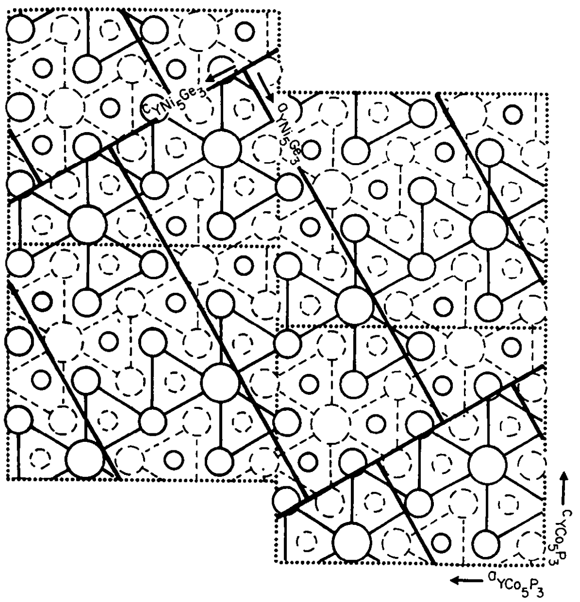

Fig. 3. The YCo_5P_3 and the YNi_5Ge_3 structures related like stacking variants. For the meaning of the different circles see Figs. 1 and 2.

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).

We wish to acknowledge the help of Mme Birgitta Kuenzler with the preparation of the drawings. This study was supported by the Swiss National Science Foundation under contract 2.035–0.86.

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Acta Cryst. (1987). C**43**, 1461–1465

Oxygen Substitution in Sn and Ni Chevrel Phases

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(*Received* 11 *September* 1986; *accepted* 24 *March* 1987)

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 $0\cdot12\,(4)$ oxygen substituted for sulfur on the $\bar{3}$ axis while $0\cdot2\,(1)$ tin was displaced from the origin along $\bar{3}$ to form an Sn—O bond of $2\cdot05\,(20)$ 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.

0108-2701/87/081461-05\$01.50

Introduction. The Chevrel phases are molybdenum chalcogenides with general composition $M_xMo_6S_8$ and they have been intensively investigated because of their superconducting and magnetic properties. Variations in physical behavior of nominally identical material have been ascribed to the nonstoichiometric composition of these compounds. An extensive review of the crystal chemistry and physical properties has been published by Yvon (1979). The structures are rhombohedral and there are two crystallographically independent sets of S atoms in $R\bar{3}$, one set in general position 18(*f*) and the other on the threefold axis in 6(*c*). It was postulated that the S atoms in 6(*c*) can be replaced by O atoms (Umarji, Subba Rao, Sankaranarayanan, Rangarajan & Srinivasan, 1980) to yield a compositon $M_xMo_6S_6O_2$. The evidence for this isomorphous substitution was not definitive, being deduced from the synthesis procedure, small changes in lattice constants obtained from powder X-ray diffraction patterns and variations in electrical properties. Hinks, Jorgensen & Li (1983, 1984) showed from a Rietveld structural refinement of neutron powder diffraction data that oxygen is present in the Sn and Pb Chevrel phases and that the limit of oxygen solubility occurs for the approximate composition $MMo_6S_6(S_{1.8}O_{0.2})$. The powder neutron diffraction data analysis is very convincing but nevertheless it is based on data obtained from a polycrystalline specimen. We undertook to grow single crystals of the Sn and Ni oxygen-containing Chevrel phases and report here the X-ray structural results.

Experimental. A mixture weighing 400 mg of Sn:$5\frac{1}{3}$Mo:6S:$\frac{2}{3}$MoO$_3$ (to yield the composition $SnMo_6S_6O_2$) was introduced into a Vycor tube 14 cm long and 7 mm internal diameter. The tube and contents were evacuated to 10^{-5} Torr (1 Torr $\simeq 1{\cdot}33\times10^2$ Pa), sealed and placed into a horizontal tube furnace. Initial heating of the tube at 783 K for 7 h was necessary to prevent explosion; this was followed by heating in a reverse gradient of 1173→1283 K for 16 h to back transport any material from the deposition zone to the source. The tube was then placed at the transport gradient, 1283→1243 K for 146 h. At the end of this period the tube was removed and quenched by running cold water over the source end of the tube. Several polyhedral crystals were seen in the deposition zone and removed for further study.

