

Fig. 1. Projection onto the *ab* plane of the structure of PNb₉O₂₅.

Thus, as well as the two P atoms statistically distributed over four positions as observed by Roth *et al.* (1965) there are also two Nb atoms split over four positions. In order to avoid the half-occupied positions, refinements were performed in the two possible noncentrosymmetric space groups $I\bar{4}$ and $I4$. In the first one the P atoms were ordered but not the Nb(1) atoms and in the second one the Nb(1) atoms were ordered but not the P atoms. In both cases the *R* and *wR* factors were higher and so it is proposed that in the 'Nb₈O₂₅' framework the P and the Nb(1) atoms occupy half of their sites, respec-

Table 2. Main atomic bond distances (Å)

Nb(1)—O(1)	× 4	1.95 (2)	Nb(3)—O(2)	1.92 (1)	
Nb(1)—O(7)		1.753 (6)	Nb(3)—O(3)	× 2	1.983 (3)
Nb(1)—O(7 ⁱ)		2.079 (6)	Nb(3)—O(4)		1.78 (1)
Nb(2)—O(1)		1.88 (2)	Nb(3)—O(5)		2.02 (1)
Nb(2)—O(2)		1.88 (1)	Nb(3)—O(6)		2.24 (1)
Nb(2)—O(3)		2.27 (1)	P—O(5)	× 4	1.64 (1)
Nb(2)—O(4)		2.15 (1)			
Nb(2)—O(6)	× 2	1.995 (4)			

Symmetry code: (i) = *x* - 1, *y*, *z*.

tively, in such a way that the polarization of the whole crystal is zero giving a centrosymmetric mean unit cell.

Related literature. The general features of the structure (Fig. 1) are very similar to those determined by Roth *et al.* (1965). Some small differences appear in the interatomic distances (Table 2), principally arising from the splitting of Nb(1). The value of the thermal motion factor for phosphorus here indicates that there is no replacement of some of the P atoms by Nb atoms in the tetrahedral site in contrast to K₇Nb_{14+x}P_{9-x}O₆₀ (Leclaire, Benabbas, Borel, Grandin & Raveau, 1989).

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Structure of Tl₂SnTe₅

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Abstract. Dithallium tin pentatelluride, $M_r = 7.40 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 1165.4$, tetragonal, $I4/mcm$, $a = 8.306(2)$, $c = 47.09 \text{ mm}^{-1}$, $F(000) = 1888$, $T = 294 \text{ K}$, final $R = 15.161(5) \text{ \AA}$, $V = 1045.9(8) \text{ \AA}^3$, $Z = 4$, $D_x = 0.041$ for 236 independent observed reflections. The

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structure of Tl_2SnTe_5 consists of SnTe_4 tetrahedra (T), TeTe_4 square-planar units (S) and two types of Tl atoms, the polyhedra of which are distorted cubes (C) and square antiprisms (A). SnTe_4 and TeTe_4 groups form chains along the c axis. They have a common edge and are situated in the following order $T-S-T-S\dots$. Between these chains, TlTe_8 cubes and antiprisms build up columns according to the sequence $A-C-A-C\dots$. The structure of Tl_2SnTe_5 contains the same types of polyhedra as observed in Tl_2GeTe_5 but their arrangement is different. In the latter, the order is $T-T-S-S\dots$ along the chains and $C-C-A-A\dots$ along the columns.

