

crystal, since the crystal is colorless. Heating experiments above 1670 K with compounds containing  $Ti^{4+}$  always make the compounds become more or less black-blue because of the reduction of  $Ti^{4+}$  to  $Ti^{3+}$ .

Iyi *et al.* (1983) prepared a single crystal with the same lattice parameters (within three times the e.s.d.) as the crystal investigated above, but they found another composition. Morgan & Shaw (1983), however, have shown that intergrowth of the Ba-poor and Ba-rich phases can occur. This makes the determination of the composition of both pure phases very difficult, especially when bulk methods such as electron probe microanalysis and density measurements (Iyi *et al.*, 1983) are used. The method of determining the composition by X-ray diffraction, used by Kimura *et al.* (1982), is in this respect more reliable. Their results for the composition of the Ba-poor phase is in agreement with our results.

This work was partly financed by the Commission of the European Community.

#### References

- CADÉE, M. C. & IJDO, D. J. W. (1982). *Mater. Res. Bull.* **17**, 481–484.  
 GRAAFF, R. A. G. DE (1973). *Acta Cryst.* **A29**, 298–301.  
 HABEREY, F., OEHLISCHLEGEL, G. & SAHL, K. (1977). *Ber. Dtsch. Keram. Ges.* **54**, 373–378.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 IYI, N., TAKEKAWA, S., BANDO, Y. & KIMURA, S. (1983). *J. Solid State Chem.* **47**, 34–40.  
 KIMURA, S., BANNAI, E. & SHINDO, I. (1982). *Mater. Res. Bull.* **17**, 209–215.  
 MATEIKA, D. & LAUDEN, H. (1979). *J. Cryst. Growth*, **46**, 85–90.  
 MORGAN, P. E. D. & SHAW, T. M. (1983). *Mater. Res. Bull.* **18**, 539–542.  
 STEVELS, A. L. N. (1978). *J. Lumin.* **17**, 121–133.

*Acta Cryst.* (1984). **C40**, 1127–1131

## Hexagonal $Y_{13}Pd_{40}Sn_{31}$ , a New Structure Type Containing Intergrown $CaCu_5$ - and $MnCu_2Al$ -Type Derived Structure Segments

BY K. CENZUAL AND E. PARTHÉ

*Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland*

(Received 29 December 1983; accepted 17 February 1984)

**Abstract.**  $M_r = 9091.2$ , hexagonal,  $hP168$ ,  $P6/mmm$ ,  $a = 19.891(7)$ ,  $c = 9.246(6)$  Å,  $V = 3168.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 9.529$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 34.9$  mm<sup>-1</sup>,  $F(000) = 7794$ ,  $T = 293$  K,  $R_w = 0.067$  for 975 independent reflections. The  $Y_{13}Pd_{40}Sn_{31}$  structure can be interpreted as an intergrowth of three kinds of structure segments: one is a ternary ordering variant of the  $CaCu_5$  type; the second has an atom arrangement similar to that of  $YPd_2Sn$  with  $MnCu_2Al$  (Heusler phase) type, a W-type derivative; and the third segment is a column of Pd-centered Sn prisms and Sn-centered Pd prisms. It is further shown that another stannide structure,  $CeNi_5Sn$ , can be interpreted as an intergrowth of binary  $CaCu_5$ -type and ternary Heusler-type slabs.

**Introduction.** There are only limited data available on the formation of ternary rare-earth–transition-element stannides and their crystal structures. In a recent crystal-chemical study of ternary rare-earth alloy structures (Parthé & Chabot, 1984) only eight ternary structure types are listed for stannides, to which has to