A 200 mg mixture 2NiO:6Mo:6S (to yield stoichiometric $Ni_2Mo_6S_6O_2$) and 3·0 mg of NH_4Cl, 0·5 mg cm^{-3} of the tube volume, were introduced into a Vycor tube which was evacuated to 10^{-5} Torr and sealed. An initial heating at 783 K for 16 h was followed by 16 h at 1173 K with the deposition zone at a higher temperature. The tube was now placed into a transport gradient of 1283→1243 K for 242 h. The tube was quenched as before and the polyhedral crystals removed from the deposition zone for further study.

A rhomb shaped crystal of the Sn compound approximately 0·08 mm on edge (6×10^{-4} mm^3) was mounted on a Syntex $P2_1$ automated single-crystal diffractometer. A least-squares refinement of 20 reflections whose 2θ values were precisely determined in the range $26 < 2\theta \le 29°$ yielded the lattice parameters. Systematic absences did not agree with those expected for $R\bar{3}$. For observed *hkil* reflections, *khil* reflections which should have been systematically absent were also observed. This indicated that a twin across $(1\bar{1}00)$ in direct space existed giving rise to three types of contributions from the two individuals: (*a*) $I(1)$ with $-h+k+l=3n$ and $I(2)$ with $-k+h+l=3n$ which superimpose. This occurs only for $l=3n$. (*b*) $I(1)$ with $-h+k+l=3n$ and $I(2)$ with $-k+h+l\neq 3n$ and the reverse. The intensities are from one individual only. (*c*) Both types of reflections are absent. ω scans of several peaks were symmetric with peak widths at half height of about 0·25°. Data were collected to $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1}, $h \le 12$, $|k| \le 12$, $|l| \le 15$, using Mo $K\alpha$ radiation monochromatized with a graphite crystal. The diffractometer was operated in the variable ω-scan mode with scan rates varying from 3 to 6° min^{-1}. Four standard reflections, $\bar{2}46$, 003, $\bar{2}\bar{2}6$, $\bar{2}\bar{2}\bar{3}$, were measured every 100 reflections and their intensities varied randomly $\pm1\%$. The 4847 measured intensities were transformed in the usual manner to structure-factor amplitudes and included an analytical absorption correction (Wehe, Busing & Levy, 1962). The transmission factors ranged from 0·33 to 0·50. Estimated standard deviations were calculated from $\sigma(I) = \{N_p + [(N_{b1}+N_{b2})/R] + pI^2\}^{1/2}$, where $p = 0{\cdot}000579$, N_p is the number of counts accumulated during the scan of the peak, N_{b1}, N_{b2} are background counts on the low- and high-2θ side respectively, R is the ratio of background time to scan time, and $I = N_p - (N_{b1} + N_{b2})/R$; $\sigma(F) = F\sigma(I)/2I$. Type 3 reflections were eliminated and equivalent reflections were averaged to give 896 unique reflections with $R_{\rm int} = 0{\cdot}034$. 811 reflections were considered observed on the basis that $F^2 > 2{\cdot}5\sigma(F^2)$.

From the 357 reflections of type 2 the volume fraction of individual 1, x_1, was estimated to be 0·445. The value of $F_o(hkl)$ from a single individual was calculated from $F_o^2(hkl) = [F_o^2(hkl) - vF_o^2(khl)]/(1-v^2)$ where $v = (1-x_1)/x_1$, which produced 539 F's, 403 of which were considered observed on the basis that $F^2 > 2{\cdot}5\sigma(F^2)$.

