determination

Preliminary X-ray investigations performed with rotating-crystal and Weissenberg techniques (Cu Kα) revealed orthorhombic symmetry. Reflections with $0kl$ where $k \neq 2n$, $h0l$ where $l \neq 2n$ and $hk0$ where $h+k \neq 2n$ were systematically absent, uniquely indicating the centrosymmetric space group *Pbcn*.

A small crystal with the approximate dimensions $0.075 \times 0.075 \times 0.05$ mm^3 was finally selected for the structure determination. The crystal was sealed at random orientation into a thin-walled glass capillary and transferred to a computer-controlled four-circle diffractometer (Nonius CAD4). Graphite monochromated Mo Kα ($\lambda = 0.71069$ Å) was used as radiation.

Intensity data were collected over one octant of the reflection sphere up to $2\theta = 52°$. Since the inspection of the peak profiles for some intense reflections indicated a slight broadening, an ω–θ scan mode was applied (maximum scan time, 120 s; conventional background peak background (BPB) scans). The scan width was varied according to $1.2° + 0.35° \tan \theta$. The regularly measured intensities of three control reflections showed no significant changes during the period of data collection, indicating good crystal and electronic stability.

A total of 1887 reflections was measured, from which 1603 were unique and not systematically absent. 685 reflections with $F_0^2 > 4\sigma(F_0^2)$ were considered to be significant. The high number of "unobserved" reflections is due to a pronounced pseudo-Bravais centring of the crystal structure.

The lattice constants given in Table 1 were determined by least-squares refinement from 24 reflections ($2\theta > 30°$) centred at four different settings.

The crystal structure was solved by direct methods (Multan 11/82) [5] (210 unitary structure factors with $E_{min} > 1.36$ and 3918 σ_2 relations). The positions of the Au atoms could be located from the E map calculated from the phase set with the highest figure of merit. The remaining atoms were taken from a series of subsequent difference Fourier syntheses. Refinement with isotropic temperature factors converged at $R = 0.07$ (unit weights). The final refinements with anisotropic temperature factors converged at $R = 0.062$

TABLE 1

Crystallographic data for $Na_7Au_5S_6$

Pearson symbol	oP72
Lattice constants (Å)	
a	10.424(6)
b	7.024(6)
c	22.27(1)
Space group	*Pbcn* (No. 60)
Cell volume (Å^3)	1630.6
Cell contents	4
Relative formula mass, RFM	1338.15
Theoretical density (g cm^{-3}) d	5.45
Absorption coefficient (cm^{-1}) $\mu_{\mathrm{Mo}\ K\alpha}$	456.6
Structure refinement	
Crystal dimensions (mm^3)	0.075×0.075×0.05
Unique reflections	1603
Observed reflections	685
σ cut-off	$4\sigma(F_0)^2$
Refined parameters	74
$R = \Sigma(\lvert F_0\rvert - \lvert F_c\rvert)/\Sigma\lvert F_0\rvert$	0.062
$R_w = [\Sigma(w\lvert F_0\rvert - \lvert \mathrm{F}_c\rvert)^2/\Sigma w\lvert F_0\rvert^2]^{1/2}$	0.059
$w = \sigma(\lvert {F_0}^2\rvert^2 + 0.01{F_0}^2)^2]^{-1/2}$	

($R_w = 0.059$) for 685 F_0s and 84 refined parameters. The final shift:error ratio was less than 0.01. A subsequent difference Fourier map was featureless.

Atomic scattering factors for the neutral atoms and anomalous dispersion corrections were taken from ref. 6. Absorption effects were approximately accounted for by a spherical absorption correction ($\mu R = 1.5$). All calculations were performed on a DEC MicroVAX 3520 computer using programs from the Enraf-Nonius crystallographic software package [7]. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Interatomic distances and bond angles are reported in Tables 3–6. (Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the Fachinformationszentrum Energie, Physik Mathematik, under C.S.D. No. 56157.)