be added the newly reported structure type of cubic  $Gd_9Ni_{24}Sn_{49}$  (Akselrud, Komarovska & Skolozdra, 1983). However, the interest in ternary stannides has grown since the discovery of superconducting phases belonging to the  $R_3T_4Sn_{13}$  family of compounds (Vandenberg, 1980; Hodeau, Chenavas, Marezio & Remeika, 1980; Remeika *et al.*, 1980; Espinosa, Cooper & Barz, 1982). In an effort to find new superconducting ternary stannides, Jorda (1984) investigated part of the Y–Pd–Sn phase diagram and found four intermetallic compounds. Among these a phase with composition  $YPd_3Sn$  was identified by Ishikawa, Jorda & Junod (1982) as having the cubic  $MnCu_2Al$  (Heusler phase) type ( $L21$  type according to *Strukturbericht*, **1**, 488), a face-centered superstructure of the W type. This paper reports on the structure determination of another of the phases found by Jorda with approximate composition  $YPd_3Sn_2$ .

**Experimental.** Sample of nominal composition  $Y_{15.5}Pd_{50}Sn_{34.5}$  prepared by levitation melting (starting materials Y 99.99%, Pd 99.9%, Sn 99.999%). As no

single crystal could be isolated after annealing at 1093 K the sample was remelted and allowed to cool slowly; needle-shaped crystals formed. Crystal 95 × 15 × 15 μm mounted on a Philips PW1100 automatic four-circle diffractometer, Mo Kα radiation. Preliminary investigations indicated a hexagonal cell with Laue symmetry 6/*mmm* and no systematic absences. Cell parameters determined by least-squares refinement of the 2θ values of 30 reflections, 16° < 2θ < 35°. 3446 reflections collected out to sinθ/λ = 0.7035 Å<sup>-1</sup> (0 ≤ *h, k* ≤ 27; 0 ≤ *l* ≤ 13), yielding 1822 unique reflections (*R*<sub>int</sub> = 0.057), of which only 417 considered significant [*I* ≥ 3σ(*I*)]. Two standard reflections (4840 and 4840): max. intensity variation 2.4%. Lorentz-polarization and spherical absorption corrections (*μR* = 0.689, 2.601 ≤ *A*\* ≤ 2.704). Atomic scattering factors for neutral atoms from Cromer & Mann (1968), *f*' and *f*'' from *International Tables for X-ray Crystallography* (1974). As the Wilson test indicated a centric distribution of intensities, centrosymmetric space group *P6/mmm* was chosen for the resolution of the structure by direct methods. 125 reflections with |*E*| > 1.8 yielded 1908 triplets. Of the 20 atom sites listed in Table 1, 18 were found from the *E* map and the remaining two in a difference electron density map. Those positions occupied by Y atoms were deduced from an examination of the interatomic distances assuming that there was no neighboring atom at a distance less than 3 Å; Pd and Sn sites were distinguished on a difference electron density map. However, we cannot exclude an exchange between Pd and Sn at certain sites. Positional coordinates and isotropic temperature factors of Table 1 (48 parameters) were refined from the *F* values of 975 reflections (416 observed and 559 less-than-calculated greater than observed) to a final *R* = 0.074 or *R*<sub>w</sub> = 0.067 [*w* = 1/σ<sup>2</sup>(*F*), *S* = 1.029].† In final cycle (*Δ*/σ)<sub>max</sub> = 0.0003; max. (min.) height of final difference electron density map = +34 (−36) e Å<sup>-3</sup>. Observed structure factor of the 0004 reflection found to be grossly underestimated and omitted in the final stages of the refinement. The temperature factor of Y(4) is unusually high. Attempts to refine the site population together with the temperature factor failed; with *U* fixed at 1.5 × 10<sup>-2</sup> Å<sup>2</sup> a partial occupation of 83 (5)% was found. The *SINGEN* and *TANGEN* programs for the direct methods as well as all other programs used are from the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

† Lists of structure factors arranged in a standard crystallographic data file (Brown, 1983) and interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39283 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic thermal parameters* (× 10<sup>2</sup>) for Y<sub>13</sub>Pd<sub>40</sub>Sn<sub>31</sub> with space group *P6/mmm*

The temperature factor is expressed as  $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$ . E.s.d.'s are given in parentheses. Regardless of the atom species occupying a site, the sites are arranged for each Wyckoff position with increasing *x* values.

