coordinated O atom is closer to N than the other two and the metal-bound O—N—O angles are significantly smaller than the other O—N—O angles, as usual in bidentate nitrate groups. The Y atom is displaced from the plane of the three nitrate groups by 0·048 (1), 0·233 (1) and 0·052 (1) Å respectively. Dihedral angles between the planes of the nitrate groups are 83·3 (5), 80·7 (4) and 67·2 (5)°. Chains of coordination polyhedra are linked together by hydrogen bonds, the water O atom forming two hydrogen bonds with two neighbouring chains [OW—O11(1 − x, 1 − y, $\bar{z}$): 2·834 (10) Å and OW—O13(x − 1, y, z): 2·922 (16) Å].

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Refinement of the Structure of Robinsonite, Pb4Sb6S13

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Abstract. The structure of robinsonite, Pb4Sb6S13, M_r = 1976·1, previously determined by Petrova, Kaplunnik, Bortnikov, Pobedimskaya & Belov [*Dokl. Akad. Nauk SSSR* (1978), **241**, 88–90] in the triclinic space group $P1$, has been refined in monoclinic $I2/m$, $a = 23·698$ (8), $b = 3·980$ (8), $c = 24·466$ (8) Å, $\beta = 93·9$ (3)°, $V = 2302$ Å^3, $Z = 4$, $D_x = 5·7$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 356·4$ cm^{-1}, $F(000) = 3368$, room temperature, $R = 0·071$, $wR = 0·064$ for 2361 independent reflections. The crystal was prepared by annealing at 723 K in the presence of I$_2$ in vacuum-sealed ampoules. The basic arrangement of atoms proposed by Petrova *et al.* (1978) is confirmed but both the space group and the cation distribution, determined by site-occupancy refinement and by bond-valence analysis, are shown to be different. A bond-valence analysis of the homeotypic Sn4Sb6S13 [Jumas, Olivier-Fourcade, Philippot & Maurin (1980). *Acta Cryst.* B36, 2940–2945], shows that it has a distribution of Sb atoms similar to that in the Pb analogue.

Introduction. Several crystallographic studies (Berry, Fahey & Bailey, 1952; Jambor & Lachance, 1968; Wang, 1977; Petrova, Kaplunnik, Bortnikov, Pobedimskaya & Belov, 1978; Ayora & Gali, 1981;

Jambor & Owens, 1982) have been devoted to both natural and synthetic robinsonite. As a result the composition of the phase has been firmly established as Pb4Sb6S13 but the symmetry and the details of the structure remain controversial. Our unit cell agrees with most previous results but only Petrova *et al.* (1978) report the structure. The space group they use ($P1$) differs from that ($B2/m$) assigned by Wang (1977) and they also appear to have permuted the lattice angles. Jumas, Olivier-Fourcade, Philippot & Maurin (1980) have reported a similar structure for Sn4Sb6S13 in the space group $I2/m$ (equivalent to Wang's $B2/m$). We have undertaken an independent structure determination to resolve these uncertainties.

Experimental. Single crystals of Pb4Sb6S13 were synthesized from elemental lead, antimony, and sulfur of 'Specpure' grade, supplied by Johnson Matthey plc. The elements were combined in the proportions of 60 mol % of PbS and 40 mol % of Sb$_2$S$_3$, sealed in evacuated silica tubes, melted at 1073 K and quenched. The ingot was then ground and pelletized. Three 1 g pellets were each placed in separate silica tubes with approximately 1 mg of I$_2$. The tubes were then evacuated, sealed and annealed in a two-zone

horizontal furnace for 3 d. The temperature gradient in the 20 cm ampoules was close to 5 K cm^{-1}, and the pellets were kept in the cooler end (723 K). Phase separation into regions of acicular crystals occurred in all the ampoules. A needle-shaped crystal, $0.15 \times 0.3 \times 0.6$ mm, was mounted with the needle axis along the X-ray goniometer axis.