4. Discussion

$Na_7Au_5S_6$ is, in addition to Na_3AuS_2 [8], $K_4Au_6S_5$ [9], KAuS [10] and the isotypic compounds RbAuS and CsAuS [11], the sixth alkali thioaurate which — so far — has been structurally characterized. Its crystal structure is of a new type. Surprisingly no discrete oligomeric anionic groups are formed, as one would probably expect from the stoichiometry. Instead two thioaurate species of different dimensionalities coexist in the crystal structure.

One of the species is an isolated, strictly linear dumbbell anion $[S–Au–S]^{3-}$, formed by Au(1) and S(1), which corresponds to the anions found in Na_3AuS_2.

TABLE 2

Atomic coordinates and equivalent isotropic thermal parameters[a] for $Na_7Au_5S_6$[b]

Atom	Wyckoff position	x	y	z	B_{eq}
Na(1)	4c	0.000	−0.004(4)[c]	0.250	2.0(5)
Na(2)	8d	0.262(3)	0.504(3)	0.5920(9)	3.4(6)
Na(3)	8d	0.378(2)	0.338(3)	0.3792(9)	1.9(5)
Na(4)	8d	0.607(2)	0.120(3)	0.544(1)	1.8(5)
Au(1)	4a	0.500	0.500	0.500	1.03(4)
Au(2)	8d	0.0023(6)	0.4711(3)	0.32740(8)	1.54(3)
Au(3)	8d	0.2453(3)	0.7288(3)	0.2519(2)	1.48(3)
S(1)	8d	0.357(1)	0.250(2)	0.501(1)	1.1(2)
S(2)	8d	0.134(1)	0.212(2)	0.3370(6)	1.1(3)
S(3)	8d	0.378(1)	0.759(2)	0.6660(7)	1.5(2)

[a] $B_{eq} = (B_{11} + B_{22} + B_{33})/3$.

[b] Space group *Pbcn*, No. 60.

[c] Estimated standard deviations are given in parentheses.

TABLE 3

Interatomic distances (Å) and bond angles for Na^+ cation coordination in $Na_7Au_5S_6$

Bond	Distance	Angle bonds	Angle
Na(1)–S(2)	2.84(1)[a]	S(2)–Na(1)–S(2)	115.0(5)°
Na(1)–S(2)	2.84(1)	S(2)–Na(1)–S(3)	124.3(2)°
Na(1)–S(3)	2.89(1)	S(2)–Na(1)–S(3)	96.0(2)°
Na(1)–S(3)	2.89(1)	S(2)–Na(1)–S(3)	96.0(2)°
		S(2)–Na(1)–S(3)	124.3(2)°
		S(3)–Na(1)–S(3)	103.2(5)°
Na(2)–S(1)	2.87(2)	S(1)–Na(2)–S(1)	91.9(5)°
Na(2)–S(1)	2.93(2)	S(1)–Na(2)–S(3)	133.5(6)°
Na(2)–S(3)	2.71(2)	S(1)–Na(2)–S(3)	101.8(4)°
Na(2)–S(3)	2.80(2)	S(1)–Na(2)–S(3)	102.5(4)°
		S(1)–Na(2)–S(3)	123.1(6)°
		S(3)–Na(2)–S(3)	106.2(5)°
Na(3)–S(1)	2.80(2)	S(1)–Na(3)–S(2)	100.3(4)°
Na(3)–S(2)	2.86(1)	S(1)–Na(3)–S(2)	122.1(5)°
Na(3)–S(2)	2.80(1)	S(1)–Na(3)–S(3)	111.4(4)°
Na(3)–S(3)	2.82(1)	S(2)–Na(3)–S(2)	98.4(4)°
		S(2)–Na(3)–S(3)	127.7(5)°
		S(2)–Na(3)–S(3)	98.3(4)°
Na(4)–S(1)	2.91(1)	S(1)–Na(4)–S(1)	107.0(4)°
Na(4)–S(1)	2.81(1)	S(1)–Na(4)–S(1)	125.9(4)°
Na(4)–S(1)	2.94(1)	S(1)–Na(4)–S(2)	104.4(5)°
Na(4)–S(2)	2.91(1)	S(1)–Na(4)–S(1)	92.9(4)°
		S(1)–Na(4)–S(2)	133.3(5)°
		S(1)–Na(4)–S(2)	95.8(4)°

[a] Experimental standard deviations are given in parentheses.

