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YNi_5Ge_3 and Isotypes with the Orthorhombic YNi_5Si_3 Structure Type

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Abstract. YNi_5Ge_3, $M_r = 600{\cdot}23$, orthorhombic, $oP36$, $Pnma$, $a = 19{\cdot}136\ (4)$, $b = 3{\cdot}8737\ (4)$, $c = 6{\cdot}801\ (1)$ Å, $V = 504{\cdot}1\ (2)$ Å^3, $Z = 4$, $D_x = 7{\cdot}908$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 48{\cdot}3$ mm^{-1}, $F(000) = 1100$, $T = 293$ K, $wR = 0{\cdot}040$ for 664 contributing unique reflections. The compounds $TbNi_5Ge_3$ [$a = 19{\cdot}118\ (5)$, $b = 3{\cdot}873\ (1)$, $c = 6{\cdot}793\ (2)$ Å], $HoNi_5Ge_3$ [$a = 19{\cdot}067\ (6)$, $b = 3{\cdot}8583\ (8)$, $c = 6{\cdot}790\ (1)$ Å] and $ErNi_5Ge_3$ [$a = 19{\cdot}031\ (5)$, $b = 3{\cdot}846\ (2)$, $c = 6{\cdot}785\ (1)$ Å] are isotypic. YNi_5Ge_3 crystallizes with the YNi_5Si_3 structure type (also called UNi_5Si_3 type) of which one Si position in the original paper of 1974 [Bodak, Yarovets & Gladyshevskii (1974). *Tesizy Dokl. Vses. Konf. Kristallokhim. Intermet. Soedin,* 2nd ed., edited by R. M. Rykhal, pp. 32–33. Lvov State Univ.] is corrected here. The YNi_5Si_3 type is compared with the isopointal YCo_5P_3 type which is shown to be a stacking variant.

Introduction. Madar, Ghetta, Chaudouet & Senateur (1986) and Madar, Ghetta, Dhahri, Chaudouet & Senateur (1987) have proposed a crystal-chemical model to correlate composition and structural features of ternary transition-metal phosphides having the metal to non-metal ratio T:P close to 2. In all phosphides studied the P atoms form face-joined triangular channels which consist – depending on the relative position of the P-atom chains parallel to the channel direction – of intergrown tetrahedra and tetragonal pyramids or of intergrown trigonal prisms. The metal atoms are ordered and, for reasons of steric hindrance, only occupy one of two successive polyhedron centers in a channel. Four different kinds of phosphorus coordination polyhedra around the T atoms can be found: a trigonal prism ($T^{[6p]}$), a tetragonal pyramid ($T^{[5y]}$), a tetrahedron ($T^{[4t]}$) and a planar triangle ($T^{[3l]}$). The crystal-chemical formulae of these phosphides can thus be written as

$$T_m^{[6p]}\,T'^{[5y]}_{m'}\,T''^{[4t]}_{m''}\,T^{*[3l]}_{m^*}\,P_n$$

where

$$m + m' + m'' + m^* = 2n. \qquad (1)$$

Madar *et al.* (1986, 1987) assigned a formal valence to each T atom. The valence has no relation to the element's position in the Periodic Table, but depends on the P-atom coordination polyhedron of the T atom; that is +3 for $T^{[6p]}$, +2 for $T^{[5y]}$, +1 for $T^{[4t]}$ and 0 for $T^{[3l]}$. The authors demonstrated that for all phosphides considered the sum of the formal charges of all T atoms equals three per P atom, three being the number of valence electrons necessary to complete the octet of a P atom. Thus

$$3m + 2m' + 1m'' + 0m^* = 3n. \qquad (2)$$

One notes that the number of formal valences of a cation is determined by its anion coordination, whereas the formal valence electron need of the anion is correlated with its position in the Periodic Table.