The unit-cell parameters were refined from 15 well centred reflections in the range $15 < 2\theta < 30°$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Intensities of 4075 reflections were measured in the range $2\theta < 50°$ and $0 \le h \le 28$, $-4 \le k \le 4$, $-29 \le l \le 29$ with a $\theta/2\theta$ scan. Two standard reflections, 631 and $\overline{1}09$, measured every 50 reflections, varied by 3.1%. The systematic absences, hkl: $h + k + l = 2n + 1$, and the symmetry of the intensities of the reflections observed on precession photographs, indicated $I2/m$, $I2$, or Im as possible space groups. The first was assumed and led to a satisfactory refinement. The absorption correction was based on ψ scans of 21 reflections (maximum correction 3.15 for the intensity of the 303 reflection) and the intensites were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{int} = 0.032$ before the absorption correction, $R_{int} = 0.029$ after) to give 2361 unique reflections.

The initial atomic positions, found by direct methods using SHELXS86 (Sheldrick, 1986), were refined using SHELX76 (Sheldrick, 1976) by full-matrix least squares (on F) with anisotropic displacement parameters for all the atoms and mixed Pb/Sb occupancies for the cation sites. Complex scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography (1974). Intensities were weighted by $w = k/[\sigma^2(F_o) + gF_o^2]$, where k refined to 0.34, g was fixed at 0.0002 and $\sigma(F_o)$ was the uncertainty derived from the counting statistics. The Pb occupation numbers of sites 13 and 14 quickly refined to values close to 1.0 and were kept fixed at this value in the subsequent refinement. The refinement converged to $wR = 0.061$, $R = 0.068$ and $S = 2.2$.

The program did not permit a constraint to be put on the total number of Pb or Sb atoms in the unit cell and the refined occupation numbers, shown in column 3 of Table 1, result in the formula of $Pb_{5.04}Sb_{4.96}S_{13}$ which is appreciably different from the electrically neutral formula $Pb_4Sb_6S_{13}$. Since this result is unsatisfactory an attempt was made to determine the site occupancies using bond valences (s). These were calculated from the bond lengths (r) using the equation

$$s = \exp[(r_0 - r)/0.37], \qquad (1)$$

where $r_0 = 2.52$ Å for Sb—S bonds and 2.541 Å for Pb—S bonds. The bond-valence analysis is presented

Table 1. *Percentage of* Sb *on cation sites in robinsonite and* $Sn_4Sb_6S_{13}$

| | Robinsonite | | | $Sn_4Sb_6S_{13}$ | |
	Petrova et al. (1978) (average)	X-ray	Bond valence	Jumas et al.	This work
M(1)	50	59	80	0	100
M(2)	0	15	18	100	0
M(3)	100	92	100	0	100
M(4)	100	84	100	0	100
M(10)	100	84	100	0	100
M(11)	100	76	88	100	48
M(12)	100	73	78	100	100
M(13)	0	0	0	100	0
M(14)	0	0	0	100	0
M(15)	50	12	36	100	35
Formula	$Pb_4Sb_6S_{13}$	$Pb_{5.04}Sb_{4.96}S_{13}$	$Pb_4Sb_6S_{13}$	$Sn_4Sb_6S_{13}$	$Sn_{4.17}Sb_{5.83}S_{13}$

in Table 2. Using the rule that the sum of bond valences (s) around each atom should be equal to its oxidation state, V, one can use the bond-valence sums to make an independent determination of the occupation numbers. Valence sums around Pb atoms are expected to be 2, for Sb they should be 3, but for most cation sites the sums fall between 2 and 3 indicating partial occupation. If x and y are the occupation numbers for Sb and Pb respectively, then the requirement that the sum of the bond valences at each site is equal to the oxidation number becomes:

$$x\Sigma s_{Sb} + y\Sigma s_{Pb} = xV_{Sb} + yV_{Pb}, \qquad (2)$$

where s_{Sb} is the bond valence calculated with $r_0 = 2.52$ Å, s_{Pb} is the valence of the same bond calculated with $r_0 = 2.541$ Å, $V_{Sb} = 3$ and $V_{Pb} = 2$. The values of x and y can then be found recognizing that $x + y = 1$. The occupation numbers determined by both X-rays and the bond-valence analysis are compared in Table 1. The results clearly depend on a suitable choice of r_0 for the Sb—S and Pb—S bonds. Initially the values $r_0(Pb—S) = 2.541$ Å and $r_0(Sb—S) = 2.474$ Å, taken from Brown & Altermatt (1985), were used in equation (1) but in order to obtain the electroneutral formula it was found necessary to change $r_0(Sb—S)$ to 2.52 Å.*

