

# The Crystal Structure of $\text{Ti}_{11+x}\text{Cu}_{1-x}\text{P}_8$ ( $x=0.34$ ) and Its Relationship to the Structures of $\text{Hf}_3\text{P}_2$ and $\text{V}_3\text{As}_2$

WILDER CARRILLO-CABRERA and TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of  $\text{Ti}_{11+x}\text{Cu}_{1-x}\text{P}_8$  with  $x=0.34$  has been determined using single-crystal X-ray diffraction data and direct methods. The space group is *Pbam*.  $Z=2$ . The cell dimensions of the crystal investigated were:  $a=18.596(4)\text{Å}$ ,  $b=9.379(3)\text{Å}$  and  $c=3.4448(7)\text{Å}$ . The structure can be described as a complex arrangement of  $\text{PTi}_6$  trigonal prisms and distorted  $\text{CuTi}_8$  b.c.c. units. It can be regarded as an intermediate between the structures of  $\text{Hf}_3\text{P}_2$  and  $\text{V}_3\text{As}_2$ .

In a previous communication on the Ti–Cu–P system<sup>1</sup> the occurrence of two orthorhombic phases, denoted  $(\text{Ti}_{1-x}\text{Cu}_x)_{-1.5}\text{P}$  and  $(\text{Ti}_{1-x}\text{Cu}_x)_{-1.6}\text{P}$ , respectively, was reported. The phases were found to contain 4.1 and 2.1 atomic percent copper respectively. In the present paper a complete structure analysis of  $(\text{Ti}_{1-x}\text{Cu}_x)_{-1.5}\text{P}$  is reported. The phase has the ideal crystallographic formula  $\text{Ti}_{11}\text{CuP}_8$ , although a moderate range of homogeneity is indicated. The crystal structure of  $\text{Zr}_{14}\text{P}_9$  (earlier<sup>2</sup>

denoted  $\text{Zr}_{-1.6}\text{P}$ ) was recently solved<sup>3</sup> and the crystallographic formula of the isostructural<sup>1</sup>  $(\text{Ti}_{1-x}\text{Cu}_x)_{-1.6}\text{P}$  can thus be given as  $\text{Ti}_{14-x}\text{Cu}_x\text{P}_9$ .

## EXPERIMENTAL

*Preparation.* Titanium filings (Koch-Light Laboratories, Colnbrook, England; claimed purity 99.95 %) and red phosphorus (Kebo, Stockholm, Sweden; better than 99 %) were reacted in an evacuated and sealed silica tube at 800 °C for three days. With the nominal composition chosen ( $\text{Ti}_{1.05}\text{P}$ ) the reaction product was found to contain TiP and  $\text{Ti}_4\text{P}_3$ . This binary alloy was subsequently arc-melted together with lumps of copper (Outokumpu Oy, Pori, Finland; as analyzed better than 99.99 %) under a purified argon atmosphere (sample I, Table 1). The (copper)/(titanium phosphide) ratio was approximately 4:1. After dissolution of the copper matrix in nitric acid aggregates of  $\text{TiCu}_2\text{P}$ <sup>1</sup> were found as well as needle-like crystals of  $\text{Ti}_{11}\text{CuP}_8$ . The crystal selected for X-ray intensity

Table 1. Unit cell dimensions for  $\text{Ti}_{11+x}\text{Cu}_{1-x}\text{P}_8$  in Ti–Cu–P alloys as measured on single crystal and powder. Standard deviations in parentheses. Sample I: arc-melted. Sample II: high-frequency melted and heat treated.

Characteristics	Copper content (at %)	Unit cell data			
		$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$
Sample I, nominal Ti/P = 1.05 single crystal	3.4 <sup>a</sup>	18.596(4)	9.379(3)	3.4448(7)	600.8
	n.d.	18.587(2)	9.3897(5)	3.4408(2)	600.5
Sample II, nominal Ti/P = 1.50 powder, (800 °C, 12d)	4.1 <sup>b</sup>	18.531(2)	9.3873(4)	3.4418(3)	598.7
	n.d.	18.473(6)	9.3918(3)	3.4446(1)	597.7

<sup>a</sup>From the present refinement. <sup>b</sup>From microprobe analysis, Ref. 1.

data collection was limited by the planes (210), (110), (010), (410) and (001). Its dimensions were approximately  $12 \times 12 \times 140 \mu\text{m}$ . Attempts to grow larger crystals by heat-treatment at 800 and 900 °C were unsuccessful.