A full-matrix least-squares refinement on F using *SHELX*76 (Sheldrick, 1976) and assuming published positions for stoichiometric $PbMo_6S_8$ (Marezio, Dernier, Remeika, Corenzwit & Matthias, 1973) converged to a conventional $R_1 = 0{\cdot}083$. A difference electron density map indicated residual Sn density in position 6(*c*) about 1 Å from the origin. In order to obtain a refined value for x_1, the least-squares program *NUCLS* (Doedens & Ibers, 1974) was modified to permit

Table 1. *Final positional coordinates and equivalent isotropic thermal parameters* ($\times 10^4$)

$U_{eq} = \frac{1}{3}$ (trace of diagonalized tensor).

	x	y	z	Occupancy	U_{eq}(Å^2)
Sn Chevrel phase					
Sn(1)	0	0	0	0·137 (15)	334 (23)
Sn(2)	0	0	607 (179)	0·034 (16)	606 (350)
Mo	8243 (1)	8398 (1)	4007·4 (7)	1	84 (4)
S(1)	9632 (3)	6726 (3)	4168 (2)	1	114 (10)
S(2)	0	0	2407 (4)	0·324 (9)	116 (15)
Ni Chevrel phase					
Ni(1)	1799 (14)	4254 (13)	7628 (10)	0·199 (10)	236 (41)*
Ni(2)	4989 (16)	7621 (16)	6829 (12)	0·214 (10)	410 (44)*
Mo	8293 (1)	8453 (1)	3885 (1)	1	49 (5)
S(1)	9647 (4)	6855 (4)	4136 (3)	1	82 (14)
S(2)	0	0	2003 (6)	0·339 (10)	132 (21)

* Isotropic refinement.

refinement of intensity data from a twin consisting of two individuals of differing volume. The quantity minimized was $D = \sum w[F_o^2 - (kF_c)^2]^2$ where $w = [\sigma(F_o^2)]^{-2}$ and $F_c^2 = x_1F^2(hkl) + (1 - x_1)F^2(khl)$. Refinement with 80% of the Sn in position 3(*a*) and the remainder in 6(*c*) and isotropic temperature factors converged to $R_2 = 0{\cdot}098$ where $R_2 = \sum|F_o^2 - (kF_c)^2|/\sum F_o^2$. The value of x_1 was determined to be 0·446 (3). Final refinement with *SHELX*76, using 31 variable parameters, included occupancy factors for Sn(1), Sn(2) and S(2), anisotropic temperature factors, and an isotropic extinction correction, $F = F(1 - 1{\cdot}4 \times 10^{-7}F^2/\sin\theta)$; scattering factors for neutral atoms corrected for real and imaginary parts of dispersion (*International Tables for X-ray Crystallography*, 1974). Final values for the observed reflections were $R_1 = 0{\cdot}0437$, $wR = 0{\cdot}0440$, $S = 1{\cdot}277$, $\Delta/\sigma \leq 0{\cdot}03$; for all reflections $R_1 = 0{\cdot}0683$, $wR = 0{\cdot}0521$. A final difference map indicated random peaks of $\pm 1{\cdot}7$ e Å^{-3}.

Diffraction intensities from a crystal of the Ni phase approximately 0·08 mm on edge ($0{\cdot}6 \times 10^{-4}$ mm^3) were collected under the same conditions as described above. A least-squares refinement of 13 reflections measured in the range $21 \leq 2\theta \leq 30°$ yielded the lattice parameters. Systematic absences $-h + k + l = 3n$ were consistent with $R\bar{3}$, the usual space group for Chevrel phases. Data were collected to $(\sin\theta)/\lambda = 0{\cdot}6$ Å^{-1}, $h \leq 12$, $|k| \leq 12$, $|l| \leq 13$. Four standard reflections, $\bar{4}2\bar{3}$, $\bar{2}\bar{2}3$, $22\bar{3}$, $4\bar{2}3$, measured every 100 reflections remained constant within statistical counting errors. The absorption coefficient was based on $Ni_{2.5}Mo_6S_8$; the minimum and maximum transmission factors were 0·660 and 0·759. 1015 reflections were collected and transformed in the usual manner to structure amplitudes; standard deviations as above with $p = 0{\cdot}0008$. Equivalent reflections were averaged to yield 320 unique reflections, $R_{int} = 0{\cdot}0273$. 255 reflections were considered observed on the basis that $F > 4\sigma(F)$. Full-matrix refinement on F, $\sum w(\Delta F)^2$ minimized, w as above, *SHELX*76, positions from the published structure (Guillevic, Bars & Grandjean, 1973) using 33 variable parameters including occupancies for Ni(1), Ni(2), S(2), anisotropic temperature factors for Mo, S(1), S(2), scattering factors for neutral atoms corrected for real and imaginary parts of dispersion (*International Tables for X-ray Crystallography*, 1974) converged for the observed reflections to $R = 0{\cdot}0421$, $wR = 0{\cdot}0407$, $S = 1{\cdot}254$, $(\Delta/\sigma)_{max} \leq 0{\cdot}02$. For all reflections $R = 0{\cdot}0633$, $wR = 0{\cdot}0505$. A final difference map had maximum and minimum values of 2 e Å^{-3}.