The orthorhombic YNi_5Si_3 (or UNi_5Si_3) structure (Bodak, Yarovets & Gladyshevskii, 1974; Aksel'rud, Yarovets, Bodak, Yarmolyuk & Gladyshevskii, 1976) poses a problem. It has the structural features of the phosphides discussed above. The sum of the formal charges divided by the number of anions is three; however, four valence electrons would be needed to complete the octet of an Si atom. Since there are further differences in the published positional parameters of one Si atom between the 1974 and the 1976 publications on the YNi_5Si_3 structure we found it of interest to restudy this structure type by investigating previously unknown germanides.

Experimental. Samples of nominal composition RNi_5Ge_3 (R = Y, Tb, Ho, Er) were prepared by arc melting under argon (R 99·99%, Ni 99·98% and Ge 99·999%). The weight losses are 0·3, 1·0, 0·7 and 0·7% respectively. The samples were annealed at 1073 K for 720 h in silica tubes under argon at 300 Torr ($4{\cdot}0 \times 10^4$ Pa). A single crystal of rectangular shape ($16 \times 52 \times 12$ μm) was obtained from the crushed YNi_5Ge_3 sample and mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator. The cell parameters were refined from 2θ values of 24 reflections (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $24 < 2\theta < 49°$) using the program *PARAM*. 1366 reflections were collected out to $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1} ($0 \le h \le 26$, $0 \le k \le 5$, $0 \le l \le 9$ and $-h$–k–l) in the ω–2θ scan mode, yielding 749 unique reflections ($R_{\text{int}} = 0{\cdot}033$). Two standard reflec-

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tions (312 and $\bar{3}1\bar{2}$) were measured with maximum intensity variations 0·9 and 0·8% respectively. Absorption corrections were made using the program *ABSCOR*, transmission factors 0·0293–0·2819. The atomic scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). The refinement of the structure was based on $|F|$ values using isotropic atomic displacement parameters and the program *CRYLSQ*. There are 29 variables refined to $R = 0\cdot072$ and $wR = 0\cdot040$ [$w = 1/\sigma^2(|F_{\rm rel}|)$, $S = 1\cdot59$] considering 664 contributing reflections. The maximum value of shift/e.s.d. in last cycle is 0·0002.* The positional and displacement parameters of YNi_5Ge_3 are given in Table 1.

The programs used to refine the structure are all from the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Isotypic compounds

The powder patterns obtained from Guinier photographs of $TbNi_5Ge_3$, $HoNi_5Ge_3$ and $ErNi_5Ge_3$ correspond to the simulated powder diagrams calculated for the YNi_5Si_3 type using the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). The cell parameters given in the *Abstract* were obtained by refining the powder diffraction lines measured on an automatic scanner (program from Johansson, Palm & Werner, 1980) using an Si standard ($a = 5\cdot4308$ Å) and the program *FINAX* (Hovestreydt, 1983).

Discussion. As mentioned above two versions of the orthorhombic YNi_5Si_3 structure have been published, one in 1974 and the second in 1976. We have calculated the interatomic distances between the atoms for both versions and we conclude that the positional coordinates of one Si atom given in the 1974 publication are incorrect because unreasonably short Si–Ni interatomic distances of 1·46 and 1·51 Å result whereas the corresponding distances based on the data published in 1976 are 2·01 and 2·12 Å. The structure data and interatomic distances of YNi_5Ge_3 (Table 2) suggest this compound to be isotypic with YNi_5Si_3 in the version of 1976 (Aksel'rud *et al.*).

In Fig. 1 two projections of the YNi_5Ge_3 structure along [010] are presented, which differ only in the way the atoms have been connected.

In Fig. 1(*a*) the coordination of the Ge atoms is emphasized. All Ge atoms are at the centers of trigonal prisms formed of four Ni and two Y atoms. The trigonal prisms have their triangular faces joined with neighboring prisms and thus form infinite prism columns perpendicular to the plane of projection. Every three columns share common Y atoms which are arranged in a row perpendicular to the plane of projection. The resulting pillar is approximately 6 Å thick. Each of these pillars is edge connected to two neighboring pillars by common Ni atoms.

