atomiques et les angles des liaisons dans le Tableau 2. La Fig. 1 représente la structure vue selon [010].

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Structure of *a*-Chloro-*b*-dichloromethylstannio-[*dc*,*ef*-bis(8-dimethylamino-1-naphthyl)]platinum(IV)

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(*Received* 20 *July* 1991; *accepted* 8 *October* 1991)

Abstract. Trichloro-1$\kappa^2 Cl$,2κCl-bis[(8-dimethylamino-2κN)-naphthyl-2κC^1]-methyl-1κC-platinumtin(*Pt*—*Sn*) dichloromethane solvate, $[PtSn(C_{12}H_{12}N)_2(CH_3)Cl_3].CH_2Cl_2$, $M_r = 860.56$, orthorhombic, $P2_12_12_1$, $a = 11.0716\,(4)$, $b = 11.6305\,(4)$, $c = 22.6463\,(9)$ Å, $V = 2916.1\,(2)$ Å^3, $Z = 4$, $D_x = 1.960$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 61.8$ cm^{-1}, $F(000) = 1648$, $T = 294$ K, $R = 0.025$ for 3239 unique observed diffractometer data with $I > 2.5\sigma(I)$. The platinum(IV) centre is octahedrally bonded to two C,N-chelate bonded dman ligands, a Cl atom and a dichloromethyltin group [Pt—Sn = 2.5489 (5) Å].

Experimental. Data were collected at 294 K on an Enraf–Nonius CAD-4F diffractometer for a yellow block-shaped crystal (0.68 × 0.35 × 0.25 mm) mounted in a Lindemann-glass capillary to prevent loss of dichloromethane solvate. Unit-cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $14.0 < \theta < 17.8°$. The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). Intensity data for 3699 reflections were collected (h 0:14, k 0:14, l 0:29) in $\omega/2\theta$ scan mode with $\Delta\omega = (0.55 + 0.35\tan\theta)°$ using Zr-filtered Mo $K\alpha$ radiation. Data were corrected for Lp, for a linear decay (4.1%) of the reference reflections (134, $\bar{1}3\bar{4}$) during the 56 h of X-ray exposure time and for absorption (*DIFABS*; Walker & Stuart, 1983), corrections in the range 0.84–1.11, resulting in 3239 unique reflections with $I > 2.5\sigma(I)$. The Pt and Sn atoms were found with standard Patterson methods (*SHELXS*86; Sheldrick, 1986), other non-H atoms were located from subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques (*SHELX*76; Sheldrick, 1976). H atoms were introduced at calculated positions (C—H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H atoms with one common isotropic thermal parameter [$U = 0.068\,(5)$ Å^2]. The dichloromethane solvate molecule was refined with bond restraints. The absolute structure was checked by refinement with opposite f'' anomalous-dispersion factors, resulting in $R = 0.061$,