*X-Ray diffraction measurements and data reduction.* Cell dimensions of powders were measured using Guinier-Hägg films, recorded with  $\text{CuK}\alpha_1$  radiation and with semiconductor grade silicon ( $a=5.431065 \text{ \AA}$ ) as internal standard. The single-crystal X-ray measurements were accomplished with a Nonius CAD 4-F automatic diffractometer, controlled by a PDP 8/A computer. The cell dimensions of the crystal used for the X-ray intensity data collection were determined by least-squares refinement of the averages,  $\theta$ , of the setting angles of 34 Friedel pairs of reflections with  $15^\circ < 2\theta < 32^\circ$ .  $\text{MoK}\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ) was used for this measurement as well as for the intensity data collection. The intensities were collected using the  $\omega - 2\theta$  scan technique. Instrumental stability and crystal setting were checked by remeasurement of three standard reflections every 25 reflections. The intensities of these reflections were within the limits of the statistical fluctuations, up to  $2\theta=20^\circ$  all reflections with  $l$  positive were measured and for  $20^\circ < 2\theta < 80^\circ$  one octant of the reciprocal lattice ( $h, k, l$  positive) was measured. The intensities were corrected for Lorentz, polarization and absorption effects.

Correction for absorption was applied using the Gaussian grid method and a linear absorption coefficient of  $89.8 \text{ cm}^{-1}$  (calculated with mass absorption coefficients from Ref. 4) assuming one atomic percent copper in the crystal. The transmission varied between 0.863 and 0.926. In total 1240 reflections were recorded. After averaging symmetry-related reflections the original data set was reduced to 1100 independent reflections. Only 27% of these had  $F_o^2 > 3\sigma(F_o^2)$ , partially a consequence of the small crystal volume. As can be seen below, this affects the refinement and results in relatively high final  $R$  values and estimated standard deviations of the parameters. 644 independent reflections displayed positive intensities and were employed in the crystal structure analysis.

*Calculations.* All calculations were performed with the computers NORD 100 and IBM 1800 using a system of programs described by Lundgren.<sup>5</sup>

## CELL DIMENSION DETERMINATIONS

The cell dimensions of  $\text{Ti}_{1-x}\text{Cu}_x\text{P}_8$  in the Ti-Cu-P system were determined and are given in Table 1. Sample I contained an excess of phosphorus while sample II was prepared with stoichiometric

amounts of the components, although it might be deficient in phosphorus due to losses during the preparation. Table 1 shows that  $\text{Ti}_{1+x}\text{Cu}_{1-x}\text{P}_8$  has a range of homogeneity.

## STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by using direct methods for sign determination. Normalized structure factors ( $E$ ) were calculated with the program EFAK. The frequency distribution of the  $E$  values corresponded to that of a centric structure. This observation together with the observed extinctions ( $h=2n+1$  and  $k=2n+1$  among  $(h0l)$  and  $(0kl)$  reflections respectively) led to the space group  $Pbam$  (No. 55), which was later confirmed in the refinement. 171 reflections with  $E > 1.0$  were included in the sign determination, which was carried out using a recent version<sup>6</sup> of the program MULTAN.<sup>7</sup> Of the five solutions obtained, the one with the highest figure of merit (1.54) was used in the calculation of an electron density map, which yielded the complete structure (seven non-equivalent metal atoms with the copper peak higher than the others and four non-equivalent phosphorus atoms). After the refinement of the structure we found that only one of the 171 signs was incorrectly determined.

The structure was refined on  $F^2$  using a full-matrix, least-squares program and the approximate coordinates obtained from the  $E$  map as initial coordinates. Complex neutral-atoms scattering factors were used.<sup>4</sup> The quantity minimized was  $\sum w(|F_o^2| - k^2|F_c^2|)^2$  with the weight  $w$  given by

$$w^{-1} = \sigma_c^2(F_o^2) + (p \cdot |F_o^2|)^2$$

where  $\sigma_c$  is the standard deviation of  $F_o^2$ , based on counting statistics, and  $p$  an empirical parameter, chosen to obtain a satisfactory weight analysis ( $p$  was 0.046 in the final refinement). The agreement indices are defined as

$$R(F^2) = \frac{\sum(|F_o^2| - |F_c^2|)}{\sum|F_o^2|}$$

$$R_w(F^2) = \frac{[\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}}$$

where  $F_o^2$  has been multiplied by  $1/k^2$ . Extinction effects were hardly discernible and thus no correction was applied.