Table 1. *Atomic positional and displacement parameters for* YNi_5Ge_3 *with space group Pnma*

The isotropic atomic displacement factors are expressed as $T = \exp[-2\pi^2U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

	Wyckoff Position	*x*	*y*	*z*	*U* (Å² × 100)
Ni(1)	4(*c*)	0·0036 (2)	$\frac{1}{4}$	0·3661 (7)	0·74 (6)
Ge(1)	4(*c*)	0·0758 (1)	$\frac{1}{4}$	0·6486 (5)	0·77 (6)
Ge(2)	4(*c*)	0·0865 (1)	$\frac{1}{4}$	0·0905 (5)	0·70 (6)
Ni(2)	4(*c*)	0·1999 (2)	$\frac{1}{4}$	0·6902 (5)	0·79 (7)
Ni(3)	4(*c*)	0·2078 (2)	$\frac{1}{4}$	0·0730 (6)	0·80 (8)
Ge(3)	4(*c*)	0·2629 (1)	$\frac{1}{4}$	0·3836 (5)	0·71 (5)
Y(1)	4(*c*)	0·3553 (1)	$\frac{1}{4}$	0·8789 (5)	0·77 (5)
Ni(4)	4(*c*)	0·3872 (2)	$\frac{1}{4}$	0·3592 (6)	1·13 (7)
Ni(5)	4(*c*)	0·4867 (2)	$\frac{1}{4}$	0·6174 (7)	0·73 (6)

Table 2. *Interatomic distances* (Å) *up to* 3·5 Å *in* YNi_5Ge_3

Y(1)–2Ge(2)	2·973 (3)*
2Ge(1)	2·975 (3)*
2Ge(3)	2·979 (3)*
2Ni(2)	3·058 (4)
Ni(5)	3·079 (5)
2Ni(3)	3·089 (4)
Ni(3)	3·117 (5)
Ni(2)	3·240 (5)
Ni(4)	3·323 (6)
2Ni(1)	3·323 (3)
Ni(1)	3·326 (5)
Ni(1)–Ge(1)	2·365 (5)†
Ge(2)	2·455 (5)†
2Ge(1)	2·464 (3)†
2Ni(5)	2·578 (5)
2Ni(1)	2·662 (5)
Ni(4)	2·704 (5)
Ni(5)	3·305 (7)
2Y(1)	3·323 (3)
Y(1)	3·326 (5)
Ni(2)–Ge(1)	2·392 (5)†
Ge(3)	2·409 (5)†
2Ge(3)	2·447 (3)†
Ni(3)	2·608 (5)
2Ni(3)	2·740 (4)
2Ni(4)	2·802 (4)
2Y(1)	3·058 (4)
Y(1)	3·240 (5)
Ge(2)	3·482 (5)
Ni(3)–Ge(2)	2·324 (4)†
Ge(3)	2·361 (5)†
2Ge(3)	2·393 (3)†
Ni(2)	2·608 (5)
2Ni(2)	2·740 (4)
2Ni(4)	3·029 (4)
2Y(1)	3·089 (4)
Y(1)	3·117 (5)
Ni(4)–Ge(3)	2·385 (4)‡
2Ge(1)	2·511 (3)‡
2Ge(2)	2·545 (4)‡
Ni(5)	2·589 (6)
Ni(1)	2·704 (5)
2Ni(2)	2·805 (4)
2Ni(3)	3·029 (4)
2Ni(5)	3·098 (4)
Y(1)	3·323 (6)
Ni(5)–Ge(1)	2·332 (5)†
Ge(2)	2·376 (5)†
2Ge(2)	2·398 (2)†
2Ni(5)	2·562 (5)
2Ni(1)	2·578 (5)
Ni(4)	2·589 (6)
Y(1)	3·079 (5)
2Ni(4)	3·098 (4)
Ni(1)	3·305 (7)
Ge(1)–Ni(5)	2·332 (5)
Ni(1)	2·365 (5)
Ni(2)	2·392 (5)
2Ni(1)	2·464 (3)
2Ni(4)	2·511 (3)
2Y(1)	2·975 (3)
Ge(2)	3·013 (5)
Ge(2)–Ni(3)	2·324 (4)
Ni(5)	2·376 (5)
2Ni(5)	2·397 (2)
Ni(1)	2·455 (5)
2Ni(4)	2·545 (4)
2Y(1)	2·973 (3)
Ge(1)	3·013 (5)
Ni(2)	3·482 (5)
Ge(3)–Ni(3)	2·361 (5)
Ni(4)	2·385 (4)
2Ni(3)	2·393 (3)
Ni(2)	2·409 (5)
2Ni(2)	2·447 (3)
2Y(1)	2·979 (3)

* Trigonal prism.
† Tetrahedron.
‡ Tetragonal pyramid.

