

Fig. 3. Layers of Au atoms in (a) $K[Au(CN)_2]$, $K[Ag(CN)_2]$ and (b) $Cs_2Na[Au(CN)_2]$.

within a layer are indicated). In $K[Au(CN)_2]$, all $Au \cdots Au$ nearest-neighbor distances within layers (3.64 \AA) are equivalent by symmetry; in $K[Ag(CN)_2]$ the $Ag \cdots Ag$ distances are the same to within experimental accuracy [$3.69(2) \text{ \AA}$]. In $Cs_2Na[Au(CN)_2]_3$, two nearest-neighbor $Au \cdots Au$ distances are observed [$3.448(1)$, $3.620(1) \text{ \AA}$]. The structures of $K[Au(CN)_2]$ and $K[Ag(CN)_2]$ show three successive

layers of anions whose stacking may be described as $\dots ABC \dots$; the structure of $Cs_2Na[Au(CN)_2]_3$ shows only two layers stacked as $\dots AC \dots$. Because of the different stacking sequences, the ratio of the c axes of the Au compounds is expected to be ~ 1.5 ; it is observed to be 1.44. The discrepancy may be understood in terms of the orientation of the linear $[Au(CN)_2]^-$ ions relative to the stacking axis. In $K[Au(CN)_2]$, they are tilted 20° to this axis. This reduces the thickness of the $[Au(CN)_2]^-$ layers compared to $Cs_2Na[Au(CN)_2]_3$ where the $[Au(CN)_2]^-$ ions are parallel to the stacking axis. There are two different types of environment for the K^+ ions in $K[Au(CN)_2]$, one similar to that of Na^+ and one similar to that of Cs^+ , respectively, in $Cs_2Na[Au(CN)_2]_3$. The tilting of the $[Au(CN)_2]^-$ ions in $K[Au(CN)_2]$ distorts the environment observed for Cs^+ in $Cs_2Na[Au(CN)_2]_3$ towards octahedral coordination, in agreement with the coordinative preferences of K^+ . For the same reasons $Ag(CN)_2$ groups in $K[Ag(CN)_2]$ are tilted by $\sim 27^\circ$ with respect to the stacking axis.

The implications of the crystal structure for the luminescence properties are discussed elsewhere (Blom, 1983).

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Structure of the Tin Antimony Sulphide $Sn_6Sb_{10}S_{21}$

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Abstract. $M_r = 2603.0$, monoclinic, $C2/m$, $a = 4.80 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 124.5 \text{ cm}^{-1}$, $44.995(5)$, $b = 3.9023(5)$, $c = 20.613(3) \text{ \AA}$, $\beta = F(000) = 4584$, $T = 293 \text{ K}$. Final $R = 0.0704$ for 1573 observed data. The structure (previously reported as

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SnSb_2S_4) consists of bands of edge-sharing half-octahedra that extend parallel to [010]. The repeat unit consists of two bands of composition $(M_{10}S_{12})_n$ and three of composition $(M_4S_6)_n$. Comparison is made with the structure of $\text{Sn}_4\text{Sb}_6\text{S}_{13}$.

Introduction. There have been several reports of the existence of a compound SnSb_2S_4 in the system $\text{SnS}-\text{Sb}_2\text{S}_3$ (Gaudin & Hamlyn, 1938; Vogel & Gilde, 1949; Sachdev & Chang, 1975; Bok & de Wit, 1963). In a study of the ternary phases in the system $\text{SnS}-\text{Sb}_2\text{S}_3$, Wang & Eppelsheimer (1976) described three compounds in the series $(\text{SnS})_m(\text{Sb}_2\text{S}_3)_n$ with $m:n$ ratios of 3:1, 2:1 and 1:1 and gave unit-cell data for these phases. The unit cell for ' SnSb_2S_4 ' was reported to be monoclinic, space group $P2_1$ or $P2_1/m$, with $a = 20.70$, $b = 3.90$, $c = 22.46$ Å, $\beta = 96.17^\circ$. In the present paper we report the structure determination of this compound and show that it has the composition $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ ($m:n = 6:5$ rather than 1:1); the unit cell, whilst clearly related to that reported by Wang & Eppelsheimer (1976), is C face-centred rather than primitive.