TABLE 4

$(AuS_2)^{3-}$ anion coordination

Bond	Distance (Å)	Angle bonds	Angle
Au(1)–S(1)	2.310(7)[a]	S(1)–Au(1)–S(1)	180°
Au(1)–S(1)	2.310(7)		

[a]Estimated standard deviations are given in parentheses.

TABLE 5

Geometry of the $^1_\infty(AuS)^-$ chain

Bond	Distance (Å)	Angle bonds	Angle
Au(2)–S(2)	2.288(8)[a]	S(2)–Au(2)–S(3)	170.3(2)°
Au(2)–S(3)	2.310(9)		
Au(3)–S(2)	2.30(1)	S(2)–Au(3)–S(3)	179.3(3)°
Au(3)–S(3)	2.30(1)	Au(1)–S(2)–Au(3)	101.8(3)°
		Au(1)–S(3)–Au(3)	103.2(4)°

[a]Estimated standard deviations are given in parentheses.

The other is an infinite chain built by the remaining gold and sulphur arranged in an alternating sequence of doubly coordinate atoms, formally corresponding to the thioaurate chain found in KAuS [10]. In the crystal structure both anionic groups are oriented in planes parallel to (001) (Fig. 1). Their relative occurrence is in the ratio 1:4; hence the crystal chemical formula of $Na_7Au_5S_6$ may be written as $(Na^+)_7(AuS_2)^{3-}[^1_\infty(AuS)^-]_4$.

The $^1_\infty(AuS)^-$ chain in the present compound shows an interesting conformation which is rather different from that found in KAuS. While the latter is a zigzag chain with all atoms lying in the same plane (S–Au–S bond angle, 180°; Au–S–Au bond angle, 90°), the infinite anion here may be described as a twisted chain with a four-fold translation period, as shown in Fig. 2(a). The Au–S–Au bond angles of 101.8(3)° and 103.2(4)° approach the tetrahedral angle indicating sp^3 hybridization of the S atoms. The sulphur coordination of Au(3) is linear while the bond angle on Au(2) is slightly bent (S–Au–S bond angle, 170.3°). In the structure the chains run parallel to the [110] and [−110] directions, crossing over each other on the Au(2) positions as shown in Fig. 2(b). The isolated $(S\text{–}Au\text{–}S)^{3-}$ groups show a herringbone-like arrangement in the planes through $z=0$ and $z=\frac{1}{2}$.

The Au–S bond lengths in both anionic groups are uniform and close to 2.30 Å, a value also found in the other thioaurates(I). The Au–S bond lengths show no dependence on the connectivity of the S atoms; bonds to the terminal S atoms and to bridging S atoms are of essentially equal length.

The crystal structure contains four independent Na^+ ions which are each surrounded by four S atoms in a flattened tetrahedral coordination. In the

TABLE 6

Cation–cation contacts up to 4 Å

Bond	Distance (Å)
Na(1)–Au(3)	3.12(1)[a, b]
Na(1)–Au(3)	3.17(1)[b]
Na(1)–Na(3)	3.34(2)[b]
Na(1)–Au(2)	3.76(2)[b]
Na(2)–Au(1)	3.21(2)
Na(2)–Au(2)	3.30(2)
Na(2)–Na(2)	3.52(2)[b]
Na(2)–Na(4)	3.53(2)
Na(2)–Au(3)	3.93(2)
Na(2)–Na(3)	3.96(3)
Na(3)–Au(2)	3.09(2)
Na(3)–Au(1)	3.18(2)
Na(3)–Au(3)	3.22(2)
Na(3)–Na(4)	3.32(3)
Na(3)–Na(4)	3.65(3)
Na(4)–Au(1)	3.05(2)
Na(4)–Au(2)	3.14(2)
Na(4)–Na(4)	3.40(3)
Au(2)–Au(2)	3.448(2)
Au(2)–Au(3)	3.539(5)
Au(2)–Au(3)	3.556(5)
Au(2)–Au(3)	3.613(5)
Au(2)–Au(3)	3.632(5)
Au(3)–Au(3)	3.513(2)

[a] Estimated standard deviations are given in parentheses.
[b] Twice.