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* A list of structure factors, arranged in a standard crystallographic data file (Brown, 1985) has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43932 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1(*b*) shows the same YNi_5Ge_3 projection with the emphasis now on the coordination of the Y and Ni atoms. The arrangement of the Ge atoms in the projection plane can be described by a slightly deformed hexagonal mesh if one ignores the fact that half of the Ge atoms are shifted by $\frac{1}{2}b$ with respect to the others (circles drawn with dashed or full lines). Each Ge triangle of the mesh is centered in the projection by a Y or an Ni atom. Depending on the relative shifts for $\frac{1}{2}b$ of the surrounding Ge atoms and the transition-metal atom in the center one can distinguish three different Ge polyhedra around the Y or Ni atoms:

a trigonal prism (3 inscribed in the circle),
a tetragonal pyramid (2 inscribed in the circle),
a tetrahedron (1 inscribed in the circle).

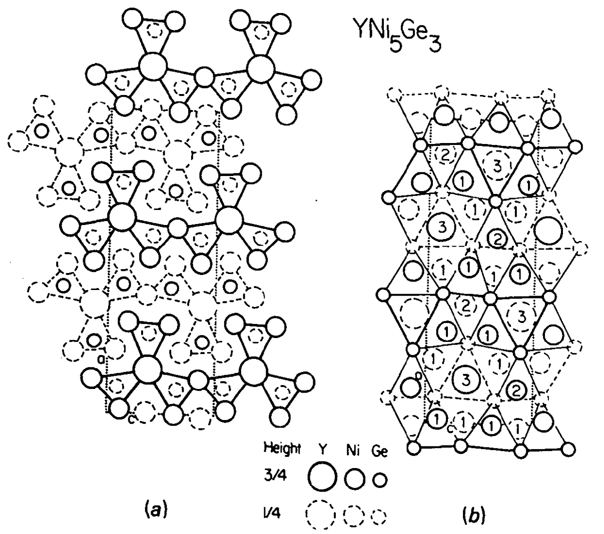

Fig. 1. Two projections of YNi_5Ge_3 along [010] with different connection lines between the atoms to emphasize different atom coordinations. (*a*) Trigonal prisms, each formed of two Y and four Ni, around Ge atoms. (*b*) Three kinds of Ge coordination polyhedra around Y and Ni atoms: trigonal prism (number 3 inscribed), tetragonal pyramid (number 2 inscribed) or tetrahedron (number 1 inscribed).

The numbers which have been inscribed in the circles to differentiate the three coordination polyhedra have been chosen such that they agree with the formal charges of the transition-metal atoms in ternary transition-metal phosphides as proposed by Madar *et al.* (1986, 1987).

The extended crystal-chemical formula of YNi_5Ge_3, considering now also the coordination of the Ge atoms but ignoring all their prism-waist contacts, can be written as

$$Y^{[,6p]}Ni^{[,5y]}Ni_4^{[,4t]}Ge_3^{[(2,4)p]}.$$

The same structural features are found with isopointal* YCo_5P_3 (*oP*36, *Pnma* – c^9; Meisen & Jeitschko, 1984) which is shown in Fig. 2 in a projection along [010]. In Fig. 2(*a*) the coordination of the P atoms is emphasized and in Fig. 2(*b*) the coordination of the Y and Co atoms is shown.