	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
Pd(1)	24( <i>r</i> )	0.1058 (2)	0.4476 (2)	0.2211 (5)	0.8 (1)
Sn(1)	12( <i>q</i> )	0.1264 (3)	0.4111 (3)	$\frac{1}{2}$	0.7 (1)
Pd(2)	12( <i>p</i> )	0.0857 (4)	0.3209 (4)	0	0.9 (1)
Pd(3)	12( <i>o</i> )	0.0884 (2)	2 <i>x</i>	0.2419 (8)	1.4 (1)
Sn(2)	12( <i>o</i> )	0.1776 (2)	2 <i>x</i>	0.2333 (7)	0.6 (1)
Pd(4)	12( <i>o</i> )	0.2603 (2)	2 <i>x</i>	0.3480 (7)	0.9 (1)
Sn(3)	12( <i>o</i> )	0.6073 (2)	2 <i>x</i>	0.1869 (6)	0.4 (1)
Y(1)	12( <i>n</i> )	0.2712 (4)	0	0.2895 (7)	1.6 (2)
Pd(5)	6( <i>m</i> )	0.1410 (3)	2 <i>x</i>	$\frac{1}{2}$	0.5 (2)
Y(2)	6( <i>m</i> )	0.5761 (4)	2 <i>x</i>	$\frac{1}{2}$	1.3 (2)
Y(3)	6( <i>l</i> )	0.2433 (4)	2 <i>x</i>	0	2.3 (3)
Pd(6)	6( <i>l</i> )	0.5452 (3)	2 <i>x</i>	0	0.8 (2)
Sn(4)	6( <i>k</i> )	0.1459 (4)	0	$\frac{1}{2}$	1.0 (2)
Pd(7)	6( <i>k</i> )	0.4225 (5)	0	$\frac{1}{2}$	0.9 (2)
Sn(5)	6( <i>j</i> )	0.1621 (4)	0	0	0.9 (2)
Sn(6)	6( <i>j</i> )	0.3862 (4)	0	0	0.8 (2)
Sn(7)	6( <i>i</i> )	$\frac{1}{2}$	0	0.2584 (9)	0.6 (2)
Y(4)	2( <i>e</i> )	0	0	0.194 (4)	5.0 (8)
Sn(8)	2( <i>d</i> )	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.7 (3)
Pd(8)	2( <i>c</i> )	$\frac{1}{2}$	$\frac{1}{2}$	0	0.9 (4)

**Discussion.** In a recent crystal-chemical study of the structures of rare-earth-transition-metal borides, silicides and their homologues (Parthé & Chabot, 1984), it was shown that a successful approach to the understanding and memorizing of complicated ternary alloy crystal structures is their interpretation as an intergrowth of segments of different simple, binary or ternary structures. The large cell and the non-trivial stoichiometry of the Y<sub>13</sub>Pd<sub>40</sub>Sn<sub>31</sub> structure made it interesting to look for a similar interpretation.

A projection in two parts of the Y<sub>13</sub>Pd<sub>40</sub>Sn<sub>31</sub> structure along [0001] is shown in Fig. 1.\* The drawing on the left contains the atom sites found between −0.3 < *z* < +0.3 and that on the right those between 0.2 ≤ *z* ≤ 0.8. The structure can be considered as an intergrowth of three kinds of structure blocks: one a ternary ordering variant of CaCu<sub>5</sub>; the second having an atom arrangement similar to the Heusler phase; and the third consisting of a column of trigonal prisms. The relative arrangement of these blocks is indicated with thin lines in the drawing.

The best known CaCu<sub>5</sub>-type derivative structure is the CeCo<sub>3</sub>B<sub>2</sub> type (Kuzma, Kripyakevich & Bilonizhko, 1969) which exists with various ternary rare-earth-transition-metal silicides, for example RRh<sub>3</sub>Si<sub>2</sub> (Chevalier, Cole, Lejay & Etourneau, 1981), but this has not yet been found with stannides. Similarly, the related PrNi<sub>2</sub>Al<sub>3</sub> structure (Fig. 2), a site-exchange variant of the CeCo<sub>3</sub>B<sub>2</sub> type where transition-metal and

\* The main-group element has been represented smaller than the transition metal in all drawings in spite of the fact that Sn is actually slightly larger than Pd.