Because the occupation numbers determined from the bond valences correspond to an electrically neutral crystal we consider these values to be more reliable. Using them as fixed parameters in SHELX76 and refining all positional and anisotropic atomic displacement parameters, we obtained $wR = 0.064$, $R = 0.071$, goodness-of-fit $S = 2.4$. Maximum final shift/e.s.d. 0.68, mean 0.12, maximum density in the final difference Fourier map 3.7 e Å^{-3}, minimum

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* An electrically neutral formula can be obtained either by decreasing the value of $r_0(Pb—S)$ or by increasing the value of $r_0(Sb—S)$ or both. Decreasing $r_0(Pb—S)$ leads to physically unreasonable occupation numbers for some sites ($x < 0$). The best solution is reached increasing only the value of $r_0(Sb—S)$.

Table 2. *Bond valences in robinsonite weighted according to X-ray occupation number*

	M(1)	M(2)	M(3)	M(4)	M(10)	M(11)	M(12)	M(13)	M(14)	M(15)	Σs
%Sb	59	15	92	84	84	76	73	0	0	12	
S(1)	0·63			0·61 × 2					0·16		−2·01
S(2)		0·52	0·30 × 2	0·32 × 2							−1·76
S(3)		0·30 × 2	1·26					0·22 × 2			−2·30
S(4)	0·20 × 2	0·39 × 2			1·20						−2·38
S(5)	0·74 × 2 + 0·27									0·16 × 2	−2·07
S(6)			0·70 × 2					0·38	0·14		−1·92
S(10)					1·13					0·48 × 2	−2·09
S(11)						1·14			0·35 × 2	0·26 × 2	−2·36
S(12)							0·97	0·35 × 2	0·28 × 2		−2·23
S(13)							0·72 × 2	0·15 + 0·12 × 2			−1·83
S(14)						0·50 × 2	0·16 × 2		0·47		−1·79
S(15)					0·19 × 2	0·38 × 2				0·58	−1·72
S(16)		0·14 × 2			0·76 × 2						−1·80
Σs	2·78	2·18	3·26	3·06	3·03	2·90	2·73	1·91	2·03	2·38	
V	2·59	2·15	2·95	2·84	2·84	2·53	2·73	2·00	2·00	2·12	

Table 3. *Atomic coordinates and equivalent isotropic displacement parameters for robinsonite*

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	U_{eq} (Å^2)
M(1)	0·6901 (1)	0·5	0·7983 (1)	0·020 (1)
M(2)	0·5053 (1)	0·5	0·8117 (1)	0·027 (1)
M(3)	0·4365 (1)	0·0	0·9438 (1)	0·026 (1)
M(4)	0·6172 (1)	0·0	0·9228 (1)	0·027 (1)
M(10)	0·5068 (1)	0·5	0·3527 (1)	0·025 (1)
M(11)	0·4206 (1)	0·5	0·5114 (1)	0·034 (1)
M(12)	0·3431 (1)	0·5	0·6706 (1)	0·029 (1)
M(13)	0·1811 (1)	0·0	0·6627 (1)	0·032 (1)
M(14)	0·2698 (1)	0·0	0·5216 (1)	0·021 (1)
M(15)	0·3559 (1)	0·0	0·3694 (1)	0·038 (1)
S(1)	0·6921 (3)	0·5	0·9088 (3)	0·015 (4)
S(2)	0·5258 (3)	0·5	0·9251 (3)	0·019 (4)
S(3)	0·4199 (3)	0·0	0·8444 (3)	0·012 (4)
S(4)	0·5934 (3)	0·0	0·8235 (3)	0·015 (4)
S(5)	0·7627 (3)	0·0	0·8132 (3)	0·020 (4)
S(6)	0·3629 (3)	0·5	0·9507 (3)	0·017 (4)
S(10)	0·4090 (3)	0·5	0·3101 (3)	0·018 (4)
S(11)	0·3279 (3)	0·5	0·4579 (3)	0·016 (4)
S(12)	0·2509 (3)	0·5	0·6108 (3)	0·013 (4)
S(13)	0·3046 (3)	0·0	0·7281 (3)	0·026 (4)
S(14)	0·3782 (3)	0·0	0·5766 (3)	0·019 (4)
S(15)	0·4545 (3)	0·0	0·4347 (3)	0·024 (4)
S(16)	0·5335 (3)	0·0	0·2896 (3)	0·031 (4)