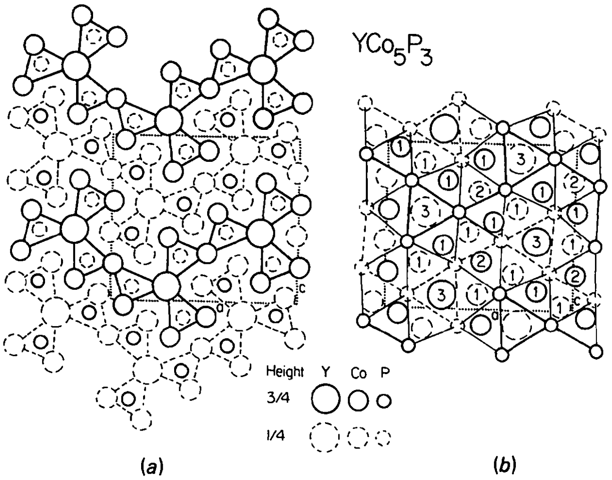

Fig. 2. Two projections of YCo_5P_3 along [010] emphasizing: (*a*) coordination of P atoms, (*b*) coordination of Y and Co atoms.

As demonstrated in Fig. 3 idealized versions of the YCo_5P_3 and the YNi_5Ge_3 structure can be considered as stacking variants of each other. Of the four idealized YCo_5P_3 unit cells shown, the two on the left are shifted by $\frac{1}{3}c$ (YCo_5P_3) along the (100) plane of YCo_5P_3. In this way slabs with YNi_5Ge_3 structure are obtained, all being one *a* (YNi_5Ge_3) translation thick (unit cells indicated with heavy lines). To get a complete correspondence with the YNi_5Ge_3 structure these slabs have to be shifted with respect to each other for $\frac{1}{2}c$ (YNi_5Ge_3) along the (100) plane of YNi_5Ge_3. For the idealized structures presented in the drawing the following relations hold: c/a (YCo_5P_3) $= 3^{1/2}/2$, c/a (YNi_5Ge_3) $= (2 \times 3^{1/2})/9$ and c (YNi_5Ge_3) $= \frac{2}{3}c$ (YCo_5P_3).

The common occurrence of phosphides and silicides or germanides with structures having the same crystal-chemical formula leads to the conclusion that the formal charges provided by the transition-metal atoms, as proposed by Madar *et al.* (1986, 1987), cannot be related to the number of valence electrons needed to complete the octets of the P and Si atoms. We note,

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* Two structures are defined as isopointal if: (1) they have the same space-group types or belong to a pair of enantiomorphic space-group types; and (2) the sites, occupied either fully or partially at random, are the same in both structures, and the complete sequence of the occupied Wyckoff positions (including the number of times each Wyckoff position is occupied) is the same for both structures, provided that the structural data are standardized (Lima-de-Faria, Hellner, Makovicky, Liebau & Parthé, 1987). In both YNi_5Ge_3 and YCo_5P_3 the Wyckoff position 4(*c*) is used nine times. Despite the fact that YNi_3Ge_5 and YCo_5P_3 contain the same kinds of polyhedra and similar interrelationships, they are not isotypic because the positional parameters (*x*, *y*, *z*) and the axial ratios are different.

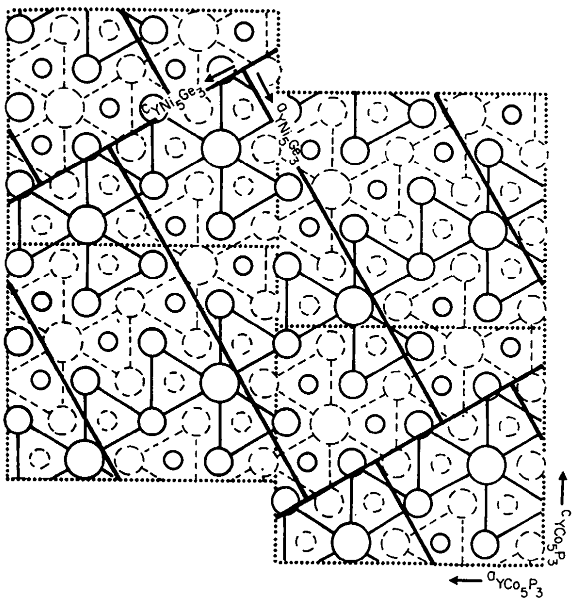

Fig. 3. The YCo_5P_3 and the YNi_5Ge_3 structures related like stacking variants. For the meaning of the different circles see Figs. 1 and 2.