Table 2. Structure data for  $Ti_{11.34}Cu_{0.66}P_8$ . Standard deviations in parentheses. Space group  $Pbam$  (No. 55),  $Z=2$ . Cell dimensions:  $a=18.596(4)$  Å,  $b=9.379(3)$  Å,  $c=3.4448(7)$  Å.

Atom	Position	Positional parameters			$B(\text{Å}^2)$
		$x$	$y$	$z$	
Ti(1)	4h	0.41152(19)	0.35481(36)	1/2	0.27(7)
Ti(2)	4h	0.56939(19)	0.31071(39)	1/2	0.29(7)
Ti(3)	4g	0.35621(19)	0.10263(36)	0	0.25(7)
Ti(4)	4g	0.69768(21)	0.22835(38)	0	0.38(7)
Ti(5)	4h	0.26950(18)	0.50860(39)	1/2	0.16(7)
Ti(6)	3d	0	1/2	1/2	0.46(10)
Cu <sup>a</sup>	2a	0	0	0	0.38(11)
P(1)	4h	0.29320(29)	0.24769(58)	1/2	0.25(10)
P(2)	4g	0.48068(27)	0.20809(55)	0	0.42(10)
P(3)	4h	0.63215(32)	0.08331(57)	1/2	0.56(10)
P(4)	4g	0.63233(31)	0.46018(53)	0	0.41(10)

<sup>a</sup>Occupancy 66(4)% Cu, the remainder Ti.

The first refinement of  $F^2$ , based on positive reflections only, gave a weighted  $R_w$  value of 0.120,  $R(F^2)=0.181$ . The refinement yielded a significantly higher temperature factor for the 2(a) position, where copper was located, than for the other positions, which indicated the occurrence of vacancies or partial substitution of titanium for copper in that position. A least-squares refinement of the substitutional model gave an occupancy of 66(4)% copper and 34(4)% titanium (reset). A refinement of the vacancy model gave an occupancy of 89(2)% for copper (*i.e.* 11% vacancies). The agreement indices and the positional and temperature parameters were, however, not significantly different in the two refinements. The choice between the two models was made on the following grounds. It can be seen from Table 1 that a phosphorus-poor composition (sample II) leads to a smaller cell volume than a phosphorus-rich composition (sample I). The vacancy model would, however, require that sample II corresponds to a phosphorus-rich composition. Furthermore, the average distance from the 2(a) position to its titanium neighbours is 2.77 Å, which is slightly larger than the Goldschmidt radius sum (2.73 Å). If vacancies were present the distance would be anticipated to be shorter than the radius sum.

Refinements under the assumption of substitution of copper for titanium in the other positions did not reveal any significant effects.

The structure data from the final refinement are presented in Table 2. The agreement factors obtained were (all 644 reflections larger than zero):

$$R_w(F^2)=0.115, R(F^2)=0.176, R(F)=0.179$$

The shifts in the final cycle were less than  $0.002\sigma$ . The total number of parameters varied was 31 (one scale factor, one occupancy factor, 18 positional parameters and 11 temperature factors).

A normal probability  $\Delta R$  plot<sup>8</sup> after the final refinement was very close to a straight line with a slope of 1.03 and an intercept of  $-0.10$  on the expected  $\Delta R$  axis. Two values fell outside the range  $\pm 4\sigma$ . The standard deviation of an observation of unit weight,<sup>9</sup>  $S$ , was 1.06, which together with the slope of the normal probability line mentioned above, indicates that the weights  $w_i$  were correctly chosen.

A final difference Fourier map calculated from the parameters obtained in the last cycle of refinement exhibited no electron density exceeding 4% of a phosphorus peak in the  $F_o$  synthesis.

The agreement factors for a refinement omitting reflections with  $F_o^2 < 3\sigma(F_o^2)$  were (298 reflections):

$$R_w(F^2)=0.101; R(F^2)=0.099; R(F)=0.061$$

The standard deviations were, however, on the average 39% larger than those for the refinement described above.

