PASSMORE, J., SUTHERLAND, G. & WHITE, P. S. (1980). *J. Chem. Soc. Chem. Commun.* pp. 330–331.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
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, MD, USA.

---

*Acta Cryst.* (1989). C45, 1853–1856

# $Sc_3Ni_2Si_3$ with $Hf_3Ni_2Si_3$-Type Structure, an Intergrowth of CrB-, $ThCr_2Si_2$- and W-Type Slabs

BY J. T. ZHAO AND E. PARTHÉ

*Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 Quai E. Ansermet, CH-1211 Geneva 4, Switzerland*

(*Received* 2 *January* 1989; *accepted* 20 *February* 1989)

**Abstract.** $Sc_3Ni_2Si_3$, $M_r = 336{\cdot}55$, orthorhombic, $oS32$, $Cmcm - f^3c^2$, $a = 3{\cdot}9812\ (7)$, $b = 9{\cdot}688\ (2)$, $c = 13{\cdot}111\ (2)$ Å, $V = 505{\cdot}7\ (1)$ Å$^3$, $Z = 4$, $D_x = 4{\cdot}420$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 11{\cdot}62$ mm$^{-1}$, $F(000) = 644$, $T = 293$ K, $wR = 0{\cdot}041$ for 431 unique reflections. The $Sc_3Ni_2Si_3$ structure with $Hf_3Ni_2Si_3$ type is a member of the structure series with general formula $R_{2+n}T_2M_{2+n}$, in which the structures can be interpreted as an intergrowth of slabs cut from the CrB, $ThCr_2Si_2$ and W types.

**Introduction.** The Sc–Ni–Si phase diagram has been investigated by Bodak, Kotur & Gladyshevskii (1976) and 15 ternary compounds were reported. Among the known structures, many, including the recently determined $Sc_3Ni_2Si_4$ structure (Zhao & Parthé, 1989), can be interpreted as an intergrowth of segments cut from simple parent structures. It was found of interest to study unknown structures and to find out how far this concept is applicable.

**Experimental.** The sample of nominal composition $Sc_2NiSi_2$, reported as a phase of unknown structure in the Sc–Ni–Si phase diagram, was prepared by arc melting under argon atmosphere (Sc 99·99, Ni 99·99 and Si 99·999%). The weight loss was 0·6%. The sample was annealed at 1073 K for 12 d in a silica tube under 300 mm Hg argon atmosphere. A single crystal with regular shape [±(100): 0·032 mm, ±(010): 0·016 mm, ±(001): 0·080 mm] obtained from the annealed sample was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The cell parameters were refined from $2\theta$ values of 29 reflections (Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $20 < 2\theta < 42°$) using the program *LATCON*. 1830 reflections were collected to $(\sin\theta)/\lambda = 0{\cdot}70$ Å$^{-1}$ $(0 \le h \le 5,\ 0 \le k \le 13,\ 0 \le l \le 18$ and the anti-reflections) in the $\omega$–$2\theta$ scan mode, yielding 437 unique reflections. Two standard reflections ($33\bar{1}$ and 141) were measured with maximum intensity variations 0·5 and 0·7% respectively. Absorption corrections were made using the program *ABSORB* with max. and min. transmission factors of 0·68871 and 0·48638. The atomic

Table 1. *Atomic positional and displacement parameters for* $Sc_3Ni_2Si_3$ *with* $Hf_3Ni_2Si_3$*-type structure (space group Cmcm)*

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

| | Wyckoff position | $x$ | $y$ | $z$ | $U$(Å$^2 \times 100$) |
|---|---|---|---|---|---|
| Sc(1) | 8($f$) | 0 | 0·0834 (2) | 0·1117 (1) | 0·50 (4) |
| Ni(1) | 8($f$) | 0 | 0·2077 (1) | 0·59583 (9) | 0·62 (3) |
| Si(1) | 8($f$) | 0 | 0·3845 (2) | 0·0389 (2) | 0·57 (5) |
| Sc(2) | 4($c$) | 0 | 0·3625 (2) | $\frac{1}{4}$ | 0·49 (5) |
| Si(2) | 4($c$) | 0 | 0·6598 (4) | $\frac{1}{4}$ | 0·56 (8) |