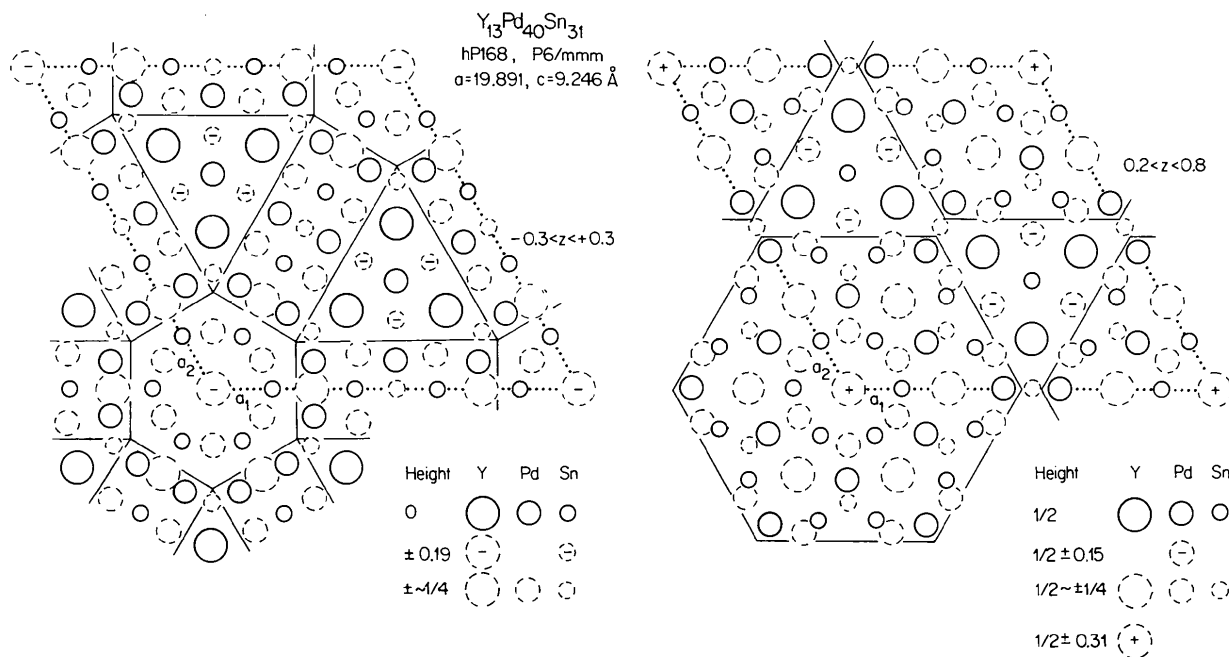


Fig. 1.  $Y_{13}Pd_{40}Sn_{31}$  in a projection along [0001]. Of the two atom sites at  $z = \frac{1}{2} \pm 0.31$  only the site occupied by Y is shown in the right-hand drawing. Thin lines are used to indicate the outlines of the different structure segments. Hexagon:  $CaCu_5$ -type segment, rectangle: Heusler-type segment; columns of trigonal prisms between these segments.