A list of observed and calculated structure factors can be obtained on request from the Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

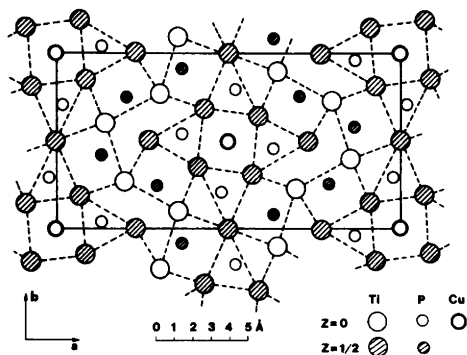


Fig. 1. Projection along the  $c$  axis of the structure of  $\text{Ti}_{11}\text{CuP}_8$ .

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A projection of the structure along the  $c$  axis is shown in Fig. 1. The structure may be regarded as built up of distorted body-centered cubic  $M'M_8$  units (with mainly copper at the center of the cube) and  $\text{PM}_6$  units, consisting of a phosphorus atom at the center of a trigonal prism of metal atoms. These structural units are also found in several other transition metal phosphides, for instance in the  $\text{Nb}_7\text{P}_4$ ,  $^{10}\text{Nb}_3\text{P}_3$ <sup>11</sup> and  $\text{Zr}_{14}\text{P}_9$ <sup>3</sup> types, which all have representatives in the Ti-Cu-P system.<sup>1</sup> There are four non-equivalent phosphorus atoms in the structure and the corresponding trigonal

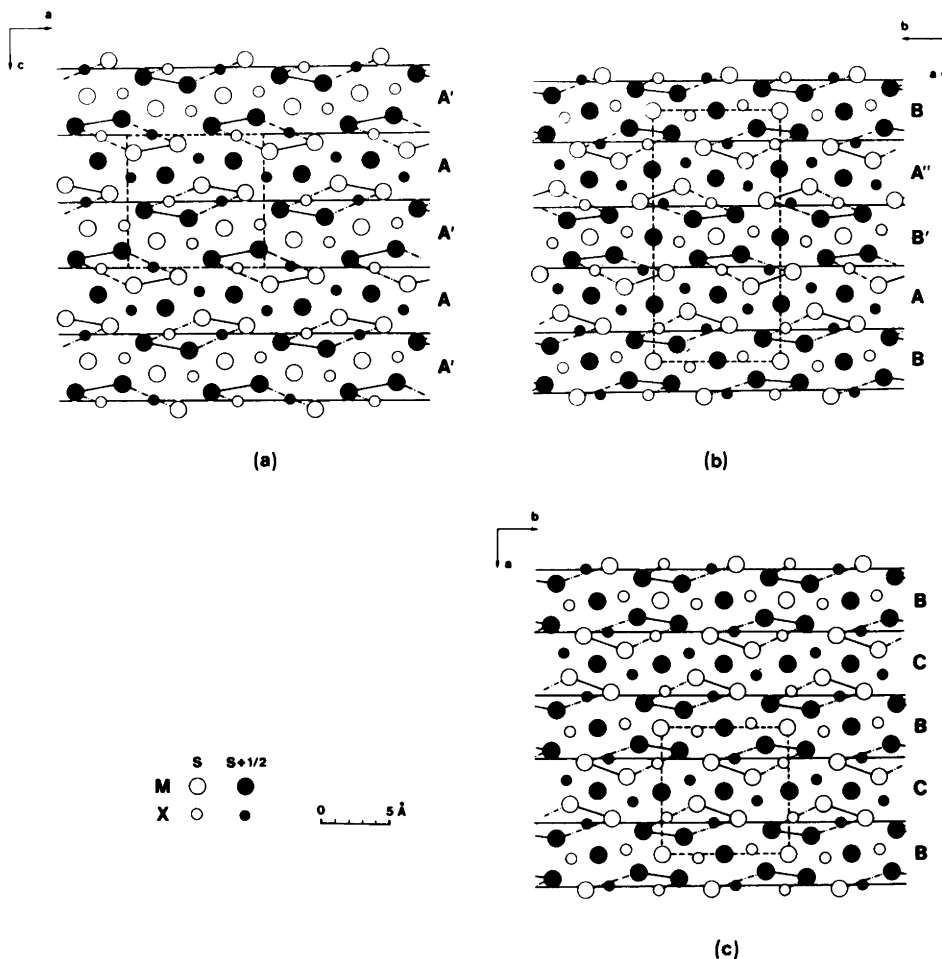


Fig. 2. Projections along the direction of the short axis of (a)  $\text{Hf}_3\text{P}_2$  ( $s=1/4$ ), (b)  $\text{Ti}_{11}\text{CuP}_8$  ( $s=0$ ), (c)  $\text{V}_3\text{As}_2$  ( $s=0$ ).