Table 4. *Bond distances (Å) less than 3·4 Å in robinsonite*

Narrow ribbon			Wide ribbon		
M(1)—S(1)	2·701 (6)		M(10)—S(10)	2·478 (7)	
	S(5) × 2	2·640 (6)		S(16) × 2	2·622 (5)
	S(5)	3·016 (7)		S(15) × 2	3·141 (6)
M(2)—S(2)	2·783 (6)		M(11)—S(11)	2·477 (7)	
	S(4) × 2	2·885 (5)		S(14) × 2	2·779 (5)
	S(3) × 2	2·986 (5)		S(15) × 2	2·885 (6)
	S(16) × 2	3·258 (6)			
M(3)—S(3)	2·437 (6)		M(12)—S(12)	2·538 (6)	
	S(6) × 2	2·657 (4)		S(13) × 2	2·633 (5)
	S(2) × 2	2·963 (5)		S(14) × 2	3·196 (6)
M(4)—S(4)	2·455 (7)		M(13)—S(6)	2·900 (7)	
	S(1) × 2	2·702 (5)		S(12) × 2	2·933 (5)
	S(2) × 2	2·946 (5)		S(3) × 2	3·109 (5)
				S(13)	3·236 (7)
				S(13) × 2	3·334 (6)
			M(14)—S(14)	2·828 (7)	
				S(11) × 2	2·932 (5)
				S(12) × 2	3·010 (5)
				S(1)	3·210 (6)
				S(6)	3·262 (6)
			M(15)—S(15)	2·739 (7)	
				S(10) × 2	2·808 (5)
				S(11) × 2	3·045 (5)
				S(5) × 2	3·211 (5)

$= -5·2$ e Å^{-3}. Since this refinement gives occupation numbers that are better than, and agreement indices that are essentially similar to, the previous refinement, it was used to generate the final atomic coordinates and equivalent isotropic displacement parameters listed in Table 3. Interatomic distances are given in Table 4.*

Discussion. Our determination confirms the correctness of the structure reported by Petrova *et al.* (1978) but indicate that they missed the mirror plane and

* Lists of observed and calculated structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52411 (51 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. The *hkl* reflections have been transformed to $\overline{h}kl$.

center of symmetry. By ignoring this higher symmetry they were able to refine a model without using sites of mixed occupancy but a valence analysis of their structure does not indicate that the segregation of different ions into sites related by a pseudo-center of symmetry is justified nor were we able to find any evidence in our diffraction patterns of the loss of monoclinic symmetry that such a separation implies. The refined atomic displacement parameters are also consistent with all atoms lying on mirror planes.

The structure of $Pb_4Sb_6S_{13}$ (Figs. 1 and 2) consists of ribbons composed of face-sharing back-to-back square-pyramidal $(Pb,Sb)S_5$ groups. There are two types of ribbon both of which are one pyramid thick and extend indefinitely in the **b** direction but which have different widths. The narrow ribbon, in which the width equals twice the basal distance of the $(Pb,Sb)S_5$ pyramid, is identical with the building

unit, Sb_4S_6, in stibnite (Bayliss & Nowacki, 1972). The second kind of ribbon is three times as wide and can be formed by insertion of four additional pairs of back-to-back pyramids in the middle of the narrow ribbon.