The first structure determination of a compound in this system was that of a further phase $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ (4:3) by Jumas, Olivier-Fourcade, Philippot & Maurin (1980). Structures reported subsequently for the 2:1 (Smith & Hyde, 1983) and 3:1 (Smith, 1984; Parise, Smith & Howard, 1984) phases show that these structures are all built from $B16$ (GeS) or $B33$ (TII)-like subunits. The end member SnS has the $B16$ structure at room temperature and inverts to $B33$ at 905 K (von Schnering & Wiedemeier, 1981). A detailed comparison of the crystal structures of the compounds in this system is in preparation.

Doubts as to the exact composition of the ' SnSb_2S_4 ' phase are raised by the following argument, based on the rather uniform packing density of S atoms in the three compounds of previously known structure. These structures all have a relatively short b axis of ~ 4 Å and it is useful to consider the number of S atoms per unit area in the projections of these structures on the (010) plane. For the 3:1, 2:1 and 4:3 phases this parameter has the value 0.0889, 0.0894 and 0.0913 Å⁻², respectively. For the primitive monoclinic cell given above this indicates a cell content of 42 S atoms (or 84 in the true C face-centred cell), corresponding to a packing parameter of 0.0909 Å⁻². If we now assume that the compound is stoichiometric and can be represented by the formula $(\text{SnS})_m(\text{Sb}_2\text{S}_3)_n$ then the only reasonable composition close to the nominal value of 1:1 is 6:5 or $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$.

Experimental. Black, needle-shaped crystals were grown from a charge of tin, antimony and sulphur (to give composition SnSb_2S_4) sealed in an evacuated silica-glass capsule and heated at 763 K for 120 h.

Guinier photographs of the sample revealed the presence of some Sb_2S_3 suggesting the composition of the needles may be tin-rich with respect to SnSb_2S_4 . Although many of the needles were multiply twinned about the elongated b axis a single crystal ($0.5 \times 0.02 \times 0.02$ mm) was obtained. The suitability of crystals for data collection was checked with $h0l$ and $h1l$ Weissenberg photographs. Zero-level photographs are consistent with the assignment of space group $P2_1/m$ by Wang & Eppelsheimer (1976). However, upper-level photographs and subsequent diffractometer measurements require a doubling of the c -axial dimension and a redefinition of the space group as $C2/m$ (absences hkl , $h+k=2n+1$). The doubled c axis becomes the a axis of the C face-centred cell. Cell parameters were obtained from Guinier-camera data, using the calculated structure factors of the final structural model to assign indices to 26 Bragg reflections in the range $24^\circ < 2\theta < 49^\circ$ ($\text{Cu K}\alpha_1$, $\lambda = 1.54056$ Å; Si standard, $a = 5.4305$ Å).

Intensity measurements made using a Philips PW1100 diffractometer; 3791 reflections measured in range $3^\circ < \theta < 25^\circ$, $h \pm 49$, $k 0 \rightarrow 4$, $l 0 \rightarrow 24$; 792 had $I < 0$ and were rejected outright from structure solution or refinement; 1359 had $I < 2\sigma(I)$ and, although included for structure solution, were excluded from structure refinement; $\theta-2\theta$ scan technique, scan range $\pm 0.45^\circ$ in 2θ from the calculated Bragg angle (with an allowance of $0.34 \tan\theta^\circ$ for dispersion), scan rate $0.02^\circ \text{ s}^{-1}$, 8 s background counting time on each side of the peak; three standard reflections measured periodically showed no systematic variation in intensity during data collection; data corrected for Lorentz and polarization effects. Although several absorption models were attempted using the program *SHELX76* (Sheldrick, 1976), there was uncertainty in indexing crystal faces parallel to the b axis as well as in the measurements of crystal dimensions; there was no improvement in the overall fit to the data of the subsequently derived model upon application of the correction, so it was abandoned. Atomic scattering factors for neutral Sn, Sb and S from *International Tables for X-ray Crystallography* (1974). All calculations performed on the Australian National University Univac 1100 computer; programs used: *SHELX76* (Sheldrick, 1976), *ORTEP* (Johnson, 1965) and *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977).