however, that P and Si (Ge) atoms are all at the centers of trigonal prisms formed by the transition-metal atoms. It is tempting to speculate that the formal negative charges of the anions are not determined by their position in the Periodic system but correspondingly by their transition-metal coordination (which is the same in both structure types).

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References

AKSEL'RUD, L. G., YAROVETS, V. I., BODAK, O. I., YARMOLYUK, YA. P. & GLADYSHEVSKII, E. I. (1976). *Sov. Phys. Crystallogr.* **21**, 210–211.

BODAK, O. I., YAROVETS, V. I. & GLADYSHEVSKII, E. I. (1974). *Tesizy Dokl. Vses. Konf. Kristallokhim. Intermet. Soedin*, 2nd ed., edited by R. M. RYKHAL, pp. 32–33. Lvov State Univ.

BROWN, I. D. (1985). *Acta Cryst.* C**41**, 820–823.

HOVESTREYDT, E. (1983). *J. Appl. Cryst.* **16**, 651–653.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHANSSON, K. E., PALM, T. & WERNER, P. E. (1980). *J. Phys. E*, **13**, 1289–1291.

LIMA-DE-FARIA, J., HELLNER, E., MAKOVICKY, E., LIEBAU, F. & PARTHÉ, E. (1987). *Acta Cryst.* In preparation.

MADAR, R., GHETTA, V., CHAUDOUET, P. & SENATEUR, J. P. (1986). 3rd Eur. Conf. Solid State Chemistry, Regensburg. Collected Abstracts, Vol. 1, pp. 33–34.

MADAR, R., GHETTA, V., DHAHRI, E., CHAUDOUET, P. & SENATEUR, J. P. (1987). *J. Solid State Chem.* **66**, 73–85.

MEISEN, U. & JEITSCHKO, W. (1984). *J. Less-Common Met.* **102**, 127–134.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

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Oxygen Substitution in Sn and Ni Chevrel Phases

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Abstract. $SnMo_6S_6S_{1.9}O_{0.1}$ (1), $M_r = 949\cdot24$, rhombohedral, $R\bar{3}$, $a = 9\cdot175\,(2)$, $c = 11\cdot367\,(2)$ Å, $V = 828\cdot7\,(2)$ Å^3, $Z = 3$, $D_x = 5\cdot71$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 100\cdot9$ cm^{-1}, $F(000) = 1287\cdot6$, room temperature, $R = 0\cdot0437$ for 403 reflections. $Ni_{2.5}Mo_6S_8$ (2), $M_r = 978\cdot93$, hexagonal, $R\bar{3}$, $a = 9\cdot508$ (2), $c = 10\cdot237\,(2)$ Å, $V = 801\cdot5\,(2)$ Å^3, $Z = 3$, $D_x = 6\cdot09$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 124\cdot4$ cm^{-1}, $F(000) = 1350$, room temperature, $R = 0\cdot0421$ for 255 reflections. The structure analysis of a crystal grown from a mixture to yield the stoichiometry $SnMo_6S_6O_2$ led to composition (1). The crystal was twinned across $(1\bar{1}00)$ and refinement showed that 0·12 (4) oxygen substituted for sulfur on the $\bar{3}$ axis while 0·2 (1) tin was displaced from the origin along $\bar{3}$ to form an Sn—O bond of 2·05 (20) Å. Oxygen substitution was confirmed by X-ray fluorescence and Auger spectroscopy. A crystal grown by vapor-phase transport, using NH_4Cl, from a reaction mixture to yield hypothetical $Ni_2Mo_6S_6O_2$, had the composition (2). No oxygen substitution was detected either from the X-ray structure refinement or by spectroscopic techniques.