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Table 1. *Final coordinates and equivalent isotropic thermal parameters* ($Å^2$) *of the non*-H *atoms*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Pt	0.50707 (2)	0.46220 (2)	0.07419 (1)	0.0281 (1)
Sn	0.44637 (5)	0.59523 (4)	0.15857 (2)	0.0348 (2)
Cl(1)	0.35624 (18)	0.51531 (19)	0.00247 (9)	0.0488 (6)
Cl(2)	0.5898 (3)	0.7351 (2)	0.18897 (12)	0.0700 (9)
Cl(3)	0.2881 (2)	0.7193 (2)	0.12759 (11)	0.0604 (8)
N(1)	0.5694 (6)	0.2887 (5)	0.0308 (3)	0.0407 (19)
N(2)	0.6435 (6)	0.5764 (6)	0.0314 (3)	0.042 (2)
C(1)	0.3878 (6)	0.3522 (6)	0.1099 (3)	0.0313 (19)
C(2)	0.2776 (7)	0.3759 (8)	0.1356 (4)	0.046 (3)
C(3)	0.2080 (8)	0.2911 (8)	0.1646 (4)	0.056 (3)
C(4)	0.2458 (8)	0.1778 (8)	0.1648 (4)	0.057 (3)
C(5)	0.3503 (8)	0.1477 (7)	0.1345 (4)	0.050 (3)
C(6)	0.3895 (10)	0.0324 (8)	0.1319 (4)	0.059 (3)
C(7)	0.4842 (12)	0.0049 (7)	0.0999 (5)	0.077 (4)
C(8)	0.5485 (9)	0.0857 (7)	0.0646 (4)	0.056 (3)
C(9)	0.5158 (7)	0.1997 (6)	0.0679 (3)	0.045 (2)
C(10)	0.4200 (7)	0.2327 (6)	0.1049 (3)	0.037 (2)
C(11)	0.7055 (8)	0.2749 (8)	0.0293 (5)	0.057 (3)
C(12)	0.5207 (8)	0.2734 (8)	−0.0299 (3)	0.054 (3)
C(13)	0.6413 (6)	0.4385 (6)	0.1327 (3)	0.0310 (19)
C(14)	0.6394 (7)	0.3753 (7)	0.1840 (3)	0.042 (3)
C(15)	0.7442 (8)	0.3629 (8)	0.2196 (4)	0.055 (3)
C(16)	0.8483 (8)	0.4157 (9)	0.2033 (4)	0.060 (3)
C(17)	0.8565 (7)	0.4818 (8)	0.1505 (4)	0.052 (3)
C(18)	0.9633 (8)	0.5326 (8)	0.1305 (5)	0.068 (4)
C(19)	0.9671 (8)	0.5920 (11)	0.0796 (5)	0.080 (4)
C(20)	0.8627 (8)	0.6067 (10)	0.0456 (5)	0.067 (4)
C(21)	0.7563 (7)	0.5614 (7)	0.0638 (3)	0.042 (2)
C(22)	0.7503 (7)	0.4962 (7)	0.1166 (3)	0.039 (2)
C(23)	0.6036 (9)	0.6992 (7)	0.0338 (5)	0.057 (3)
C(24)	0.6589 (9)	0.5478 (10)	−0.0331 (4)	0.059 (3)
C(25)	0.3920 (10)	0.5404 (9)	0.2435 (4)	0.062 (3)
Dichloromethane solvate				
Cl(4)	0.0934 (5)	0.5829 (5)	0.3218 (3)	0.183 (3)
Cl(5)	0.0536 (8)	0.3426 (5)	0.3333 (3)	0.200 (4)
C(26)	0.1500 (10)	0.4536 (9)	0.3462 (6)	0.150 (11)

$wR = 0.081$. Weights were introduced in the final refinement cycles, convergence with 332 parameters was reached at $R = 0.025$ $\{wR = 0.029$, $w = [\sigma^2(F) + 0.000377F^2]^{-1}$, $S = 1.87$, $(\Delta/\sigma)_{av} = 0.049\}$. The final difference Fourier map shows no residual densities outside the range -0.50 to 0.52 e $Å^{-3}$. Scattering factors from Cromer & Mann (1968), anomalous-dispersion corrections from Cromer & Liberman (1970). The program package *EUCLID* (Spek, 1982) was used for geometrical calculations and illustrations. All calculations were carried out on a MicroVAX II cluster. Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Bond distances and angles are given in Table 2. Fig. 1 shows the molecular structure with the adopted labelling scheme.

Related literature. Reaction of $Pt(dman)_2$ (dman = 8-dimethylamino-1-napthyl) with $SnCl_3Me$ results in the selective formation of a racemic mixture of one $PtCl(SnCl_2Me)(dman)_2$ diastereoisomer, *i.e.* in an overall oxidative-addition reaction, and not in the formation of an η^2-$ClSnCl_2Me$ bonded platinum(II) complex {*cf.* $[IrBr(C_6H_4CH_2NMe_2\text{-}2)(cod)(\eta^2\text{-}BrSnBrMe_2)]$; van der Zeijden, van Koten, Wouters, Wijsmuller, Grove, Smeets & Spek, 1988}. The crystal structure of the related complex [*ad*,*be*-bis(8-dimethylamino-1-naphthyl)]-*f*-ethyl-*c*-iodo-platinum(IV) will also be published (Smeets, Spek, van Beek & van Koten, 1992). A search in the 1991 version of the Cambridge Structural Database for Pt^{IV}—Sn bonds gave no results. Details of the chemistry will