Structure solved using the automatic centrosymmetric direct-methods package in *SHELX76* to find metal-atom positions; S atoms located in subsequent difference Fourier syntheses. Full-matrix least-squares refinement on F of positional and isotropic thermal parameters followed by several cycles in which metal atoms were refined with anisotropic thermal parameters using individual reflection weights $[\sigma^2(F) + 0.002F^2]^{-1}$ resulted in final $R = 0.0704$, $wR = 0.0488$ [$R = \sum A / \sum |F_o|$, $wR = (\sum wA^2 / \sum wF_o^2)^{1/2}$, where $A =$

$|F_o - F_c|$. Several models for ordered arrangements of Sn and Sb in the 16 available metal sites were tested. Models chosen on the basis of thermal parameters (the larger thermal parameters being indicative of the presence of Sn), intuition and guesswork were essentially indistinguishable on the basis of their ability to affect the overall fit to the data. No evidence is found which can justify the assignment of any particular metal site to either Sn or Sb. Fractional site occupancies consistent with the 6:5 (SnS:Sb₂S₃) chemistry of Sn₆Sb₁₀S₂₁ were used to define the scattering from the 16 metal sites. In final cycle of least-squares refinement no parameter shift exceeded 0.2% of the e.s.d. of that parameter. Residual electron density ranged from -2.5 to 2.5 e Å⁻³ in final difference Fourier synthesis.

Discussion. Final parameters (with their e.s.d.'s) are presented in Table 1.* *M*-*S* distances are given in Table 2.

Fig. 1 shows the structure projected along [010]. In the upper part of the figure the structure is depicted as isolated bands of edge-sharing *MS*₅ half-octahedra that extend parallel to [010], the elongation direction of the crystals. The metal atoms lie close to the square face of the pyramids but are offset towards one edge as a result of the stereochemical activity of the lone pair of electrons, giving [1 + 2 + 2] coordination. The repeat unit consists of two diad-related bands of composition (*M*₁₀*S*₁₂)_n, two of composition (*M*₄*S*₆)_n, also diad-related, and an independent (*M*₄*S*₆) band that lies on a diad axis. As in the case of Sn₄Sb₆S₁₃ (Jumas *et al.*, 1980), these bands are linked by weaker *M*-*S*...*M* and *M*-*E*...*M* interactions, where *E* denotes the lone pair of electrons on the metal atom.

The lower left part of Fig. 1 shows how these sheets of half-octahedra combine to form elements of the SnS-type structure, which consists of alternate layers of trigonal prisms and half-octahedra (Wiedemeier & von Schnering, 1978). The two symmetry-related (*M*₄*S*₆)_n bands are juxtaposed to create four face-sharing trigonal prisms with their axes parallel to [010]. The (*M*₁₀*S*₁₂)_n bands are arranged *en échelon* with two distinct types of overlap: one forming four trigonal prisms parallel to [010], and the other forming a unit of three trigonal prisms that have their axes in the (010) plane. The structural unit built from the (*M*₁₀*S*₁₂)_n bands thus has the MoB structure in which alternate layers of trigonal prisms are rotated 90° with respect to each other.

It is interesting to note that the SnS (or MoB) units shown in the bottom left part of Fig. 1 contain the shortest *M*-*M* distances of the structure between the

Table 1. Final positional ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	<i>U</i> _{eq} */ <i>U</i>
<i>M</i> (1)†	3213 (1)	0	988 (2)	18
<i>M</i> (2)	2214 (1)	0	527 (2)	13
<i>M</i> (3)	5626 (1)	½	1194 (2)	17
<i>M</i> (4)	2217 (1)	0	2607 (2)	18
<i>M</i> (5)	3025 (1)	½	3006 (2)	29
<i>M</i> (6)	6393 (1)	0	1715 (2)	24
<i>M</i> (7)	4849 (1)	½	838 (2)	15
<i>M</i> (8)	6786 (1)	0	3597 (2)	27
<i>M</i> (9)	7729 (1)	½	4546 (2)	26
<i>M</i> (10)	9322 (1)	½	3924 (2)	23
<i>M</i> (11)	307 (1)	½	4422 (2)	20
<i>M</i> (12)	5917 (2)	0	-322 (2)	27
<i>M</i> (13)	3539 (1)	½	4871 (2)	28
<i>M</i> (14)	5922 (2)	½	3365 (2)	38
<i>M</i> (15)	8879 (1)	0	2359 (2)	25
<i>M</i> (16)	9886 (1)	0	2871 (2)	27
<i>S</i> (1)	1935 (3)	0	4458 (7)	19 (4)
<i>S</i> (2)	5447 (4)	0	210 (8)	20 (4)
<i>S</i> (3)	6815 (3)	0	243 (7)	9 (3)
<i>S</i> (4)	2572 (3)	½	3699 (8)	19 (4)
<i>S</i> (5)	2308 (3)	0	-629 (7)	17 (4)
<i>S</i> (6)	2100 (3)	½	1839 (7)	12 (4)
<i>S</i> (7)	2 (3)	½	1616 (8)	19 (4)
<i>S</i> (8)	2754 (3)	0	2297 (7)	17 (4)
<i>S</i> (9)	3517 (3)	0	2446 (7)	18 (4)
<i>S</i> (10)	4436 (3)	0	2779 (6)	10 (3)
<i>S</i> (11)	181 (3)	0	5934 (8)	22 (4)
<i>S</i> (12)	1752 (3)	½	5857 (7)	16 (4)
<i>S</i> (13)	-664 (3)	0	1125 (7)	18 (4)
<i>S</i> (14)	1259 (3)	½	3986 (7)	15 (4)
<i>S</i> (15)	1413 (3)	0	9034 (7)	16 (4)
<i>S</i> (16)	-695 (3)	0	5427 (7)	19 (4)
<i>S</i> (17)	1075 (3)	0	6350 (7)	18 (4)
<i>S</i> (18)	853 (3)	½	1999 (6)	8 (3)
<i>S</i> (19)	1482 (3)	0	2562 (7)	14 (4)
<i>S</i> (20)	-340 (3)	½	6749 (7)	19 (4)
<i>S</i> (21)	1098 (3)	0	671 (7)	15 (4)