Table 2. *Interatomic distances up to* 3·5 Å *in* $Sc_3Ni_2Si_3$

| | |
|---|---|
| Sc(1)—2Si(2) | 2·792 (2) |
| 2Si(1) | 2·821 (2) |
| Ni(1) | 2·828 (2) |
| 2Ni(1) | 2·847 (1) |
| 2Si(1) | 2·930 (2) |
| Ni(1) | 2·976 (2) |
| Si(1) | 3·070 (3) |
| Sc(2) | 3·256 (3) |
| Sc(1) | 3·346 (2) |
| 2Sc(2) | 3·439 (2) |
| Sc(2)—2Si(1) | 2·776 (3) |
| 2Si(2) | 2·797 (3) |
| Si(2) | 2·880 (4) |
| 4Ni(1) | 2·917 (1) |
| 2Sc(1) | 3·256 (3) |
| 4Sc(1) | 3·439 (2) |
| Ni(1)—2Si(1) | 2·306 (1) |
| Si(2) | 2·395 (2) |
| Si(1) | 2·461 (3) |
| Sc(1) | 2·828 (2) |
| Ni(1)—2Sc(1) | 2·847 (1) |
| 2Sc(2) | 2·917 (1) |
| Sc(1) | 2·976 (2) |
| 2Ni(1) | 3·309 (1) |
| Si(1)—2Ni(1) | 2·306 (1) |
| Si(1) | 2·459 (3) |
| Ni(1) | 2·461 (3) |
| Sc(2) | 2·776 (3) |
| 2Sc(1) | 2·821 (2) |
| 2Sc(1) | 2·930 (2) |
| Sc(1) | 3·070 (3) |
| 2Si(1) | 3·435 (3) |
| Si(2)—2Ni(1) | 2·395 (2) |
| 4Sc(1) | 2·792 (2) |
| 2Sc(2) | 2·797 (3) |
| Sc(2) | 2·880 (4) |

0108-2701/89/121853-04$03.00

scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). The systematic absences led to three possible space groups $Cmc2_1$, $Ama2$ and $Cmcm$. According to the cell parameters and the possible space groups an isotype of the $Hf_3Ni_2Si_3$ type (Yarmolyuk, Grin' & Gladyshevskii, 1977) was considered as the first possibility. This was confirmed by the structure refinement. The structure refinement was based on $|F|$ values and the atomic positional parameters of $Hf_3Ni_2Si_3$ using isotropic atomic displacement parameters and the program *SFLSX*.