[001] direction the Na^+ ions separate the $(AuS_2)^{3-}$ groups from the chains – except Na(1), which is located in an interstitial site between the thioaurate chains. The average Na–S distances in the individual tetrahedra vary from 2.82 to 2.88 Å; these values are comparable with the sum of the ionic radii for tetracoordinate Na^+ (r = 1.13 Å) and S^{2-} (r = 1.70 Å) [12].

In contrast to KAuS [10] and $K_4Au_6S_5$ [9] no Au–Au contacts closer than 3.45 Å are found. Since typical distances, for which Au–Au attractions are discussed, occur in the range 3.0–3.2 Å, such interactions may rather be ruled out for the present compound.

The crystal structure of $Na_7Au_5S_6$ represents one of the rare examples of a structure which can be derived from a b.c.c. anion packing. Since for ionic structures this type of packing is commonly regarded as unfavourable with respect to c.c.p. and h.c.p. anion packings, the underlying geometry of the crystal structure of $Na_7Au_5S_6$ will be described in more detail.

As can be seen from Fig. 3, the arrangement of S atoms may be expressed as a tiling of body-centred cubes. The unit cell contains 12 (slightly distorted) cubes, which are oriented in such a way that two coplanar face diagonals are oriented in the [010] and [001] directions respectively, while the edge

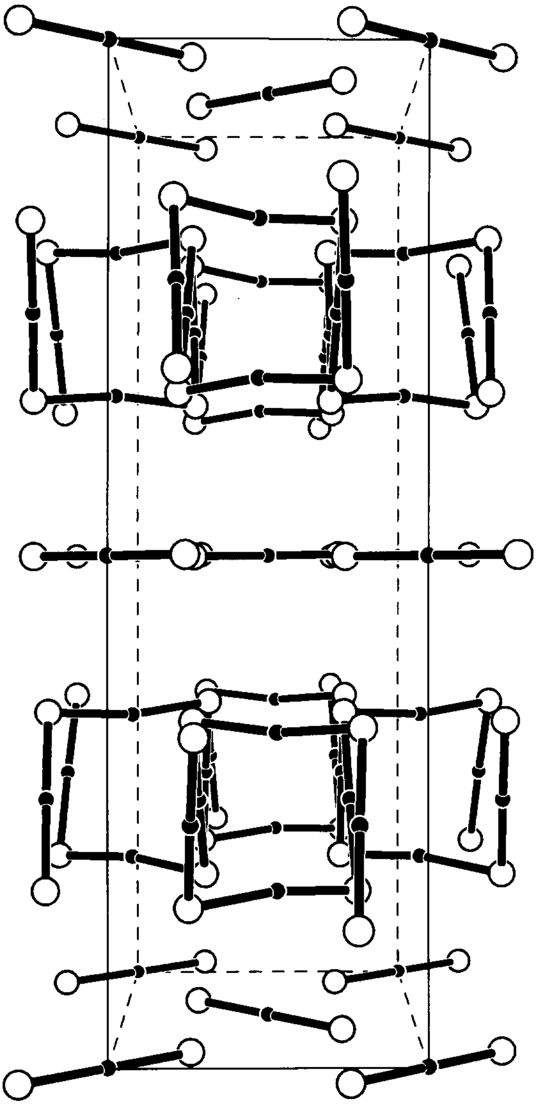

Fig. 1. Perspective view of the crystal structure of $Na_7Au_5S_6$ along the [100] direction: ●, Au atom; ○, S atom. Sodium positions are omitted for the sake of clarity.

normal to them is collinear with the *a* axis which comprises two edge lengths.

Based on the unit cell volume of 1630 $Å^3$ the edge length for an undistorted body-centred cube is calculated as $a_0 = 5.14$ Å. The ideal lattice constants can be expressed as $a = 2a_0 = 10.28$ Å, $b = 2^{1/2}a_0 = 7.27$ Å and $c = 2^{1/2}(3a_0) = 21.81$ Å. The actual cell dimensions follow these values closely within a few per cent.