* *U*_{eq} (for metal positions) = $\frac{1}{3}(U_{11} + U_{22} + U_{33})$.

† Sn and Sb are assumed to be randomly distributed over the 16 available metal sites.

metal atoms of adjacent trigonal prisms. These distances are *M*(3)-*M*(7) 3.492 (5), *M*(4)-*M*(8) 3.548 (6), *M*(9)-*M*(9) 3.520 (7) and *M*(10)-*M*(11) 3.629 (6) Å, all other *M*-*M* distances being greater than 3.84 Å. These may be compared with the equivalent distance in SnS itself of 3.494 Å (Wiedemeier & von Schnering, 1978). Similar short *M*-*M* distances occur in Sn₄Sb₆S₁₃, and they may be ascribed to interactions of the kind *M*-*E*...*M* (Jumas *et al.*, 1980).

The lower right corner of Fig. 1 shows how the coordination polyhedra of all the metal atoms may be considered as capped trigonal prisms, with the prism axes either parallel to [010] or lying in the (010) plane. With the exception of *M*(14) these prisms have a single cap on a square face, the cap being a half-octahedron of one of the bands described above. Fig. 2 shows a typical example, the coordination polyhedron around *M*(3). In this case the two longest *M*-*S* distances are related by mirror symmetry; in the prisms that have their axis in (010) this no longer holds and the two longest bonds are independent [*e.g.* *M*(9), see Table 2].

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39631 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) with *e.s.d.*'s