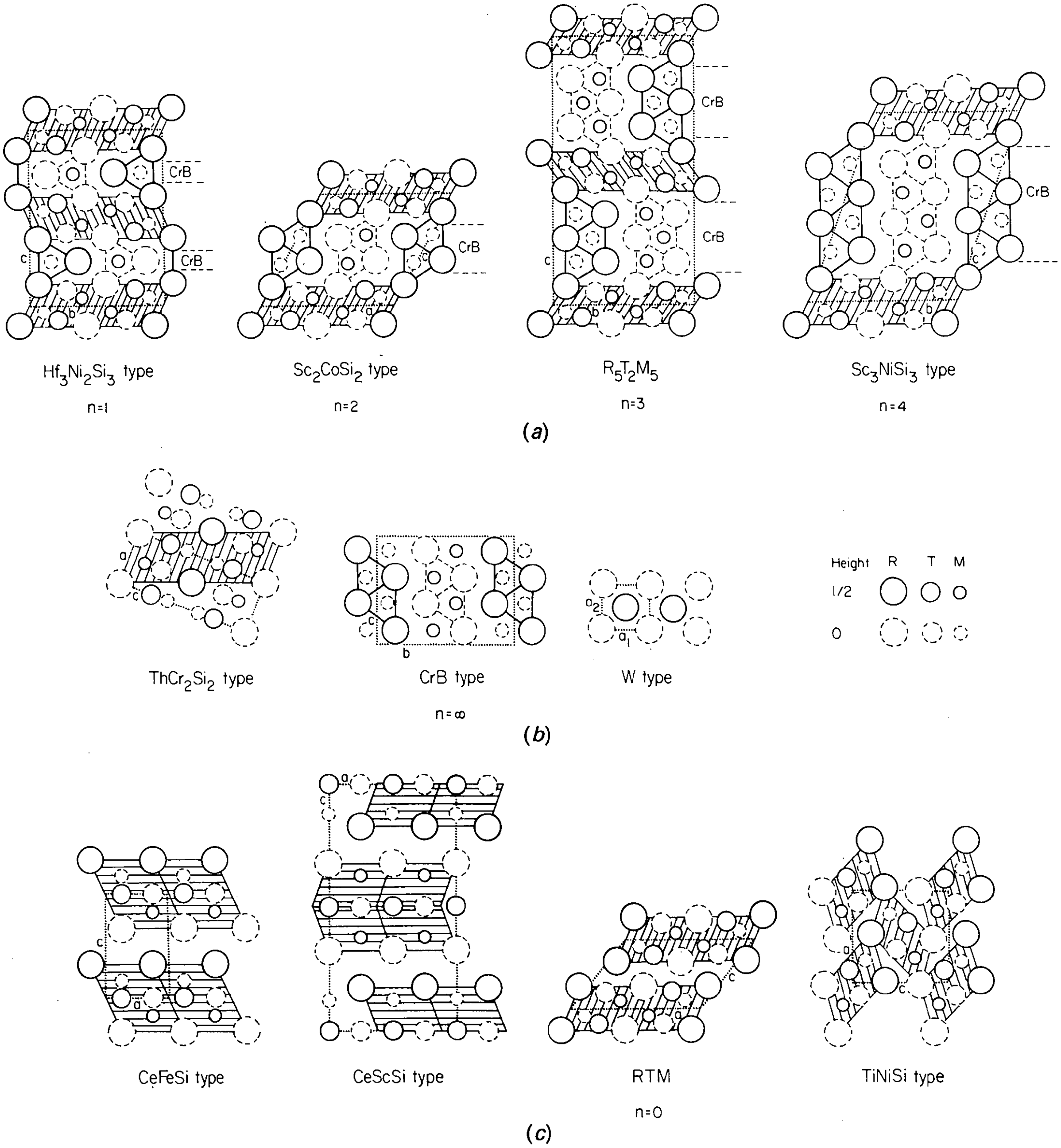

Fig. 1. (*a*) The members of the $R_{2+n}T_2M_{2+n}$ structure series which can be interpreted as an intergrowth of the $ThCr_2Si_2$-, CrB- and W-type slabs. The limits of the CrB slabs are indicated by lines beside the drawings and the $ThCr_2Si_2$ slabs are shaded in the drawings. The $R_5T_2M_5$ type is a hypothetical structure which is the member of the $R_{2+n}T_2M_{2+n}$ series with $n = 3$. The atom heights are shown in (*b*). (*b*) The $ThCr_2Si_2$, CrB and W types and the segments which are used to construct the structures shown in (*a*) and (*c*). The $ThCr_2Si_2$-type segments are shaded in the drawing. (*c*) The ternary equiatomic structures which are built up of the segments cut from the $ThCr_2Si_2$ type and W type. The $ThCr_2Si_2$-type segments are shaded in the drawings. The *RTM* type is a hypothetical structure which is the member of the $R_{2+n}T_2M_{2+n}$ series with $n = 0$. The atom heights are shown in (*b*).