Table 3. Interatomic distances in  $Ti_{1.1.34}Cu_{0.66}P_8$ . The table shows all M–P and M–M distances less than 4.00 Å and P–P distances less than 3.41 Å. Standard deviations in parentheses.

Ti(1)–P(1)	2.419(6)	Ti(6)–2P(3)	2.579(6)
–2P(2)	2.552(5)	–4P(2)	2.628(4)
–2P(4)	2.577(5)	–2Ti(2)	3.187(4)
–2Cu(1)	2.744(3)	–4Ti(3)	3.323(3)
–Ti(2)	2.965(5)	–2Ti(6)	3.445(1)
–Ti(5)	3.009(5)	–2Ti(1)	3.712(4)
–2Ti(3)	3.101(4)		
–Ti(2)	3.157(5)	Cu(1)–2P(4)	2.489(6)
–2Ti(1)	3.445(1)	–4Ti(1)	2.744(3)
–Ti(6)	3.712(4)	–2P(2)	2.761(5)
		–4Ti(2)	2.790(3)
		–2Cu(1)	3.445(1)
Ti(2)–P(3)	2.431(7)	P(1)–Ti(1)	2.419(6)
–2P(4)	2.510(5)	–2Ti(4)	2.484(5)
–2P(2)	2.572(5)	–Ti(5)	2.486(7)
–2Cu(1)	2.790(3)	–2Ti(3)	2.488(5)
–Ti(1)	2.965(5)	–Ti(5)	2.527(7)
–2Ti(4)	3.042(4)	–P(3)	3.389(8)
–Ti(1)	3.157(5)	–P(3)	3.401(8)
–Ti(6)	3.187(4)		
–Ti(5)	3.442(5)	P(2)–Ti(3)	2.517(6)
–2Ti(2)	3.445(1)	–2Ti(1)	2.552(5)
		–2Ti(2)	2.572(5)
		–2Ti(6)	2.628(4)
		–Cu(1)	2.761(5)
Ti(3)–2P(3)	2.461(5)	P(3)–Ti(2)	2.431(7)
–2P(1)	2.488(5)	–2Ti(3)	2.461(5)
–P(2)	2.517(6)	–2Ti(4)	2.510(5)
–2Ti(5)	3.035(4)	–Ti(6)	2.579(6)
–2Ti(1)	3.101(4)	–Ti(5)	2.696(7)
–Ti(4)	3.262(5)	–P(1)	3.389(8)
–2Ti(6)	3.323(3)	–P(1)	3.401(8)
–Ti(4)	3.347(5)		
–2Ti(3)	3.445(1)	P(4)–Cu(1)	2.489(6)
		–Ti(4)	2.491(6)
		–2Ti(2)	2.510(5)
		–2Ti(5)	2.527(5)
		–2Ti(1)	2.577(5)
Ti(4)–2P(1)	2.484(5)		
–P(4)	2.491(6)		
–2P(3)	2.510(5)		
–2Ti(2)	3.042(4)		
–2Ti(5)	3.070(4)		
–2Ti(5)	3.113(4)		
–Ti(3)	3.262(5)		
–Ti(3)	3.347(5)		
–2Ti(4)	3.445(1)		
Ti(5)–P(1)	2.486(7)		
–2P(4)	2.527(5)		
–P(1)	2.527(7)		
–P(3)	2.696(7)		
–Ti(1)	3.009(5)		
–2Ti(3)	3.035(4)		
–2Ti(4)	3.070(4)		
–2Ti(4)	3.113(4)		
–Ti(2)	3.442(5)		
–2Ti(5)	3.445(1)		

prism axes are oriented parallel (two) to or perpendicular (two) to the  $c$  axis of the unit cell. In addition to the six metal atoms of the prism the phosphorus atom coordinates further metal atoms, situated outside the quadrilateral faces of the prism. The coordination numbers are 7, 7 (+1), 7 and 8 for the atoms P(1), P(2), P(3) and P(4), respectively.