The b.c.c. packing can be conceived as a space-filling arrangement of flattened tetrahedra with the edges a_0 (twice) and $(3^{1/2}/2)a_0$ (four times).

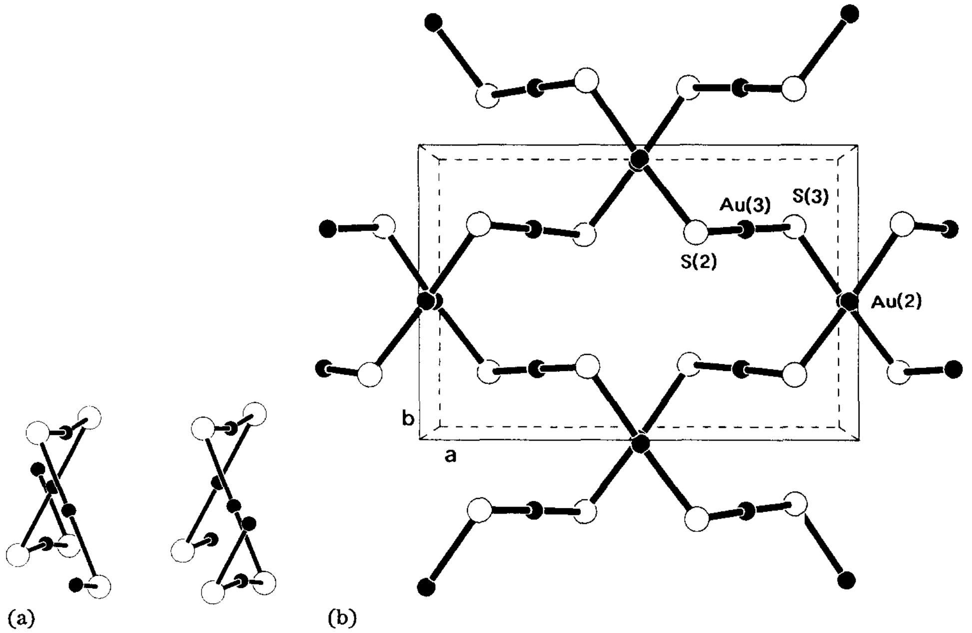

Fig. 2. (a), two $^1_\infty(\mathrm{AuS})^-$ chains viewed in projection along [110]; (b), view of the $^1_\infty(\mathrm{AuS})^-$ chains as seen in projection along [001].

The centres of the tetrahedra are located on the faces of the basic body-centred cube at the positions $(0, \pm\frac{1}{4}, \frac{1}{2})\curvearrowright$(Fig. 4) and represent the potential cationic sites. However, because of their short distances neighbouring centres are not simultaneously accessible for occupation.

In $Na_7Au_5S_6$ a fraction of these sites is occupied by sodium, whereas gold — in order to attain a linear coordination — is shifted from the centre of the tetrahedron to one of its shorter edges, thus centring half of one body diagonal of the body-centred cube.

Simple considerations on the idealized crystal structure lead to an Na–S distance of $(5^{1/2}/4)a_0 = 2.87$ Å which compares well with the actual mean Na–S distance of 2.85 Å. Idealized S–Na–S bond angles in the tetrahedron are 2 arctan $2 = 126.7°$ (twice) and 2 arcsin $[(3/5)^{1/2}] = 101.5°$ (four times). Though the actual angles are different, these values may principally explain the sequence of the S–Na–S bond angles found in the structure. The idealized Au–S distance is calculated as $(3^{1/2}/4)a_0 = 2.23$ Å, which is too short for an Au–S bond length. Hence the distortion of the actual packing from the idealized b.c.c. model may be largely due to the necessity of attaining Au–S bond distances of reasonable length.

With respect to the occupation of the body-centred cubes by the cations, two different types can be distinguished in the structure (Fig. 5). Type 1 contains the $(S\text{–}Au\text{–}S)^{3-}$ group as its body half-diagonal; all faces are occupied by Na^+. Type 2 contains an S–Au–S–Au–S fragment of the chain and has only four occupied faces.