Table 3. *Crystallographic data of the structures in the* $R_{2+n}T_2M_{2+n}$ *series*

(The unit cell data for the last line refer to the isotypic ScSi.)

| $n$ | Structure type | Unit cell parameters (Å and °) | Pearson code | Space group and Wyckoff sequence |
|---|---|---|---|---|
| 0 | $RTM$ | $a \approx 10$, $b \approx 4$, $c \approx 6·5$; $\beta \approx 135$ | $mS12$ | $C2/m - i^3$ |
| 1 | $Hf_3Ni_2Si_3$ | $a = 3·831$, $b = 9·862$, $c = 13·003$ | $oS32$ | $Cmcm - f^3c^2$ |
| 2 | $Sc_2CoSi_2$ | $a = 9·74$, $b = 3·954$, $c = 9·39$; $\beta = 118·27$ | $mS20$ | $C2/m - i^5$ |
| 3 | $R_5T_2M_5$ | $a \approx 4$, $b \approx 10$, $c \approx 19$ | $oS48$ | $Cmcm - f^5c^2$ |
| 4 | $Sc_3NiSi_3$ | $a = 9·801$, $b = 3·974$, $c = 12·8168$; $\beta = 110·08$ | $mS28$ | $C2/m - i^7$ |
| ∞ | CrB(ScSi) | $a = 3·988$, $b = 9·882$, $c = 3·659$ | $oS8$ | $Cmcm - c^2$ |

There are 14 variables refined to $wR = 0·041$ [$w = 1/\sigma^2(|F_{\rm rel}|)$, $S = 3·591$] considering 431 contributing reflections. 6 ($F < 0$) unobserved reflections. The max. shift/e.s.d. in the last cycle is 0·00009. Final residual electron density $-2·9$–$3·4$ e Å$^{-3}$. The programs used to refine the structure are all from the *XTAL*2·4 system (Hall & Stewart, 1988). The atomic positional and displacement parameters are given in Table 1.* The data have been standardized with the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). Interatomic distances up to 3·5 Å are given in Table 2.

**Discussion.** All the structures of compounds in the Sc–Ni–Si phase diagram with less than 50 atom% Ni can be interpreted as an intergrowth of segments cut from simple parent structures, the segments being either columns or slabs (Zhao & Parthé, 1989). The $Sc_3Ni_2Si_3$ structure with $Hf_3Ni_2Si_3$ type, shown in Fig. 1(*a*), fits in here. It can be constructed of intergrown slabs cut from ScSi with CrB type, $ScNi_2Si_2$ with $ThCr_2Si_2$ type and deformed W type. The indices of the stacking interfaces of the $ThCr_2Si_2$-type, CrB-type and W-type slabs are (101), (001) and (130) respectively. The slabs are shown in Fig. 1(*b*).

The $Hf_3Ni_2Si_3$ type forms part of a structure series with general formula $R_{2+n}T_2M_{2+n}$ [$RT_2M_2$($ThCr_2Si_2$) + $R$(W) + $R_nM_n$($n$CrB)]. The letter $R$ denotes here rare earth or early transition metal elements (Sc, Y, Hf, *etc.*), $T$ a late transition metal (Fe, Co, Ni, *etc.*) and $M$ a B main-group element (Si, Ge, Ga, *etc.*). The parameter $n$ of the formula for the series indicates the number of CrB-type slabs which are sandwiched between the joined W-type, $ThCr_2Si_2$-type and W-type slabs. The $Hf_3Ni_2Si_3$ type is the member with $n = 1$. The other known members of this structure series are $Sc_2CoSi_2$ with $n = 2$ (Gladyshevskii & Kotur, 1978) and $Sc_3NiSi_3$ with $n = 4$ (Kotur & Gladyshevskii, 1983). In Fig. 1(*a*) is also shown one unknown member: the $R_5T_2M_5$ structure with $n = 3$. From Table 3, in which the crystallographic data of the structure types in this series are listed, we can see that the space group for the structures with $n$ even is $C2/m$ and for structures with $n$ odd is $Cmcm$. This is due to the symmetry elements of the CrB layer in the structure. The mirror plane in the direction parallel to the CrB layer will be lost when even numbers of CrB slabs are found in the structure.