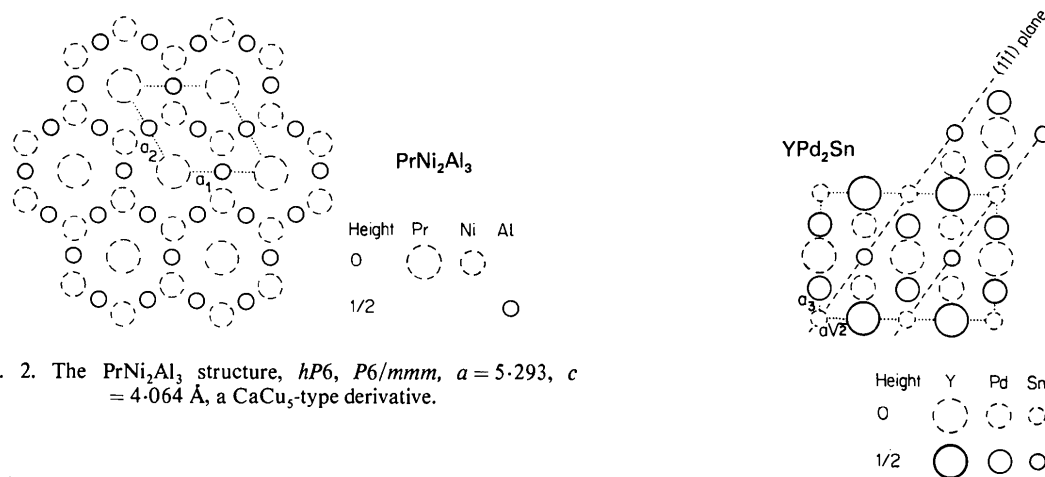


Fig. 2. The  $PrNi_2Al_3$  structure,  $hP6$ ,  $P6/mmm$ ,  $a = 5.293$ ,  $c = 4.064$  Å, a  $CaCu_5$ -type derivative.

Fig. 3. Cubic  $YPd_2Sn$ ,  $cF16$ ,  $Fm\bar{3}m$ ,  $a = 6.720$  Å, with  $MnCu_2Al$  (Heusler phase) type in a projection along [110]. The dotted lines correspond to the limits of the projection of the cubic cell. A rectangular structure block with the central Y atom replaced by Sn is found in  $Y_{13}Pd_{40}Sn_{31}$ . The dashed lines correspond to the traces of (111) planes which are the borders of a two-dimensional slab found in the  $CeNi_3Sn$  structure.

main-group-element sites have been interchanged (Rykhail, Zarechnyuk & Kuten, 1978), is not known in the stannide series. The projection of the  $PrNi_2Al_3$  structure shown in Fig. 2 has the same dimensions as the hexagonal ternary  $CaCu_5$ -type segment indicated in the right-hand drawing of Fig. 1. This segment in  $Y_{13}Pd_{40}Sn_{31}$  is continued in the [0001] direction, however, with a reduced cross section at  $z = 0$  (smaller hexagon in the drawing on the left). The site occupation close to the  $c$  axis corresponds to the atom ordering in  $PrNi_2Al_3$ . However, further out from the axis, Pd and Sn sites are in part interchanged.

In Fig. 3 is shown a projection along [110] of  $YPd_2Sn$  (Ishikawa, Jorda & Junod, 1982) which

crystallizes with the cubic  $MnCu_2Al$  type. The site occupation in the rectangular structure segments of  $Y_{13}Pd_{40}Sn_{31}$  (left-hand side of Fig. 1) is identical to the atom ordering in  $YPd_2Sn$ , except for the central site which is occupied by Sn instead of Y.

The third structure segment, shown in Fig. 4, consists of a column of Sn-centered Pd prisms alternating with Pd-centered Sn prisms turned by 60°, each kind of prism having three Y atoms in prism waist contact. To our knowledge this type of prism column has not been found in any other structure; however, centered trigonal prisms with rare-earth waist contact occur in the hexagonal ZrNiAl structure type, a Fe<sub>2</sub>P-type derivative, reported for example with HoPdSn\* and HoPtSn (Dwight, Harper & Kimball, 1973). The site occupation in these phases was not refined but a comparison between calculated and observed intensities for HoPtSn indicates that Pt atoms should be at the centers of Sn prisms.