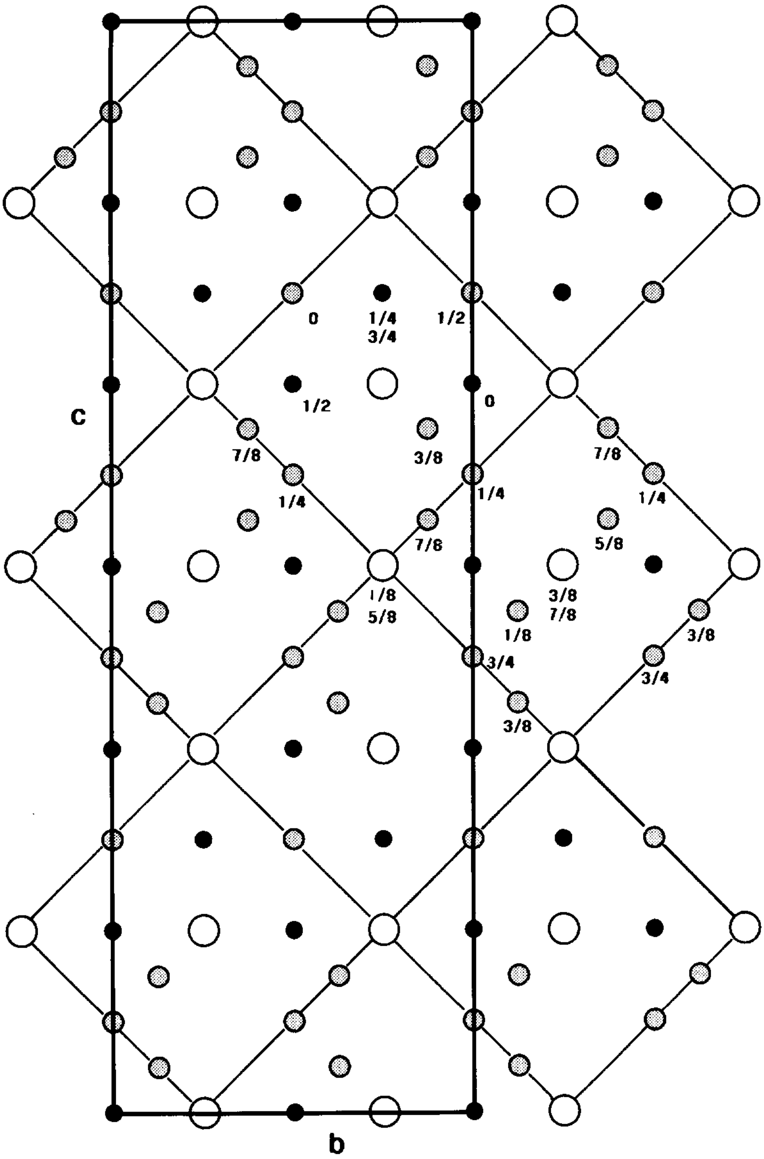

Fig. 3. View of the idealized structure of $Na_7Au_5S_6$, stressing the underlying b.c.c. packing of S atoms: ○, S atom; ●, Au atom; ◎, Na atom. The crystallographic *a* axis comprises twice the edge length of the basic body-centred cube.

The validity of the structure interpretation developed above may also be estimated from Table 7 which lists the positional parameters calculated for the idealized model, showing a good agreement with the experimental values.

The appearance of the unusual b.c.c. anion packing in $Na_7Au_5S_6$ may be due to its peculiar geometric conditions which meet the coordination