The structure with $n = 0$ has composition $RTM$ and the hypothetical structure is shown in Fig. 1(*c*). The construction based on intergrown $ThCr_2Si_2$- and W-type slabs leads to $T$—$T$ contacts. This is probably the reason why this structure has not been found. If there are intergrown CrB-type slabs there are no $T$—$T$ contacts. In Fig. 1(*c*) are shown three experimentally observed structure types with $RTM$ composition: TiNiSi (Shoemaker & Shoemaker, 1965), CeFeSi (Bodak, Gladyshevskii & Kripyakevich, 1970) and CeScSi (Mokraya & Bodak, 1979). The latter, however, cannot be properly called an $RTM$ compound. All these structure types are built up of segments cut from the $ThCr_2Si_2$ type and W type, which are joined in a different way.

The CeFeSi and CeScSi types can be built up of slabs only cut from $ThCr_2Si_2$ type and W type; however, the indices of the stacking interfaces of the $ThCr_2Si_2$ slab and W slab are (001) and (100). The interfaces are not the desired ones to construct the $R_{2+n}T_2M_{2+n}$ series. The $ThCr_2Si_2$ type layer in CeScSi is different from the layer in CeFeSi. CeScSi can be considered as a microtwinned CeFeSi structure.

The TiNiSi can be built up of columns cut from the $ThCr_2Si_2$ type and columns of the W type. Here the interfaces of the columns are the same as the interfaces of the slabs in the $R_{2+n}T_2M_{2+n}$ series. These columns can be joined to form a continuous slab which corresponds to the slab in the hypothetical $RTM$ structure discussed above.

Because the TiNiSi type can be considered as an intergrowth of the $ThCr_2Si_2$- and W-type segments, the $R_{2+n}T_2M_{2+n}$ structure series had been described before (Gladyshevskii & Kotur, 1978; Kotur &

---

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51976 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Gladyshevskii, 1983; Parthé & Chabot, 1984) as an intergrowth of CrB-type slabs and slabs composed of TiNiSi segments. The TiNiSi and the hypothetical *RTM* structure are composed of the same kind of $ThCr_2Si_2$- and W-type columns; however, there are no *T*—*T* contacts in the first.

We wish to acknowledge the help of Mme. Birgitta Künzler with the preparation of the drawings. This study was supported by the Swiss National Science Foundation under contract 2–5.537.

### References

Bodak, O. I., Gladyshevskii, E. I. & Kripyakevich, P. I. (1970). *J. Struct. Chem. USSR*, **11**, 283–288.

Bodak, O. I., Kotur, B. Ya. & Gladyshevskii, E. I. (1976). *Dokl. Akad. Nauk Ukr. SSR Ser. A*, pp. 656–659.

Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.

Gladyshevskii, E. I. & Kotur, B. Ya. (1978). *Sov. Phys. Crystallogr.* **23**, 533–535.

Hall, S. R. & Stewart, J. M. (1988). Editors. *XTAL*2.4 *Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Kotur, B. Ya. & Gladyshevskii, E. I. (1983). *Sov. Phys. Crystallogr.* **28**, 271–273.

Mokraya, I. R. & Bodak, O. I. (1979). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 312–315.

Parthé, E. & Chabot, B. A. (1984). In *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, edited by K. A. Gschneidner Jr & L. Eyring, Ch. 48, pp. 113–334. Amsterdam: North-Holland.

Shoemaker, C. B. & Shoemaker, D. P. (1965). *Acta Cryst.* **18**, 900–905.

Yarmolyuk, Ya. P., Grin', Yu. N. & Gladyshevskii, E. I. (1977). *Sov. Phys. Crystallogr.* **22**, 416–419.