Our description of the wide ribbons is equivalent to that given by Smith & Hyde (1983), where they picture the wide ribbons as obtained by the introduc-
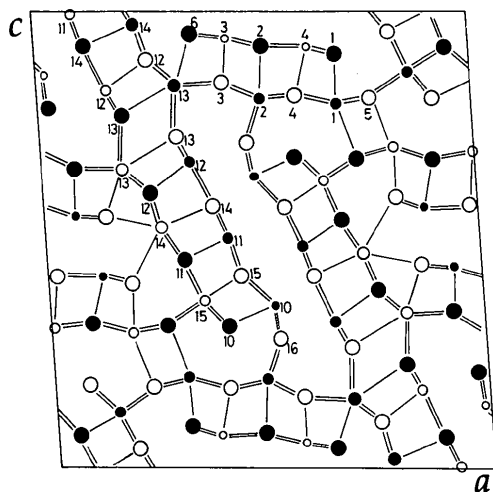

Fig. 1. The unit cell of robinsonite projected down [010]. In order of decreasing size, the circles denote S, Pb, mixed sites and Sb. Atoms at $z = 0$ and $z = 0.5$ are indicated by open and full circles respectively.
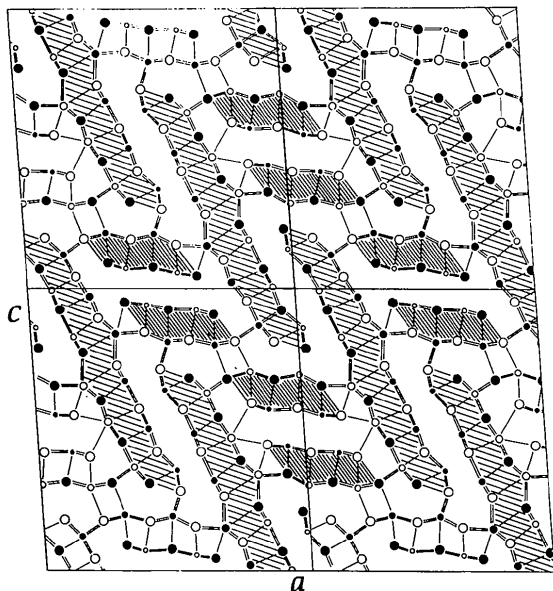
Fig. 2. Four unit cells of the crystal structure of robinsonite projected down [010] with the wide and narrow ribbons indicated by coarse and fine ruling respectively. Conventions for indicating atoms are the same as in Fig. 1.

tion of layers of the thallium iodide type structure (B33) into the stibnite structure. Makovicky (1981), on the other hand, describes robinsonite as built of lozenge-shaped rods (double ribbons in our description) of SnS or TlI archetype structure, depending on whether there is a mirror plane present (TlI) or not (SnS).

The stoichiometry of the crystal is determined by the stoichiometries of the neutral ribbons, viz $2Sb_2S_3$ for the narrow ribbon and $2Sb_2S_3.8PbS$ for the wide one. However, the Pb atoms are not found only in the middle of the wide ribbons. Antimony favors the five-coordinated metal sites found where one ribbon faces a parallel ribbon. The Pb atoms occupy positions of higher coordination number found at sites where the face of one ribbon meets the edge of a different ribbon.

Jumas et al. (1980) refined the structure of the homeotypic $Sn_4Sb_6S_{13}$ from single-crystal X-ray diffraction measurements in space group $I2/m$, but the difficulty in distinguishing Sn from Sb by X-rays made the assignment of the cation-site occupancies difficult. They assigned antimony mostly to the wide ribbon and tin to the narrow but this results in unsatisfactory bond-valence sums. To compare the metal distribution in $Sn_4Sb_6S_{13}$ with that in robinsonite we performed a bond-valence analysis on $Sn_4Sb_6S_{13}$ using $r_0 = 2.437$ Å for Sn—S and $r_0 = 2.52$ Å for Sb—S bonds. The resulting Sn/Sb distribution is presented in Table 1 together with the authors' orginal assignment. The distribution of Sb atoms is very similar in both the Sn and Pb analogues.