The interatomic distances are given in Table 3. 64 % of the Ti–P distances are shorter than the sum of the Goldschmidt metal radius and the tetrahedral covalent radius for phosphorus. The shortest Ti–P distance is 2.42 Å as compared to the corresponding radius sum of 2.55 Å. The shortest Ti–Ti distance is 2.97 Å, which is slightly larger than the radius sum 2.90 Å. The average distance between the atoms in the 2(a) position and its eight titanium neighbours is 2.77 Å in close agreement with the radius sum 2.79 Å (weighted radius for the atoms in the 2(a) position used). There are no P–P bonds in the structure, since the shortest P–P distance is 3.39 Å.

Ti<sub>11</sub>CuP<sub>8</sub> crystallizes with a new structure type. The structure does, however, display structural features common to the structures of V<sub>3</sub>As<sub>2</sub><sup>12</sup> as well as Hf<sub>3</sub>P<sub>2</sub>.<sup>13</sup> This is demonstrated in Fig. 2, where the structures have been partitioned into slabs (A, B, C) to show the common structural units. Furthermore, a six-atom unit is indicated to facilitate the comparison. A slab of type A is related to one of type A' by a center of symmetry while A' is related to A'' by a translation in the direction of the short axis by one half of that axis. B' is generated from B by the operation of a reflection glide plane. Using the notations given, the three structures can be described by the stacking sequences of slabs:

Hf <sub>3</sub> P <sub>2</sub>	AA'AA'...
Ti <sub>11</sub> CuP <sub>8</sub>	ABA''B'ABA''B'...
V <sub>3</sub> As <sub>2</sub>	BCBC...

There are thus slabs of type A common to the structures of Hf<sub>3</sub>P<sub>2</sub> and Ti<sub>11</sub>CuP<sub>8</sub> and slabs of type B common to the structures of V<sub>3</sub>As<sub>2</sub> and Ti<sub>11</sub>CuP<sub>8</sub>. The non-metal atoms in the B type slabs (B, B') have coordination number eight while those in the other slabs (A, A', A'', C) have coordination number seven. It should be observed as well that the structure of Ti<sub>11</sub>CuP<sub>8</sub> is related to those of phosphides with compositions different from M<sub>3</sub>P<sub>2</sub>. The Nb<sub>8</sub>P<sub>5</sub> structure<sup>14</sup> can, for instance, be described by the stacking sequence of slabs in the  $c$  direction:

ADA''D'ADA''D'...

where A and A'' denote the same slabs as above while D is a new slab, containing fragments of the B slab.

*Acknowledgements.* This investigation has been supported by the Swedish Natural Science Research Council. One of us (W. C.-C.) is indebted to the Swedish Institute for financial support.

## REFERENCES

1. Carrillo-Cabrera, W. and Lundström, T. *Acta Chem. Scand. A* 33 (1979) 401.
2. Lundström, T. *Acta Chem. Scand.* 20 (1966) 1712.
3. Tergenius, L.-E., Nöläng, B. N. and Lundström, T. *Acta Chem. Scand. A* 35 (1981) 693.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
5. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Report UUIC-B13-4-02, Institute of Chemistry, University of Uppsala, Uppsala 1975, Sweden.
6. Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. and Woolfson, M. M. *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from the X-Ray Diffraction Data*, University of York, York 1978.
7. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
8. Abrahams, S. C. and Keve, E. T. *Acta Crystallogr. A* 27 (1971) 157.
9. Abrahams, S. C. *Acta Crystallogr. A* 25 (1969) 165.
10. Rundqvist, S. *Acta Chem. Scand.* 20 (1966) 2427.
11. Hassler, E. *Acta Chem. Scand.* 25 (1971) 129.
12. Berger, R. *Acta Chem. Scand. A* 31 (1977) 287.
13. Lundström, T. *Acta Chem. Scand.* 22 (1968) 2191.
14. Anugul, S., Pontchour, C.-O. and Rundqvist, S. *Acta Chem. Scand.* 27 (1973) 26.

Received January 30, 1981.