Experimental. Single crystals of Tl_2SnTe_5 were obtained by heating at 543 K a molten stoichiometric mixture of Tl, Sn and Te in an evacuated silica tube for several weeks. Platelet-like crystal: $0.090 \times 0.080 \times 0.030$ mm. Enraf-Nonius CAD-4 diffractometer, lattice parameters refined from 25 reflections having $6.40 \leq \theta \leq 15.51^\circ$, $\theta-2\theta$ scan technique with scan width $(0.85 + 0.35 \tan \theta)^\circ$; $0.039 \leq (\sin \theta)/\lambda \leq 0.661 \text{ \AA}^{-1}$, $0 \leq h \leq 7$, $0 \leq k \leq 10$, $0 \leq l \leq 19$. Three standard reflections: 024, 600 and 008, no significant deterioration in intensity, average $\sigma(I)/I$ (standard reflections) = 0.011. Empirical correction for absorption using *DIFABS* (Walker & Stuart, 1983), max. and min. values of the coefficient 1.47 and 0.78. 361 independent reflections, 125 unobserved reflections [$I < 3\sigma(I)$]. Direct methods, program *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), full-matrix least-squares refinements on F , refined parameters: x , y , z and β_{ij} . $R = 0.041$, $wR = 0.051$, $w = 1/\sigma^2(F)$ for all reflections, $S = 1.66$, $(\Delta/\sigma)_{\max} = 0.03$, $|\Delta\rho|_{\max} = 2.2(4) \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99 and 149). Computer programs of *SDP* (B. A. Frenz & Associates, Inc., 1982) system. Atomic parameters are given in Table 1, bond lengths and angles in Table 2.*

The Sn and Te atoms cannot be distinguished by X-rays, but the most probable distribution of these atoms on the corresponding positions was drawn from the following arguments. One of the two undetermined sites is at the centre of a tetrahedron which is common to tin atoms (e.g. in α -Sn). Moreover, the four distances from this site to the vertex of its polyhedron are equal to $2.792(2) \text{ \AA}$ and correspond approximately to the sum of Sn^{4+} and Te^{2-} ionic radii (Shannon, 1976). The second site has a

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (abc\cos\gamma)\beta_{12} + (accos\beta)\beta_{13} + (bccos\alpha)\beta_{23}].$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Tl(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	1.34 (3)
Tl(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	3.71 (7)
Te(1)	1863 (3)	6863 (3)	1357 (1)	0.80 (2)
Te(2)	0	$\frac{1}{2}$	0	0.99 (6)
Sn	$\frac{1}{2}$	0	$\frac{1}{4}$	0.65 (6)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Tl(1)—Te(1)	3.491 (2)	Te(1)—Te(2)	3.004 (2)
Tl(2)—Te(1)	3.663 (2)	Te(1)—Sn'	2.792 (2)
Tl(1)—Tl(2)	3.790		
Te(1 ^{iv})—Te(2)—Te(1 ⁱⁱⁱ)	93.54 (5)	Te(1 ^{iv})—Sn—Te(1 ^v)	103.27 (5)
Te(1 ^{iv})—Sn—Te(1 ⁱⁱⁱ)	112.66 (3)		

Symmetry code: (i) $-y, x, z$; (ii) $-x, 1-y, -z$; (iii) $x, y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (v) $\frac{1}{2}+x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

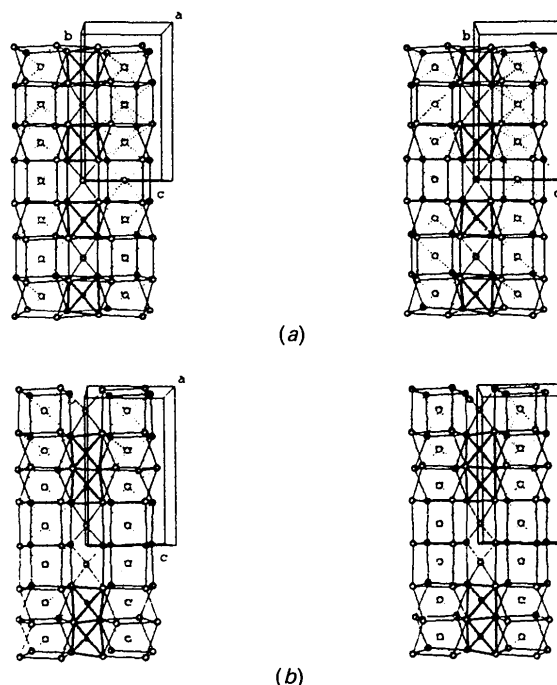


Fig. 1. Stereoviews of (a) Tl_2SnTe_5 and (b) Tl_2GeTe_5 in the unit cells (black circles Sn or Ge, grey circles Te and white circles Tl).

square-planar environment which has been found in the Te compounds such as Tl_2GeTe_5 (Touré, Kra, Eholié, Olivier-Fourcade, Jumas & Maurin, 1990; Marsh, 1990) and complexes of Te with thiourea and substituted thioureas (Foss, Husebye & Maroy, 1963).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53646 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Figs. 1(a) and 1(b) show stereoviews of the crystal structures of Tl₂SnTe₅ and Tl₂GeTe₅, respectively, realized by *MolDraw* (Cense, 1989). The latter is made using the crystal data of Marsh (1990).

