

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* \geq 6.0 σ (*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.

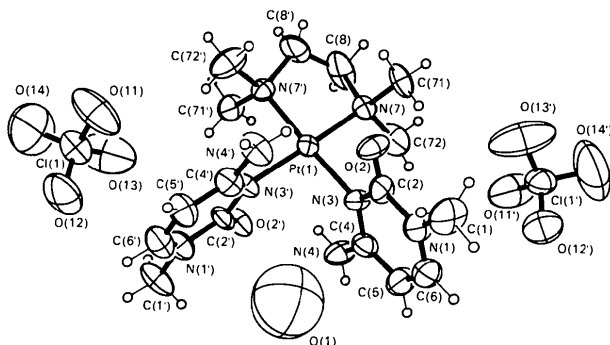
References

- B. A. FRENZ & ASSOCIATES, INC. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
 CENSE, J.-M. (1989). *Tetrahedron Comput. Methodol.* **2**, 65–71.
 FOSS, O., HUSEBYE, S. & MAROY, K. (1963). *Acta Chem. Scand.* **17**, 1806–1807.
 JANIAC, C. & HOFFMANN, R. (1990). *J. Am. Chem. Soc.* **112**, 5924–5946.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MARSH, R. E. (1990). *J. Solid State Chem.* **87**, 467–469.
 SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–756.
 TOURÉ, A. A., KRA, G., EHOlié, R., OLIVIER-FOURCADE, J., JUMAS, J.-C. & MAURIN, M. (1990). *J. Solid State Chem.* **84**, 245–252.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 159–166.

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 $2.0 \leq 2\theta \leq 50.0^\circ$ (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,

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Pt(1)	0.0	0.09288 (7)	0.25	314
Cl(1)	0.3076 (3)	0.1380 (4)	0.2318 (4)	646
O(11)	0.303 (1)	0.108 (1)	0.338 (1)	1289
O(12)	0.310 (1)	0.247 (1)	0.225 (2)	1188
O(13)	0.251 (1)	0.095 (2)	0.138 (1)	1645
O(14)	0.373 (2)	0.102 (2)	0.228 (3)	2040
N(1)	-0.1305 (8)	0.307 (1)	0.343 (1)	530
C(1)	-0.134 (1)	0.336 (2)	0.458 (2)	795
C(2)	-0.0794 (9)	0.232 (1)	0.348 (1)	446
O(2)	-0.0393 (6)	0.1903 (8)	0.4424 (9)	504
N(3)	-0.0762 (7)	0.2050 (9)	0.240 (1)	378
C(4)	-0.1189 (9)	0.256 (1)	0.135 (1)	464
N(4)	-0.1107 (8)	0.231 (1)	0.035 (1)	569
C(5)	-0.171 (1)	0.330 (1)	0.134 (2)	599
C(6)	-0.176 (1)	0.354 (1)	0.237 (2)	622
N(7)	-0.0748 (7)	-0.023 (1)	0.232 (1)	375
C(71)	-0.095 (1)	-0.034 (1)	0.337 (1)	554
C(72)	-0.147 (1)	-0.013 (2)	0.122 (1)	731
C(8)	-0.042 (1)	-0.122 (1)	0.214 (2)	870
O(1)	0.0	0.448 (6)	0.25	3375

Fig. 1. General view (*SHELXTL-Plus* graphic), showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries.

the max./min. transmission factors were 1.00/0.89, and averaged ($R_{int} = 0.050$) to 2395 unique reflections, 1957 of which had $F \geq 6.0\sigma(F)$. The systematic absences (hkl) $h + k = 2n + 1$, ($h0l$) $l = 2n + 1$ conform to space groups $C2/c$ and Cc . The structure was solved *via* Patterson function and $\Delta\rho$ maps in the space group $C2/c$. It was refined (on F) using full-matrix least squares with anisotropic displacement parameters for all non-H atoms and a common isotropic displacement parameter for the H atoms, which were placed in geometrically calculated positions (C—H, N—H 0.96 \AA and CCH 120 or 109.5°). 171 parameters were refined. Weights $w = 1.0/[\sigma^2(F) + 0.000057F^2]$ led to a featureless analysis of variance in terms of $\sin\theta$ and F_o . The refinement converged to $S = 3.60$, $R = 0.071$, $wR = 0.064$, $(\Delta/\sigma)_{max} = 0.004$ (no extinction correction). The largest peaks in final $\Delta\rho$ map were ± 3.0 (6) $e \text{\AA}^{-3}$ (near Pt). Atomic scattering factors for neutral atoms