Discussion. The final atomic parameters for the Sn and Ni phases are shown in Table 1.* Bond lengths are similar to those previously reported for the Chevrel phases. The only noteworthy length is 2·05 (20) Å between Sn(2) and S(2), which represents the oxygen substitution.

A single-crystal X-ray structure determination of the Sn Chevrel phase had not been previously published although it is known that the compounds containing large metal ions, *e.g.* Pb, Sn, rare earth, are nearly stoichiometric with composition MMo_6S_8 (Marezio *et al.*, 1973; Yvon, 1979). On the basis of a Rietveld analysis of neutron powder diffraction data from oxygen-containing Sn and Pb Chevrel phases, Hinks *et al.* (1983, 1984) showed that Sn was disordered, with most of the Sn at the origin, positon 3(*a*) of $R\bar{3}$, and the rest displaced along the $\bar{3}$ axis in site 6(*c*), about 0·8 Å from the origin. They observed a correlation between the amount of Sn displaced and the oxygen substitution in the 6(*c*) site. Their reported displacement of 0·04 Sn for the 'pure' sulfur composition indicates the presence of some oxygen. Our results show that 2·5 (3) Sn is present at the origin in 3(*a*) and 0·6 (3) Sn in 6(*c*) of $R\bar{3}$, 0·7 Å from the origin. The occupancy factors were not constrained during the refinement and within the error of measurement a total of one Sn atom is present in the formula. The site occupancy of the S atom on the threefold axis was determined from the refinement of the occupancy factor using the S scattering factor. The difference from full occupancy is ascribed to the presence of oxygen. The least-squares refinement yielded 5·83 (16) S which was attributed then to 5·66 S and 0·34 O in that site. Although the components in the reaction mixture were present in the proportion to form the hypothetical $SnMo_6S_6O_2$, the actual composition of the crystal grown by sublimation is initially unknown. The composition of this crystal based on the structure refinement is $[Sn_{0.82(9)}Sn_{0.20(10)}]Mo_6S_6[S_{1.88(5)}O_{0.12}]$ and within the experimental errors of the determination confirms the correlation between oxygen content and

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* Lists of anisotropic thermal parameters, bond lengths and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43921 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Sn displacement. The ratio $c/a = 1{\cdot}239$ for this crystal yields $x = 0{\cdot}1$ using Fig. 1 of Hinks *et al.* (1983).

If the maximum oxygen substitution is 0·2 in site 6(*c*) (Hinks *et al.*, 1984), the scattering power at that site is decreased by 0·8 electrons and in our case the difference is approximately 0·5 electrons. It is not surprising that a least-squares analysis, which also showed strong correlations among the Sn(1), Sn(2) and S(2) parameters, yields values of the estimated standard deviation for the occupancy of S(2) that are not significantly different from full occupancy. It was therefore essential to obtain independent verification of the presence of oxygen.

Qualitative X-ray fluorescence analysis was carried out on single crystals of the Sn and Ni phases using a Kevex 7000 EDS/WDS X-ray analysis system attached to a Jeol JSM-35C SEM fitted with a Jeol four-crystal wavelength spectrometer. At an operating voltage of 25 kV and using the energy-dispersive technique the presence of Sn or Ni was established but the Mo and S peaks overlap. Using wavelength-dispersive analysis with a pentaerythritol crystal at 25 kV, resolved Mo and S peaks were observed. Operating at 10 kV and using a lead myristate analyzing crystal indications of an oxygen presence in the Sn phase could be inferred but the intensity at the oxygen position was barely above background. No indication of an oxygen presence was seen in the Ni phase.