$M(1)-S(3)$	2.53 (1)	$M(9)-S(12)$	2.56 (1)
-S(15)	2.58 (1) × 2	-S(4)	2.66 (1) × 2
-S(5)	3.08 (2) × 2	-S(1)	3.11 (1) × 2
-S(9)	3.16 (2)	-S(1)	3.56 (1)
-S(8)	3.57 (2)	-S(4)	4.00 (1)
$M(2)-S(5)$	2.46 (1)	$M(10)-S(10)$	2.47 (1)
-S(3)	2.67 (1) × 2	-S(17)	2.66 (1) × 2
-S(5)	2.89 (1) × 2	-S(11)	2.96 (1) × 2
-S(6)	3.42 (1) × 2	-S(16)	3.67 (1) × 2
$M(3)-S(21)$	2.49 (1)	$M(11)-S(20)$	2.44 (1)
-S(18)	2.69 (1) × 2	-S(16)	2.61 (1) × 2
-S(2)	2.87 (1) × 2	-S(11)	2.97 (1) × 2
-S(7)	3.60 (1) × 2	-S(11)	3.77 (1) × 2
$M(4)-S(6)$	2.53 (1) × 2	$M(12)-S(2)$	2.48 (2)
-S(8)	2.56 (2)	-S(13)	2.73 (1) × 2
-S(4)	3.26 (1) × 2	-S(21)	2.88 (1) × 2
-S(19)	3.30 (1)	-S(15)	3.35 (1) × 2
-S(1)	4.15 (1)	-S(3)	4.08 (1)
$M(5)-S(4)$	2.61 (2)	$M(13)-S(1)$	2.66 (1)
-S(8)	2.65 (1) × 2	-S(12)	2.71 (1) × 2
-S(12)	3.13 (1) × 2	-S(14)	3.12 (1) × 2
-S(9)	3.25 (1) × 2	-S(17)	3.21 (1)
-S(17)	4.12 (2)	-S(16)	3.51 (1)
$M(6)-S(18)$	2.56 (1)	$M(14)-S(14)$	2.71 (1) × 2
-S(19)	2.62 (1) × 2	-S(16)	2.79 (1)
-S(21)	3.10 (1) × 2	-S(19)	3.16 (1)
-S(6)	3.16 (1)	-S(20)	3.25 (1) × 2
-S(3)	3.75 (1)	-S(18)	3.41 (1) × 2
$M(7)-S(13)$	2.45 (1)	$M(15)-S(9)$	2.56 (1) × 2
-S(7)	2.57 (1) × 2	-S(17)	2.65 (1)
-S(2)	3.10 (1) × 2	-S(15)	3.03 (1)
-S(2)	3.67 (1) × 2	-S(10)	3.22 (1) × 2
		-S(13)	3.44 (1)
$M(8)-S(14)$	2.58 (1)	$M(16)-S(11)$	2.51 (1)
-S(1)	2.67 (1) × 2	-S(10)	2.80 (1) × 2
-S(19)	3.10 (1) × 2	-S(20)	2.87 (1) × 2
-S(4)	3.52 (1)	-S(7)	3.33 (1) × 2
-S(6)	4.03 (1)	-S(13)	4.14 (1)

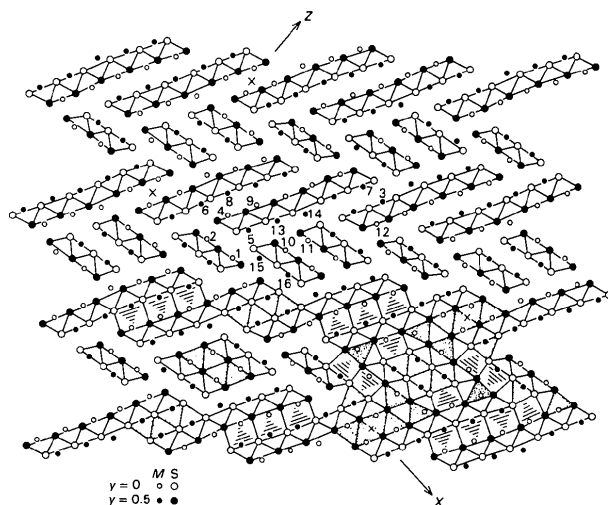


Fig. 1. Projection of the structure of $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ on (010). Dot shading denotes trigonal prisms viewed end on (prism axis parallel to [010]); line shading denotes trigonal prisms with their axes lying in (010). The four crosses mark the corners of one unit cell.

The coordination of $M(14)$ is somewhat different, being a bicapped trigonal prism with the metal atom located approximately midway between the two capped faces (Fig. 3). As a result of this configuration the shortest $M-S$ distance for this atom is 2.71 (1) Å, the distance to the S atoms common to the two capped faces. $M(14)$ has a relatively large temperature factor, with the thermal ellipsoid elongated between the two caps. The coordination of $M(14)$ is very similar to that of $\text{Sb}(6)$ in $\text{Sn}_4\text{Sb}_6\text{S}_{13}$, which also has an elevated thermal parameter. In both cases the distinctive coordination arises from the fact that the metal atom in question can be considered to belong to half-octahedra of two alternative sheets.

Another feature of the structure of $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$ that is also observed in $\text{Sn}_4\text{Sb}_6\text{S}_{13}$ is that the thermal parameters for the metal atoms are greater than those of the S atoms. The reasons for this have been discussed by Jumas *et al.* (1980) and will not be pursued here.

In conclusion, the phase 'SnSb₂S₄' of Wang & Eppelsheimer (1976) has the formula $\text{Sn}_6\text{Sb}_{10}\text{S}_{21}$. This compound is structurally related to $\text{Sn}_4\text{Sb}_6\text{S}_{13}$, both structures consisting of bands of edge-sharing MS_3 pyramids extending along [010].