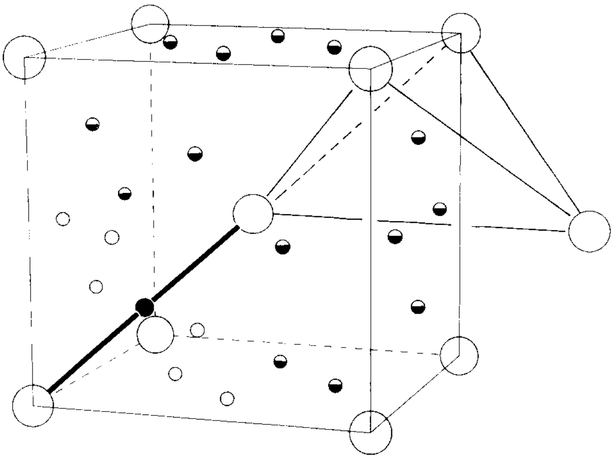

Fig. 4. The body-centred cube and its potential tetrahedral centres. The small open circles indicate that positions are at unfavourably short distances to the Au atom (●) and therefore must remain void. One of the remaining sites on each face of the cube may be occupied by Na$^+$. (The sites on the rear are omitted.)

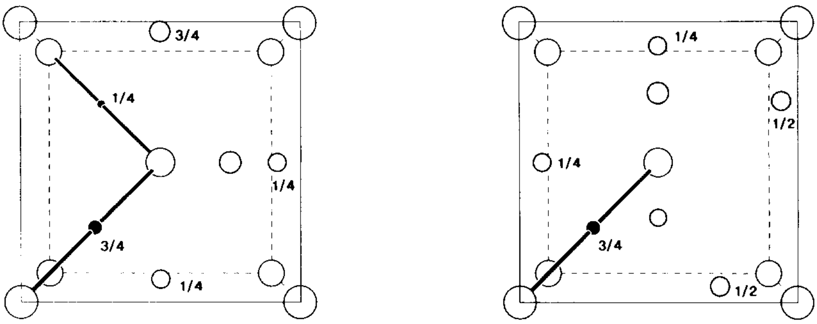

Fig. 5. Two different types of body-centred cube in the structure of $Na_7Au_5S_6$ containing a fragment of the $^1_\infty(AuS)^-$ chain (left) or the isolated $(AuS_2)^{3-}$ group (right) respectively. The numbers indicate the heights in fractions of the cube edge a_0.

demands of the metal atoms. It is interesting to note that the crystal structure of Na_3AuS_2 [8] is based on the same type of packing. Compared with the very different composition, the volume change of the elementary body-centred cube with respect to $Na_7Au_5S_6$ is relatively small. This means that the packing is rather insensitive to changes in the Na:Au ratio provided the metal:sulphur ratio is maintained.

In this context it may be of interest that investigations in the Na_2S–Au_2S pseudobinary section indicate the existence of still another thioaurate with higher gold content. This thioaurate crystallizes with a large unit cell ($V \approx 4V_{Na_7Au_5S_6}$). Pronounced substructure effects have, however, so far been a severe obstacle to solving the crystal structure by direct methods. It is likely that this new compound is based on a b.c.c. sulphur packing as well, and we are confident that in this case the application of the geometric packing

TABLE 7

Idealized positional parameters for $Na_7Au_5S_6$ obtained under the assumption of an undistorted b.c.c. packing of chalcogen atoms

Atom	x	y	z
Na(1)	0.000	0.000	0.2500
Na(2)	0.250	0.500	0.5833
Na(3)	0.375	0.375	0.3750
Na(4)	0.625	0.125	0.5417
Au(1)	0.500	0.500	0.5000
Au(2)	0.000	0.500	0.3333
Au(3)	0.250	0.750	0.2500
S(1)	0.375	0.250	0.5000
S(2)	0.125	0.250	0.3333
S(3)	0.375	0.750	0.6667

principles discussed here will finally lead to a successful determination of the structure.

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References

1 P. K. Mehrotra and R. Hofmann, *Inorg. Chem.*, *17* (1978) 2187.
2 P. Pyykkö and Y. F. Zhao, *Angew. Chem.*, *103* (1991) 622.
3 H. Schmidbaur, *Angew. Chem.*, *88* (1976) 830.
4 H. Schmidbaur, *Gold Bull.*, *23* (1990) 11.
5 P. Main, *Multan 11/82*, Department of Physics, University of York, 1982.
6 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974.
7 *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, 1990.
8 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, *132* (1987) 173.
9 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, *137* (1987) 13.
10 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, *127* (1987) 65.
11 W. Bronger and H. U. Kathage, personal communication, 1991.
12 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, *25* (1969) 925.