Table 2. Bond distances (\AA), bond angles ($^\circ$), torsion angles ($^\circ$), least-squares planes, dihedral angle ($^\circ$) and possible hydrogen bond (\AA , $^\circ$)

Pt(1)—N(3)	2.05 (1)	C(2)—N(3)	1.39 (2)
Pt(1)—N(7)	2.05 (1)	N(3)—C(4)	1.36 (2)
Cl(1)—O(11)	1.39 (2)	C(4)—N(4)	1.33 (2)
Cl(1)—O(12)	1.42 (2)	C(4)—C(5)	1.40 (3)
Cl(1)—O(13)	1.33 (2)	C(5)—C(6)	1.33 (3)
Cl(1)—O(14)	1.38 (3)	N(7)—C(71)	1.50 (2)
N(1)—C(1)	1.48 (3)	N(7)—C(72)	1.49 (2)
N(1)—C(2)	1.38 (2)	N(7)—C(8)	1.49 (2)
N(1)—C(6)	1.37 (2)	C(8)—C(8')	1.49 (3)
C(2)—O(2)	1.21 (2)		
N(3)—Pt(1)—N(7)	93.0 (5)	O(2)—C(2)—N(3)	121 (2)
N(3)—Pt(1)—N(7')	176.8 (5)	Pt(1)—N(3)—C(2)	116 (1)
N(3)—Pt(1)—N(3)	89.2 (5)	C(2)—N(3)—C(4)	121 (1)
N(7)—Pt(1)—N(7')	85.0 (5)	Pt(1)—N(3)—C(4)	123 (1)
N(7)—Pt(1)—N(3)	176.7 (5)	N(3)—C(4)—C(5)	120 (1)
O(13)—Cl(1)—O(14)	106 (2)	N(3)—C(4)—N(4)	118 (1)
O(12)—Cl(1)—O(14)	106 (2)	N(4)—C(4)—C(5)	122 (1)
O(12)—Cl(1)—O(13)	114 (1)	C(4)—C(5)—C(6)	119 (2)
O(11)—Cl(1)—O(14)	111 (2)	N(1)—C(6)—C(5)	121 (2)
O(11)—Cl(1)—O(13)	110 (1)	Pt(1)—N(7)—C(8)	108 (1)
O(11)—Cl(1)—O(12)	110 (1)	Pt(1)—N(7)—C(72)	113 (1)
C(2)—N(1)—C(6)	122 (2)	Pt(1)—N(7)—C(71)	114.3 (9)
C(1)—N(1)—C(6)	121 (2)	C(72)—N(7)—C(8)	104 (1)
C(1)—N(1)—C(2)	118 (1)	C(71)—N(7)—C(8)	109 (1)
N(1)—C(2)—N(3)	117 (1)	C(71)—N(7)—C(72)	107 (1)
N(1)—C(2)—O(2)	121 (2)	N(7)—C(8)—C(8')	110 (1)

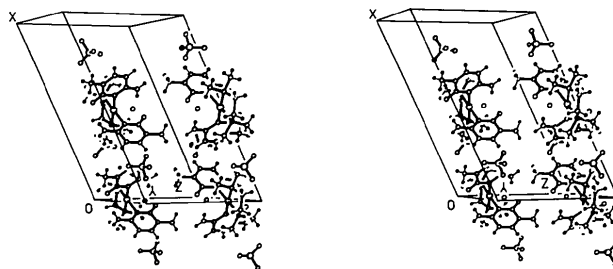
Pt(1)—N(7)—C(8)—C(8')	35 (2)	N(7)—C(8)—C(8')—N(7')	-48 (2)
N(7)—Pt(1)—N(7)—C(8)	-12 (1)		

No.	Plane through atoms	Equation of the plane (x along a, y in the plane ab, z along c*)	χ^2
1	N(1), C(2), N(3), C(4), C(5), C(6)	$-0.694x - 0.698y - 0.177z = -0.47 \text{\AA}$	6.0
2	Pt(1), N(3), N(7)	$-0.110x - 0.030y + 0.9935z = 2.851 \text{\AA}$	0.0

Dihedral angle: 1,2 94.5 (5)

Possible hydrogen bond

$D \cdots A$	$H \cdots A$	$D-H \cdots A$
N(4) \cdots O(2)	2.87 (2)	H(42) \cdots O(2)
		2.17 (2)
		N(4) \cdots H(42) \cdots O(2)
		135 (1)

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs used were *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982) and *MISSYM* (Le Page, 1987). The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit-cell contents in Fig. 2.