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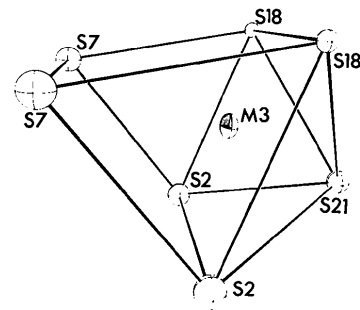


Fig. 2. Coordination polyhedron of metal atom $M(3)$.

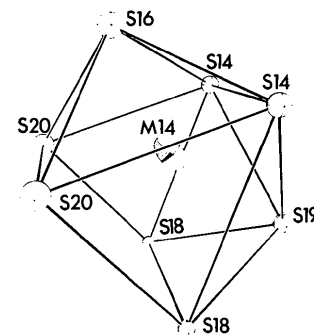


Fig. 3. Coordination polyhedron of metal atom $M(14)$.

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Digold(III) Strontium Hydroxide, Au₂Sr(OH)₈*

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Abstract. $M_r = 617.6$, tetragonal, $I422$, $a = 5.588$ (1), $c = 11.853$ (3) Å, $V = 370.1$ (1) Å³, $Z = 2$, $D_x = 5.542$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 465$ cm⁻¹, $F(000) = 536$, $T = 293$ K, $R = 0.027$ for 324 observed reflections. The structure contains Au(OH)₄⁻ ions with crystallographic symmetry 4 (but actual symmetry close to $4/mmm$) and Au—O 1.980 (8) Å. The strontium ions are weakly coordinated by eight hydroxide ions [Sr—O 2.641 (8) Å] in a distorted Archimedean antiprism with crystallographic symmetry 422. The absolute structure was determined with an η refinement. The isostructural Au₂Ba(OH)₈ has cell constants $a = 5.722$ (2), $c = 12.104$ (4) Å.

Introduction. Little structural information is available for compounds containing the Au—OH unit. Tetrahydroxoaurate(III) salts as prepared by Jander & Krien (1960) were amorphous or polycrystalline. Organometallic derivatives with bridging hydroxide have been structurally characterized, but the structures were of low accuracy (Glass, Konnert, Miles, Britton & Tobias, 1968; Peteau-Boisdenghien, Meunier-Piret & Van Meerssche, 1975). Professor E. Schwarzmann and co-workers in this Institute have recently succeeded in obtaining single crystals of several hydroxoaurate(III) derivatives; here we report the structure of

Au₂Sr(OH)₈. Details of the preparation will be published elsewhere.

Experimental. Pale-yellow square or rectangular prisms were sealed in glass capillaries. Preliminary photographic investigations showed a tetragonal cell, Laue group $4/mmm$, systematic absences hkl , $h + k + l$ odd, crystals elongated along c .

Crystal 0.08 × 0.06 × 0.02 mm, 720 profile-fitted intensities (Clegg, 1981) measured on Stoe—Siemens four-circle diffractometer ($2\theta \leq 65^\circ$, monochromated Mo $K\alpha$ radiation); three standard reflections with no significant intensity change; empirical absorption corrections (azimuthal scans, transmissions 0.42–0.48); index ranges $|h|, |k| < 8$, $|l| < 17$ in octants hkl and $\bar{h}\bar{k}\bar{l}$; averaging equivalent reflections gave 340 unique reflections ($R_{\text{int}} = 0.026$, Friedel opposites not merged), 324 with $F > 4\sigma(F)$ used for all calculations (*SHELXTL*, Sheldrick, 1978); cell constants refined from 2θ values of 40 reflections in the range 20–24°.

Au and Sr positions, from inspection of Patterson function, consistent with any of five space groups: $I422$, $I4mm$, $I4m2$, $I42m$, $I4/mmm$. Only in $I422$ could a chemically reasonable O atom be located in a subsequent difference synthesis. Refinement on $|F|$ to $R = 0.027$, $wR = 0.026$ [Au and Sr anisotropic, H not located; 11 parameters, $w^{-1} = \sigma^2(F) + 0.0003F^2$, extinction correction in the form $F_{\text{corr}} = F_c(1 + xF_c^2/\sin 2\theta)^{0.25}$ with $x = 2.8$ (3) × 10⁻⁶, $S = 1.1$], max. Δ/σ

* Hydroxy Complexes of Gold. Part 1.