A list of interatomic distances up to 4 Å and their relative dilatation [ $\Delta = (d - \sum r) / \sum r$ ] using atomic radii for 12-coordinated atoms (Teatum, Gschneidner & Waber, 1960) has been deposited. For Sn the radius of 1.545 Å, corresponding to valence 4, has been chosen. There is only one distance between Sn atoms shorter than twice the atomic radius [ $d[\text{Sn}(4) - \text{Sn}(4)] = 2.902$  (11) Å,  $\Delta = -6\%$ ] and none between Pd or Y atoms; minimum distances between Y and Pd, Y and Sn, and Pd and Sn atoms are 3.041 (6) Å ( $\Delta = -4\%$ ), 3.057 (11) Å ( $\Delta = -9\%$ ) and 2.610 (12) Å ( $\Delta = -11\%$ ) respectively. All Pd atoms have between four and six Sn atoms and between two and four Y atoms at short distances but only in a few cases do the Sn atoms form simple polyhedra such as tetrahedra [Pd(2) and Pd(7)] or a trigonal prism [Pd(8)]. In most cases larger coordination polyhedra, including Pd atoms and containing up to 13 atoms, must be considered. In the same way all Sn atoms have six to eight Pd and two to four Y atoms at contact distances. Simple polyhedra formed by the Pd atoms are trigonal prisms [Sn(4), Sn(5) and Sn(8)] and a cube at the center of the Heusler-type segment [Sn(6)], but here too larger, mixed, coordination polyhedra containing up to 15 atoms must generally be considered. Y(1), Y(2) and Y(3) are all surrounded by 17 atoms, while Y(4), which appears to have partial occupation, has only 13 atoms at a distance shorter than 4 Å (the coordination polyhedron as defined by the method of Frank and Kasper, however, contains 20 atoms). Among its 13 closest neighbors there is another Y(4) atom at a distance equal to twice the radius of 12-coordinated Y [ $d[\text{Y}(4) - \text{Y}(4)] = 3.60$  (5) Å].

#### Intergrowth of CaCu<sub>5</sub>- and W-type derived segments in other structures

Other rare-earth alloy structures are known where CaCu<sub>5</sub>-type segments and W-type derived segments are intergrown without the use of a third segment. One example is the CeNi<sub>5</sub>Sn structure, shown in Fig. 5

\* HoPdSn also has a second modification with orthorhombic TiNiSi type (Dwight, 1983).

(Skolozdra, Mandzyk & Akselrud, 1981), where slabs of binary CaCu<sub>5</sub> type, cut along the (0001) plane, are intergrown with slabs, previously unidentified, which are actually cut parallel to a (111) plane from a cubic Heusler phase [see traces of (111) planes in Fig. 3].\* Another example is the orthorhombic CeCu<sub>6</sub> structure

\* The hexagonal Y<sub>2</sub>Fe<sub>4</sub>Si<sub>10-x</sub> (x ~ 1) structure (Gladyshevskii, Bodak, Yarovets, Gorelenko & Skolozdra, 1978) can be described as an intergrowth of two kinds of slabs. The first contains trigonal prisms of the NbAs type, but it had previously not been possible to identify the second one from a simpler structure (see Fig. 64 in Parthé & Chabot, 1984). Dr B. Chabot has now drawn our attention to the fact that the atom sites in the second slab correspond to those of the Heusler-type slab in CeNi<sub>5</sub>Sn. The site occupation is, however, similar to that of the CsCl type except for the partially occupied Si site which should have been occupied by Fe in order to respect the model.

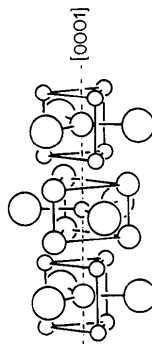


Fig. 4. Columns of Pd prisms centered by Sn atoms which alternate with Sn prisms centered by Pd, each prism having three Y atoms in waist contact. These columns are found in Y<sub>13</sub>Pd<sub>40</sub>Sn<sub>31</sub> with their axes at  $\frac{1}{3}\frac{2}{3}z$  and  $\frac{2}{3}\frac{1}{3}z$ . Large circles: Y, medium circles: Pd, Small circles: Sn.