Positional parameters and the equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths, bond angles, torsion angles, least-squares planes, dihedral angles and possible hydrogen bonds are given in Table 2.

Related literature. The title compound was structurally characterized in order to rationalize its poor reactivity with excess cyanide (Frommer & Lippert, 1990). This reaction has been studied with regard to differences of cisplatin-nucleobases adducts removal from DNA (Raudaschl-Sieber & Lippert, 1985). We have previously postulated that a fixed head-tail orientation of two bases carrying exocyclic oxygens adjacent to the Pt binding site successfully prevents ligand substitution by CN⁻. The present crystal structure confirms this assumption and strongly suggests that the single set of 1-MeC resonances in the ¹H NMR spectra (D₂O) of the title compound up to 348 K is due to a single rotamer (head-tail) rather than to rapid ligand rotation. While the CH₃ groups of the tmeda ligand further increase the steric bulk for rotation of 1-MeC (Reily & Marzilli, 1986)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53594 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(tmeda = *N,N,N',N'*-tetramethylethylenediamine), these groups are not inherently responsible for the non-reactivity of the title compound towards CN⁻. Neither (tmeda)PtCl₂ nor [(tmeda)Pt(py)₂](ClO₄)₂ display similar behaviour. Rather, all ligands undergo rapid substitution by CN⁻. We have also characterized the latter compound by X-ray analysis [orthorhombic, *P*2₁2₁2₁, *a* = 10.936 (3), *b* = 13.000 (3), *c* = 16.985 (4) Å, *V* = 2415 (1) Å³, *Z* = 4], but the present refinement (*R* = 0.073), because of unreasonable displacement parameters is not satisfactory.

References

- DHARA, S. C. (1970). *Indian J. Chem.* **8**, 193–194.
 FROMMER, G. & LIPPERT, B. (1990). *Inorg. Chem.* **29**, 3259–3260.
 LE PAGE, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
 NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
 PREUT, H., FROMMER, G. & LIPPERT, B. (1990). *Acta Cryst.* **C46**, 1326–1328.
 RAUDASCHL-SIEBER, G. & LIPPERT, B. (1985). *Inorg. Chem.* **24**, 2426–2432.
 REILY, M. D. & MARZILLI, L. G. (1986). *J. Am. Chem. Soc.* **108**, 6785–6793.
 SHELDRICK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE. Oxford: Clarendon Press.
 WILLIAMS, D. E. (1984). *PCK83*. Crystal and molecular packing analysis program. Univ. of Louisville, USA. QCPE Program No. 481. Dept. of Chemistry, Indiana Univ., Indiana, USA.

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Structure of Tris(η^5 -cyclopentadienyl)uranium Iodide

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Abstract. [U(C₅H₅)₃]I, *M_r* = 560.22, orthorhombic, *P*2₁2₁2₁, *a* = 8.109 (3), *b* = 13.346 (3), *c* = 13.626 (3) Å, *V* = 1475 (1) Å³, *Z* = 4, *D_x* = 2.523 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 124.9 cm⁻¹, *F*(000) = 1000, *T* = 295 (1) K, *R* = 0.037 for 902 observed unique reflections [*I* ≥ 1.5σ(*I*)]. The title compound is not isostructural with its bromide,

chloride or fluoride analogues. The four halide derivatives exhibit, however, identical coordination polyhedra about the U atom. This atom is surrounded by three η^5 -covalently bonded cyclopentadienyl rings and by one iodide atom in a distorted tetrahedral configuration.

Experimental. [U(C₅H₅)₃]I was prepared from uranium iodide and potassium cyclopentadienide in

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