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Refinement of the Structure of Boulangerite, Pb5Sb4S11

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Abstract. The structure of boulangerite, $Pb_5Sb_4S_{11}$, $M_r = 1875.7$, previously determined by Born & Hellner [*Am. Mineral.* (1960), **45**, 1266–1271] and by Petrova, Kuznetzov, Belokoneva, Simonov, Pobedimskaya & Belov [*Dokl. Akad. Nauk SSSR* (1978), **242**, 337–340] has been refined in the orthorhombic space group *Pnam*, $a = 23.490$ (5), $b = 21.245$ (5), $c = 4.020$ (1) Å, $V = 2006$ Å^3, $Z = 4$, $D_x = 6.21$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 462.8$ cm^{-1}, $F(000) = 3160$, room temperature, $R = 0.077$, $wR = 0.068$ for 2035 independent reflections. The crystal was prepared by annealing at 860 K in the presence of I_2 in vacuum-sealed ampoules. The basic arrangement of atoms previously proposed is confirmed but the cation distribution is determined more accurately by site-occupancy refinement and by bond-valence analysis.

Introduction. Although the structure of boulangerite has been the object of several studies the cation distribution has not been reliably determined. Berry (1940) and Palache & Berman (1942) determined the unit cell. Born & Hellner (1960) proposed a structure for natural boulangerite using $hk0$ and $hk2$ Weissenberg photographs. The structure was later confirmed by Petrova, Kuznetzov, Belokoneva, Simonov, Pobedimskaya & Belov (1978) on a synthetic crystal. Although the general features found in these studies were the same, we undertook an independent structure determination as part of a broader investigation into cation distributions in lead antimony sulfides in order to establish the correct cation distribution.

Experimental. Single crystals of $Pb_5Sb_4S_{11}$ were synthesized from elemental lead, antimony and sulfur of 'Specpure' grade, supplied by Johnson Matthey plc. Three samples were prepared by weighing the elements in proportions corresponding to 65, 66, 67 mol % of PbS. The samples were sealed in evacuated silica tubes, melted at 1150 K for 2 d and then annealed at 873 K for 2 d. Considerable ingot separation occurred in all the ampoules. The separate portions of the ingots were then ground and pressed into seven 1 g pellets which were separately annealed for 3 d in evacuated silica tubes in a two-zone horizontal furnace after the addition of approximately 1 mg of I_2 to each. At the end of the 20 cm ampoules where the pellets were placed the temperature was 860 K. The other end was kept at 880 K. Acicular crystals of $Pb_5Sb_4S_{11}$ and $Pb_2Sb_2S_5$ grew in various parts of the ampoules, most often near the cooler end. The structure of $Pb_2Sb_2S_5$ is reported by Skowron & Brown (1990*b*). Good quality crystals of $Pb_5Sb_4S_{11}$ were found in the sample prepared from 66 mol% PbS. A needle-shaped crystal, 0.15 × 0.3 × 0.6mm, was mounted with the needle axis along the goniometer axis for the X-ray study.

The unit-cell parameters were refined from 15 well centered reflections in the range $19 < 2\theta < 26°$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Intensities of 3700 reflections were measured in the range $2\theta < 50°$ and $0 \le h \le 27$, $0 \le k \le 25$, $-4 \le l \le 4$ with a $\theta/2\theta$ scan. Two standard reflections, $\overline{9}61$ and $10,\overline{4},0$, measured every 50 reflections, varied by 1.4%. The systematic absences, $0kl$: $k + l = 2n + 1$; $h0l$: $h = 2n + 1$, found using precession photographs indicate space groups *Pnam* or *Pna2*$_1$. The former was chosen and led to a satisfactory refinement. The absorption correction was based on ψ scans of 20 reflections (maximum correction 1.67 for the intensity of the 15,0,4 reflection). The intensities were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{int} = 0.037$ before the absorption correction, $R_{int} = 0.035$ after) to give 2035 unique reflections.

The initial atomic positions, found by direct methods using *SHELXS*86 (Sheldrick, 1986), were refined using *SHELX*76 (Sheldrick, 1976) by full-matrix least squares (on F) with anisotropic atomic