Single crystals of each of the Sn and Ni phases were analyzed using Auger electron spectroscopy. Both crystals were placed into a Physical Electronics SAM 590 instrument which operated at 3×10^{-9} Torr at a 3 keV beam voltage. As expected, oxygen signals were observed initially from the surfaces of each crystal. When the surface of the Ni compound was subjected to Ar gas sputtering for 4 min no oxygen peak was detected even at a scale factor setting 10× that for sulfur. When the surface of the Sn compound was subjected to Ar sputtering for 6 min the initially seen oxygen signal decreased in amplitude, but was clearly evident at a scale factor setting 10× that for the sulfur peak. Using the semi-quantitative procedure described in *Handbook of Auger Electron Spectroscopy* (1976) the following atom percentages were obtained: (*a*) for the composition $Ni_{2.5}Mo_6S_8$: Ni 6·0 (15·2), Mo 39·7 (36·4), S 54·3 (48·5) (numbers in parentheses are theoretical values); (*b*) for the composition $SnMo_6S_{7.9}O_{0.1}$: Sn 2·9 (6·7), Mo 42·6 (40·0), S 54·2 (52·7), O 0·4 (0·7). The experimental values for the Sn phase are the average of three sets of results after three successive 6 min sputterings of the surface of the same crystal, the range of values was 2·7–2·9, 41–44, 53–56 and 0·4 respectively. Further evidence to support the presence of oxygen in the Sn phase is based on the displacement of Sn along the $\bar{3}$ axis. The structure cannot be refined to *R* less than 0·09 with Sn having full occupancy on the origin. The extent of the Sn displacement is directly related to the oxygen substitution (Hinks *et al.*, 1983, 1984). These results together with the excellent agreement with the conclusions from the neutron diffraction data give strong credence to the determination of oxygen substitution in the Sn phase only.

Chevrel phases containing small metal ions, *e.g.* Ni, Co, Fe, can incorporate two ions to yield a stoichiometry $M_2Mo_6S_8$. Umarji *et al.* (1980) also reported the syntheses of $MMo_6S_6O_2$ (M = Co, Ni, Cu) and we studied a single crystal of an Ni phase, grown from a mixture to yield the composition $Ni_2Mo_6S_6O_2$, in order to determine the extent of oxygen substitution. A single-crystal X-ray structure study had been reported for $Ni_2Mo_6S_8$ (Guillevic *et al.*, 1973) and our parameters are in excellent agreement with their published values. We also observe the same disordered Ni arrangement around the threefold axis and our refinement does not indicate oxygen replacing S on the threefold axis. The stoichiometry based on our X-ray results is $[Ni_{1.13(7)}Ni_{1.29(11)}]Mo_6S_6S_{2.06(9)}$. The Ni composition in excess of 2 is not unusual since additional metal ions can enter the chalcogen channels (Yvon, 1979; Tarascon, DiSalvo, Murphy, Hull, Rietman & Waszczak, 1984).

The partial replacement of S by O in the Sn and Pb Chevrel phases but not in the Ni phase may be connected to the position of the metal atom in the structure. Large metal atoms are at the origin and move along the $\bar{3}$ axis to form a bond with oxygen. The limited solubility of 0·20 (Hinks *et al.*, 1984) may be due to the strain introduced with increasing oxygen substitution. The Sn—O bond of 2·05 (20) Å (Sn—O = 2·06 Å in SnO_2 and 2·22 Å in SnO) compared to 3·1 Å for Sn—S causes the *c*-axis length to decrease with increasing substitution until the strain is relieved by the formation of a second phase (Hinks *et al.*, 1984). Oxygen replacement also occurs only in one position of the $\bar{3}$ axis with the Sn moving towards oxygen from the origin. If oxygen substituted randomly in the 6(*c*) site one should expect Sn to remain at the origin. Such substitution requires severe distortion of the sulfur cube around the Mo_6 octahedron and is energetically unfavorable.