Zhao, J. T. & Parthé, E. (1989). *J. Less-Common Met.* **154**, 31–37.

---

*Acta Cryst.* (1989). C**45**, 1856–1858

# Crystal Chemistry of *cyclo*-Hexaphosphates. III. Structure of Dilithium Dimanganese *cyclo*-Hexaphosphate Decahydrate

By M. T. Averbuch-Pouchot

*Laboratoire de Cristallographie, Laboratoire associé à l'Université J. Fourier, CNRS*, 166*X*,
38042 *Grenoble CEDEX, France*

(*Received* 21 *January* 1989; *accepted* 4 *April* 1989)

**Abstract.** $Li_2Mn_2P_6O_{18}.10H_2O$, $M_r = 777{\cdot}732$, triclinic, $P\overline{1}$, $a = 7{\cdot}286\,(5)$, $b = 9{\cdot}761\,(7)$, $c = 10{\cdot}026\,(6)$ Å, $\alpha = 118{\cdot}31\,(5)$, $\beta = 110{\cdot}62\,(5)$, $\gamma = 86{\cdot}27\,(5)°$, $V = 583\,(2)$ Å$^3$, $Z = 1$, $D_x = 2{\cdot}215$ Mg m$^{-3}$, $\lambda$(Mo $K\overline{\alpha}$) = 0·7107 Å, $\mu = 1{\cdot}673$ mm$^{-1}$, $F(000) = 390$, $T = 294$ K, final $R = 0{\cdot}027$ for 2386 reflections. The $P_6O_{18}$ ring anion is centrosymmetric. The two associated cation polyhedra, a tetrahedron built up of three O atoms and one water molecule for the Li atom and an octahedron made up of three water molecules and three O atoms for the Mn atom, do not share any O atoms. Two of the ten water molecules [O(*W*2)] do not take part in the metal coordinations. The hydrogen-bond scheme is reported. Crystal data for the isotypic zinc salt are given.

**Introduction.** This work is part of a systematic investigation of *cyclo*-hexaphosphate crystal chemistry. We previously reported chemical preparations and crystal structures for various monovalent cation or mixed monovalent cation *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*a*,*b*,*c*,*d*) and for some divalent cation *cyclo*-hexaphosphates (Averbuch-Pouchot, 1989*e*,*f*).

The title compound is the first example of a hydrated divalent–monovalent-cation *cyclo*-hexaphosphate.

The corresponding zinc salt $Li_2Zn_2P_6O_{18}.10H_2O$ is isotypic, with the following unit-cell dimensions: $a = 7{\cdot}160\,(5)$, $b = 9{\cdot}741\,(7)$, $c = 9{\cdot}928\,(6)$ Å, $\alpha = 118{\cdot}49\,(5)$, $\beta = 110{\cdot}57\,(5)$, $\gamma = 86{\cdot}96\,(5)°$. Its chemical preparation is similar to that described for the title compound.

**Experimental.** $Li_2Mn_2P_6O_{18}.10H_2O$ crystals have been obtained by mixing an aqueous solution of manganese chloride and an aqueous solution of lithium *cyclo*-hexaphosphate hexahydrate so as to obtain a ratio Li/Mn = 2 in the final solution. After some days of evaporation at room temperature pale-pink calcite-like triclinic prisms appear in the solution.

Crystal size: $0{\cdot}16 \times 0{\cdot}16 \times 0{\cdot}16$ mm. Density not measured. Nicolet diffractometer, graphite monochromator. 14 reflections ($9 < \theta < 11°$) for refining unit-cell dimensions. $\omega$ scan, scan width: 1·40°, scan-speed variable between 1·20 and 3·60° min$^{-1}$, total background measuring time: 20% of the scan. 3382 reflections collected, $2 < \theta < 30°$, $\pm h$, $\pm k$, $l$, $h_{\max}$

0108-2701/89/121856-03\$03.00 © 1989 International Union of Crystallography