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

Pt—Sn	2.5489 (5)	N(1)—C(12)	1.487 (10)
Pt—Cl(1)	2.410 (2)	N(2)—C(21)	1.459 (10)
Pt—N(1)	2.348 (6)	N(2)—C(23)	1.496 (11)
Pt—N(2)	2.233 (7)	N(2)—C(24)	1.508 (11)
Pt—C(1)	2.009 (7)	C(1)—C(2)	1.380 (10)
Pt—C(13)	2.010 (7)	C(1)—C(10)	1.439 (10)
Sn—Cl(2)	2.375 (3)	C(9)—C(10)	1.405 (10)
Sn—Cl(3)	2.376 (2)	C(13)—C(14)	1.375 (10)
Sn—C(25)	2.114 (9)	C(13)—C(22)	1.428 (10)
N(1)—C(9)	1.459 (9)	C(21)—C(22)	1.417 (10)
N(1)—C(11)	1.516 (11)		
Sn—Pt—Cl(1)	99.61 (5)	Pt—N(1)—C(11)	113.1 (5)
Sn—Pt—N(1)	155.90 (16)	Pt—N(1)—C(12)	112.5 (5)
Sn—Pt—N(2)	98.20 (18)	C(9)—N(1)—C(11)	110.0 (6)
Sn—Pt—C(1)	84.9 (2)	C(9)—N(1)—C(12)	107.4 (6)
Sn—Pt—C(13)	77.5 (2)	C(11)—N(1)—C(12)	109.1 (7)
Cl(1)—Pt—N(1)	98.16 (17)	Pt—N(2)—C(21)	106.8 (5)
Cl(1)—Pt—N(2)	91.36 (18)	Pt—N(2)—C(23)	110.6 (5)
Cl(1)—Pt—C(1)	88.8 (2)	Pt—N(2)—C(24)	111.5 (6)
Cl(1)—Pt—C(13)	172.6 (2)	C(21)—N(2)—C(23)	110.4 (7)
N(1)—Pt—N(2)	97.5 (2)	C(21)—N(2)—C(24)	111.3 (6)
N(1)—Pt—C(1)	79.3 (3)	C(23)—N(2)—C(24)	106.2 (7)
N(1)—Pt—C(13)	86.6 (3)	Pt—C(1)—C(2)	128.6 (6)
N(2)—Pt—C(1)	176.8 (3)	Pt—C(1)—C(10)	114.9 (5)
N(2)—Pt—C(13)	82.4 (3)	C(2)—C(1)—C(10)	116.4 (7)
C(1)—Pt—C(13)	97.7 (3)	N(1)—C(9)—C(10)	117.2 (6)
Pt—Sn—Cl(2)	117.18 (7)	C(1)—C(10)—C(9)	119.8 (6)
Pt—Sn—Cl(3)	109.98 (6)	Pt—C(13)—C(14)	128.2 (5)
Pt—Sn—C(25)	125.0 (3)	Pt—C(13)—C(22)	113.1 (5)
Cl(2)—Sn—Cl(3)	99.36 (9)	C(14)—C(13)—C(22)	118.7 (6)
Cl(2)—Sn—C(25)	97.7 (3)	N(2)—C(21)—C(22)	116.6 (7)
Cl(3)—Sn—C(25)	104.0 (3)	C(13)—C(22)—C(21)	120.4 (7)
Pt—N(1)—C(9)	104.4 (4)		

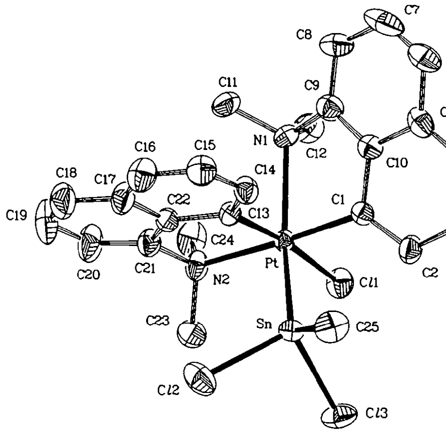

Fig. 1. Thermal ellipsoid plot (drawn at the 40% probability level) of the molecular structure, with the adopted atom labelling. H atoms are omitted for clarity.