Small metal atoms in Chevrel phases are disordered in the channels around the $\bar{3}$ axis. The Ni—S bond lengths are 2·1–2·3 Å in the Chevrel phase, consistent with values observed for this bond, and generally Ni—O is about 2·1 Å. Thus, oxygen substitution should occur more readily and to a larger extent in these phases because the bond distances are more comparable and much less strain should be introduced into the crystal. The fact that no oxygen is observed in this crystal may be due to the growth process employed here or it may be an intrinsic property due to the different metal-atom arrangement. The question of oxygen substitution is still unresolved in this type of compound.

This research was supported by the National Science Foundation under Grant DMR 8520028 and by the R. A. Welch Foundation of Houston, Texas.

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Acta Cryst. (1987). C**43**, 1465–1467

Structure of the Second Crystalline Form of Uranium(IV) Tetrahydroborate

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(*Received* 17 *November* 1986; *accepted* 18 *March* 1987)

Abstract. $[U(BH_4)_4]$, $M_r = 297{\cdot}4$, orthorhombic, *Cmcm*, $a = 8{\cdot}014$ (2), $b = 7{\cdot}940$ (3), $c = 11{\cdot}673$ (3) Å, $V = 742{\cdot}7$ (7) Å^3, $Z = 4$, $D_x = 2{\cdot}66$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 20{\cdot}60$ mm^{-1}, $F(000) = 512$, room temperature, $R = 0{\cdot}023$ for 342 observed reflections. The structure is of two-dimensional polymeric type. Each U atom is coordinated to four coplanar bridging bidentate [U—B(1) 2·84 (1) Å] and two terminal tridentate BH_4 ligands [U—B(2) 2·51 (1) Å] in *trans* position. H atoms are observed in a residual Fourier map: the most striking feature is the bending of the $U—B—H_{\text{terminal}}$ line in tridentate BH_4 [162 (6)°] which renders the three bonding H atoms inequivalent.

Introduction. The structure of $U(BH_4)_4$ was established in 1972 from both X-ray (Bernstein, Keiderling, Lippard & Mayerle, 1972) and neutron (Bernstein, Hamilton, Keiderling, La Placa, Lippard & Mayerle, 1972) single-crystal diffraction data. The surprising feature of the $U(BH_4)_4$ structure consisted in its polymeric nature in the solid state. Four of the six BH_4^- ions surrounding each U atom are attached to it by two H atoms, the two other H atoms bridging to neighboring U atoms in a polymeric structure. The two terminal tridentate BH_4 ligands in *cis* configuration complete the coordination sphere of each U atom.

We have reported (Charpin, Marquet-Ellis & Folcher, 1978) the evidence for a second crystalline form of $U(BH_4)_4$ (form II) differing by higher volatility and solubility in benzene and by its color (form I: yellow green; form II: emerald green). Though no good-quality single crystals could be obtained, we have suggested a possible two-dimensional polymerization involving terminal tridentate BH_4^- in *trans* position. Recently, we have been able to obtain in a sublimation process a mixture of both forms as single crystals suitable for an X-ray analysis and we now report the structure of $U(BH_4)_4$ form II.

Experimental. Freshly sublimated $U(BH_4)_4$ is added under Ar atmosphere to molten diphenylacetylene: a brownish color is observed, part of the borohydride is then vaporized and deposited as yellow-green $[U(BH_4)_4$ I] and emerald-green $[U(BH_4)_4$ II] crystals on the top of the tube; crystal 0·25 × 0·20 × 0·12 mm; Enraf–Nonius CAD-4 diffractometer; unit-cell parameters refined from 25 reflections in range $16 < 2\theta < 24°$; three standard reflections monitored at 100-reflection intervals, loss of 0·2% in 8 h, linearly corrected; scans by ω–2θ method; Lorentz and polarization corrections; empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983), transmission coefficients min. 0·78 and max. 1·56; 799 reflections collected, 371 unique, 342 with $I > 3\sigma(I)$; $2 < 2\theta < 40°$; $-9 \leq h \leq 0$, $-9 \leq k \leq 0$, $0 \leq l \leq 13$; structure solved by Patterson method for U, remaining atoms

0108-2701/87/081465-03$01.50