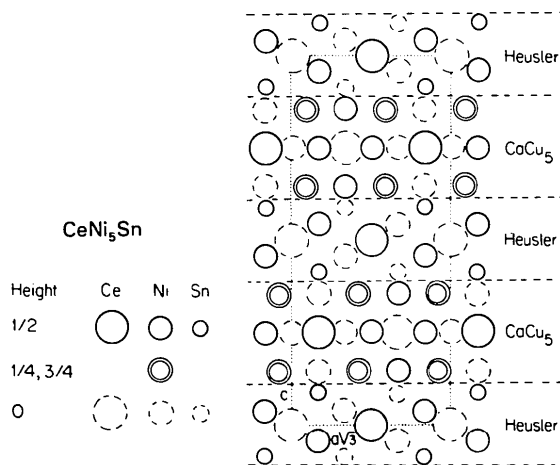


Fig. 5. The CeNi<sub>5</sub>Sn structure, *hP28*, *P6<sub>3</sub>/mmc*, *a* = 4.9049, *c* = 19.731 Å (projection along [1120]), interpreted as an intergrowth of two kinds of slabs, one built as the binary CaCu<sub>5</sub> type and the second with an arrangement as in the MnCu<sub>2</sub>Al (Heusler phase) type.

(Cromer, Larson & Roof, 1960) which can be considered as an intergrowth of  $\text{CaCu}_5$ , and an ordering variant of the  $\text{CsCl}$  type, but here structural columns are intergrown instead of slabs (see Fig. 61 in Parthé & Chabot, 1984).

We would like to thank Dr J. L. Jorda for the preparation of the samples and Dr B. Chabot for many helpful discussions. Further, we would like to acknowledge the help of Mrs I. Jequier who typed the manuscript and Mrs B. Künzler who prepared the drawings. This study has been supported by the Swiss National Science Foundation under contract No. 2.858-0.83. One of us (KC) would like to thank the Stiftung Entwicklungsfonds Seltene Metalle, Zürich, for financial help.

#### References

- AKSELUD, L. G., KOMAROVSKA, L. P. & SKOLOZDRA, R. V. (1983). *Dopov. Akad. Nauk Ukr. RSR Ser. B*, pp. 33–35.  
 BROWN, I. D. (1983). *Acta Cryst.* A **39**, 216–224.  
 CHEVALIER, B., COLE, A., LEJAY, P. & ETOURNEAU, J. (1981). *Mater. Res. Bull.* **16**, 1067–1075.  
 CROMER, D. T., LARSON, A. C. & ROOF, R. B. (1960). *Acta Cryst.* **13**, 913–918.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A **24**, 321–324.  
 DWIGHT, A. E. (1983). *J. Less-Common Met.* **93**, 411–413.  
 DWIGHT, A. E., HARPER, W. C. & KIMBALL, C. W. (1973). *J. Less-Common Met.* **30**, 1–8.  
 ESPINOSA, G. P., COOPER, A. S. & BARZ, H. (1982). *Mater. Res. Bull.* **17**, 963–969.