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* Lists of anisotropic thermal parameters, H-atom positions, complete lists of bond distances and bond angles, selected torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54725 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0285]

be published elsewhere (van Beek, Wehman-Ooyevaar, Grove, Smeets, Spek & van Koten, 1992).

Data were collected by A. J. M. Duisenberg. This work was supported in part (WJJS, JAMvB and ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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Acta Cryst. (1992). C**48**, 747–749

Structure of 4′-Demethylepipodophyllotoxin

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(*Received* 12 *March* 1991; *accepted* 10 *September* 1991)

Abstract. [5*R*-(5α,5aβ,8aα,9β)]-5,8,8a,9-Tetrahydro-9-hydroxy-5-(4-hydroxy-3,5-dimethoxyphenyl)furo-[3′,4′:6,7]naphtho[2,3-*d*]-1,3-dioxol-6(5a*H*)-one, $C_{21}H_{20}O_8$, $M_r = 400.38$, orthorhombic, $P2_12_12_1$, $a = 11.483\ (1)$, $b = 19.345\ (3)$, $c = 8.459\ (1)$ Å, $V = 1879.0\ (5)$ Å^3, $Z = 4$, $D_m = 1.35\ (9)$, $D_x = 1.415$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1.54178$ Å, $\mu = 8.78$ cm^{-1}, $F(000) = 840$, $T = 296$ K, final $R = 0.040$ and $wR = 0.05$ for 1333 unique reflections. The title compound, synthesized from podophyllotoxin, was demethylated at the C4′ position, and epimerized at the C4 position while maintaining chirality at all other stereo centres. The chair conformation of the cyclohexyl ring was not affected by the synthetic modification.

Experimental. The title compound (DMEP) was synthesized from podophyllotoxin (POD) according to the method of Kuhn, Keller-Juslen & von Wartburg (1969). DMEP was crystallized from a 4/1 ethanol/water solution by slow evaporation at 277 K. A rod-like crystal, having approximate dimensions of 0.3 × 0.3 × 0.2 mm, was mounted on a glass fibre. Measurements were made on a Rigaku AFC-6*R* diffractometer with graphite-monochromated Cu $K\alpha$ radiation and a 12 kW rotating anode generator. Intensities were measured at 296 K using ω–2θ scans to a maximum 2θ value of 120.1°. Cell constants were obtained from a least-squares refinement of the setting angles of 24 reflections in the range $50.13 < 2\theta < 76.48°$. *h*,*k*,*l* ranged from 0,0,0 to 12,21,9. Of 1650 reflections collected, 1621 were unique ($R_{\text{int}} = 0.142$) (22 were systematically absent). Number of unobserved reflections = 288 defined by $I \leq 3.0\sigma(I)$. The intensities of three representative reflections ($2\bar{9}\bar{2}$, $\bar{2}92$ and $0,\bar{1}\bar{0},\bar{1}$) remained constant throughout data collection and thus no decay correction was applied. The data were corrected for Lorentz and polarization effects. An empirical absorption correction (North, Phillips & Mathews, 1968) was applied, based on azimuthal scans of several reflections, with transmission factors ranging from 0.91 to 1.00. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984). Refinement of the two enantiomorphs did not reveal statistically significant differences; hence, enantiomorph selection was made by knowledge of the precursor compound's stereochemistry. H atoms were generated using optimum bonding geometry and included in F_c. H-atom thermal parameters and positions were not refined. Non-H atoms were refined anisotropically. Parameters were refined on *F*, with function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/\text{Lp}^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, $p = p$ factor.

0108-2701/92/040747-03$03.00