Related literature. Tl^I—Tl^I and In^I—In^I interactions. The structural behaviour of several Tl compounds (geometry of polyhedra, interatomic distances, orbitals) from the molecular to the solid state is reported by Janiak & Hoffman (1990).

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cis-Bis(1-methylcytosine- κ N)(*N,N,N',N'*-tetramethylethylenediamine- κ^2 N,N')platinum(II) Diperchlorate Monohydrate

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Abstract. [Pt(C₅H₇N₃O)₂(C₆H₁₆N₂)](ClO₄)₂·H₂O, *M*_r = 778.47, monoclinic, *C*2/*c*, *a* = 19.513 (7), *b* = 12.994 (5), *c* = 12.178 (4) Å, β = 114.74 (2)°, *V* = 2804 (2) Å³, *Z* = 4, *D*_x = 1.844 Mg m⁻³, *F*(000) = 1536, λ (Mo *K* α) = 0.71073 Å, μ = 5.31 mm⁻¹, *T* = 291 K, final *R* = 0.071 for 1957 unique observed [*F* ≥ 6.0σ(*F*)] diffractometer data. The number of observations per refined parameter is 1957/171 = 11.4. The cation contains chelating *N,N,N',N'*-tetramethylethylenediamine and two 1-methylcytosine nucleobases bound through the N(3) positions. Owing to the bite of the ethylenediamine {N(7)—Pt(1)—N(7) 85.0 (5)° [(i) *-x*, *y*, *-z* + $\frac{1}{2}$]}], the angles of the Pt coordination sphere display some deviations from ideal square planarity. Pt—N distances as well as geometries of the 1-methylcytosine ring and the diamine ligand are normal [Preut, Frommer & Lippert (1990). *Acta Cryst.* **C46**, 1326–1328, and references therein]. The 1-methylcytosine rings are almost at right angles to the Pt coordination plane [94.5 (5)°] and are oriented such that O(2) and (O²) are on opposite sides of the plane (head–tail orientation). The only short hydrogen bond [2.87 (2) Å] is intramolecular and involves exocyclic O(2) and NH₂(4) groups.

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Experimental. The title compound was prepared by reaction of Pt(C₆H₁₆N₂)I₂, obtained according to a modified Dhara method (Dhara, 1970) from K₂PtCl₄ and C₆H₁₆N₂, with AgClO₄ (2 equiv.) and 1-methylcytosine (2 equiv.) at pH 2–3, 14 h, 323 K. On slow evaporation, colorless needles were isolated in 52% yield. A well developed crystal of size ~0.05 × 0.04 × 0.25 mm was used. The crystal was mounted in a Lindemann glass capillary along *c*. *D*_m was not determined. Intensity data were collected with $\omega/2\theta$ scans, variable scan speed 1.5–14.6° min⁻¹ in θ , scan width 1.2° + dispersion. A Nicolet R3m/V diffractometer with graphite-monochromated Mo *K* α radiation was used. The lattice parameters were determined from a least-squares fit of 25 reflections with $2\theta_{\max}$ = 29.80°. ω scans of low-order reflections along the three crystal axes showed acceptable mosaicity. Six standard reflections (310, 021, 002, $\bar{3}10$, $0\bar{2}1$, 00 $\bar{2}$) were recorded every 300 reflections, only random deviations were detected during 149 h of X-ray exposure; 5349 reflections with with $2.0 \leq 2\theta \leq 50.0^\circ$ (8960 accessible), $-24 \leq h \leq 24$, $0 \leq k \leq 16$, $-15 \leq l \leq 15$ were measured. The data were corrected for Lorentz-polarization and for absorption effects, the latter *via* ψ scans of nine reflections,