- GLADYSHEVSKII, E. I., BODAK, O. I., YAROVETS, V. I., GORELENKO, YU. K. & SKOLOZDRA, R. V. (1978). *Ukr. Fiz. Zh. (Russ. Ed.)* **23**, 77–82.  
 HODEAU, J. L., CHENEVAS, J., MAREZIO, M. & REMEIK, J. P. (1980). *Solid State Commun.* **36**, 839–845.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 ISHIKAWA, M., JORDA, J. L. & JUNOD, A. (1982). *Superconductivity in d- and f-Band Metals*. Proc. IVth Conf., Kernforschungszentrum Karlsruhe, Karlsruhe, June 28–30, edited by W. BUCKEL & W. WEBER, pp. 141–144.  
 JORDA, J. L. (1984). *J. Less-Common Met.* To be published.  
 KUZMA, YU. B., KRIPYAKEVICH, P. I. & BILONIZHKO, N. S. (1969). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 939–941.  
 PARTHÉ, E. & CHABOT, B. (1984). *Handbook on Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner Jr & L. Eyring, Vol. 6, ch. 48, pp. 113–334. Amsterdam: North-Holland.  
 REMEIK, J. P., ESPINOSA, G. P., COOPER, A. S., BARZ, H., ROWELL, J. M., MCWHAN, D. B., VANDENBERG, J. M., MONCTON, D. E., FISK, Z., WOOLF, L. D., HAMAKER, H. C., MAPLE, M. B., SHIRANE, G. & THOMLINSON, W. (1980). *Solid State Commun.* **34**, 923–926.  
 RYKHAL, R. M., ZARECHNYUK, O. S. & KUTEN, YA. I. (1978). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 1136–1138.  
 SKOLOZDRA, R. V., MANDZYK, V. M. & AKSELUD, L. G. (1981). *Sov. Phys. Crystallogr.* **26**, 272–274.  
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 TEATUM, E., Gschneidner, K. Jr & Waber, J. (1960). Cited in *The Crystal Chemistry and Physics of Metals and Alloys* (1972) edited by W. B. Pearson, p. 151. New York: John Wiley.  
 VANDENBERG, J. M. (1980). *Mater. Res. Bull.* **15**, 835–847.

*Acta Cryst.* (1984). C **40**, 1131–1135

## Structures of Copper(II) Complexes with *N,N'*-Bis( $\beta$ -carbamoyl ethyl)ethylenediamine and Its Deprotonated Form, $[\text{Cu}(\text{NO}_3)(\text{C}_8\text{H}_{18}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\cdot\text{NO}_3\cdot\text{H}_2\text{O}$ and $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}^*$

By TSONG-JEN LEE, TIAN-HUEY LU, SI-HAN LIU, CHUNG-SUN CHUNG AND TSENG-YUH LEE

National Tsing Hua University, Hsinchu, Taiwan 300

(Received 21 November 1983; accepted 13 February 1984)

**Abstract.** (I)  $[\text{Cu}(\text{NO}_3)(\text{C}_8\text{H}_{18}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\cdot\text{NO}_3\cdot\text{H}_2\text{O}$ ,  $M_r = 425.84$ , triclinic,  $P\bar{1}$ ,  $a = 7.663$  (3),  $b = 10.725$  (6),  $c = 10.767$  (5) Å,  $\alpha = 91.82$  (4),  $\beta = 108.18$  (9),  $\gamma = 90.14$  (4)°,  $U = 840.3$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.683$ ,  $D_m = 1.653$  (4) Mg m<sup>-3</sup>,  $F(000) = 476.8$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.842$  mm<sup>-1</sup>,  $T = 296$  (4) K. (II)  $[\text{Cu}(\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ ,  $M_r = 299.82$ , monoclinic,  $P2_1/c$ ,  $a = 6.795$  (7),  $b = 16.872$  (8),  $c = 12.103$  (13) Å,  $\beta = 118.02$  (8)°,  $U =$

$1224.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.660$ ,  $D_m = 1.653$  (4) Mg m<sup>-3</sup>,  $F(000) = 629.2$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.736$  mm<sup>-1</sup>,  $T = 296$  (4) K. Final  $R(F) = 0.068$  and  $0.060$  for 2197 and 1861 observed reflections for (I) and (II), respectively. (I) is a six-coordinate octahedral complex with a nitrate O atom and a water O atom in *trans* positions. The quadridentate ligand *bcen* coordinates to the Cu atom with two tertiary N atoms and two O atoms. In contrast to this, (II) exhibits fivefold tetragonal pyramidal coordination, where the deprotonated ligand,  $(\text{H}_{-2}\text{bcen})^{2-}$ , coordinates to the Cu atom with four N atoms and the fifth site is occupied by a water O atom.

\* Aqual[3,3'-(ethylenediimino)dipropionamide]nitratocopper(II) nitrate monohydrate and aqual[3,3'-(ethylenediimino)dipropionamido(2-)]copper(II) monohydrate.