Tableau 3. *Distances* (Å) *et angles* (°) *dans les molécules de pyridine*

	Molécule 1	Molécule 2	Molécule 3	Molécule 4
N–C(1)	1,34 (3)	1,37 (3)	1,34 (3)	1,32 (3)
C(1)–C(2)	1,45 (5)	1,45 (3)	1,40 (3)	1,40 (3)
C(2)–C(3)	1,36 (5)	1,34 (3)	1,41 (3)	1,39 (4)
C(3)–C(4)	1,40 (4)	1,37 (4)	1,37 (3)	1,41 (5)
C(4)–C(5)	1,39 (4)	1,43 (3)	1,42 (3)	1,42 (4)
C(5)–N	1,33 (3)	1,33 (3)	1,36 (3)	1,36 (3)
C(5)–N–C(1)	117 (2)	121 (2)	118 (2)	118 (2)
N–C(1)–C(2)	120 (3)	119 (2)	123 (2)	125 (2)
C(1)–C(2)–C(3)	121 (4)	119 (3)	119 (3)	118 (3)
C(2)–C(3)–C(4)	118 (3)	122 (3)	119 (3)	118 (3)
C(3)–C(4)–C(5)	117 (3)	118 (3)	119 (3)	119 (3)
C(4)–C(5)–N	126 (3)	121 (2)	122 (3)	121 (3)
Equation du plan	$X + 1{,}34Y - 2{,}83Z = 0{,}05$	$X + 0{,}23Y + 0{,}66Z = -0{,}18$	$X - 2{,}83Y + 0{,}19Z = -18{,}63$	$X - 2{,}02Y - 6{,}25Z = -45{,}23$
Distances au plan moyen				
N	0,04 (2)	0,01 (2)	0,00 (2)	−0,02 (2)
C(1)	−0,01 (3)	0,00 (2)	0,02 (2)	0,01 (2)
C(2)	−0,03 (3)	0,01 (2)	0,02 (2)	0,02 (2)
C(3)	0,06 (3)	0,01 (2)	0,00 (2)	0,04 (3)
C(4)	−0,03 (3)	0,00 (2)	0,01 (2)	0,04 (3)
C(5)	−0,03 (2)	0,01 (2)	0,02 (2)	0,00 (2)

Les octaèdres qui constituent l'environnement du magnésium ne sont liés entre eux que par de faibles interactions du type van der Waals; en effet les distances les plus courtes entre les atomes des molécules de pyridine sont de 3,66 Å.

Les calculs ont été effectués sur l'ordinateur CII Iris 80 de l'Université Pierre et Marie Curie.

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Isothiocyanato[tris(2-dimethylaminoethyl)amine]palladium(II) Thiocyanate

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Abstract. $C_{13}H_{30}N_5PdS^+.SCN^-$, $[Pd(C_{12}H_{30}N_4)(NCS)](SCN)$, $M_r = 453{\cdot}0$, monoclinic, $a = 8{\cdot}845$ (1), $b = 17{\cdot}290$ (3), $c = 14{\cdot}430$ (2) Å, $\beta = 110{\cdot}70$ (1)°, $V = 2064{\cdot}3$ Å^3, $Z = 4$, $D_c = 1{\cdot}46$ Mg m^{-3}, $F(000) = 936$; space group $P2_1/c$ from systematic absences ($h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$); Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}08$ mm^{-1}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final R of 0·091 for 3223 independent observed reflections. The crystal structure contains discrete $[Pd(NCS)(Me_6tren)]^+$ cations and SCN^- anions. The Pd atom is four-coordinated in a square-planar environment by an isothiocyanato N [Pd–N 1·987 (8) Å] and three N atoms [Pd–N 1·985 (8) (*trans* to isothiocyanate), 2·054 (9) and 2·055 (9) Å] of the Me_6tren ligand. The fourth N of the Me_6tren ligand takes no part in the coordination scheme. The S atom of a symmetry-related isothiocyanato ligand lies above the coordination plane with Pd···S 3·640 (5) Å and N–Pd···S 84·2–98·1°.

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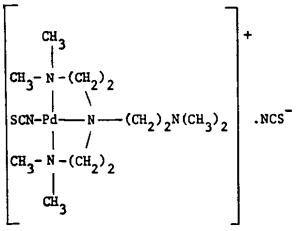
Introduction. Attempts to prepare five-coordinate palladium(II) complexes (Senoff, 1978; Bhattacharya

& Senoff, 1979) analogous to those obtained with nickel (Orioli & Nardi, 1975) using tris(2-dimethylaminoethyl)amine (= Me_6tren), led us to examine crystals of composition $[Pd(NCS)(Me_6tren)].NCS$. We report here the results of our studies which establish unequivocally that the Pd is not coordinated by the four N atoms of the Me_6tren ligand but only by three as shown in (I); a somewhat similar four-coordination was found in $[PdCl(Me_6trenH)].Cl.PF_6$ (Ferguson & Roberts, 1978).



(I)

Small yellow plate-like crystals of (I), elongated along the *a* axis, were grown from acetone. Difficulty was experienced in obtaining good single crystals, and the one eventually used for data collection was slightly split and did not diffract well. However, as the aim of the analysis was mainly to establish gross details of stereochemistry we judged this to be no great impediment.

Preliminary space group and unit-cell parameters were obtained by photographic methods; precise lattice parameters were obtained from a least-squares refinement of the setting angles of 12 reflections with θ(Mo $K\alpha$) between 10 and 20°. Intensity data for 3627 independent reflections with $2 \leq \theta \leq 25°$ were collected on a computer-controlled Hilger & Watts Y290 four-circle diffractometer as described previously for $[PdCl(Me_6trenH)].Cl.PF_6$ (Ferguson & Roberts, 1978). The intensities of three standard reflections, recorded after every 100 measurements, decreased by 6% during data collection; this was corrected for by appropriate scaling. After correction for Lorentz, polarization and absorption factors, 3223 reflections with $I > 3\sigma(I)$ were retained as observed and used in subsequent calculations.

The structure was solved [using the programs of Sheldrick (1976)] by a combination of Patterson and Fourier methods and refined by full-matrix least-squares calculations minimizing $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$ and $\sigma(F)$ is derived from counting statistics. All the H atoms were successfully located from a difference synthesis and were included (but not refined) in subsequent calculations at their idealized positions (tetrahedral geometry, C—H 0·95 Å) with an overall thermal parameter U_{iso} = 0·10 Å^2. The scattering factors of Stewart, Davidson & Simpson (1965) were used for the H atoms, and those of Cromer & Mann (1968) for the non-hydrogen atoms.

At convergence, final values of R and R^1 [$= (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] are 0·091 and 0·090 respectively. A final difference synthesis showed no chemically significant maxima. Atomic coordinates and standard deviations are in Table 1. Fig. 1 shows the structure of the cation with the same numbering scheme as in $[PdCl(Me_6trenH)]^{2+}$; details of molecular geometry are in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, and the calculated hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34475 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates (fractional,* $\times 10^5$ *for* Pd, $\times 10^4$ *for others)*

	x	y	z	$U_{av} \times 10^3$*
Pd	1204 (7)	8645 (3)	19272 (4)	38
S(1)	−2834 (5)	−939 (3)	−532 (3)	118
S(2)	7123 (7)	985 (3)	3683 (4)	127
N(1)	1417 (10)	101 (5)	3006 (7)	63
N(2)	1242 (9)	1708 (4)	2846 (6)	54
N(3)	−1261 (11)	1748 (5)	1099 (7)	61
N(4)	3172 (10)	3379 (5)	2557 (6)	50
N(5)	−948 (10)	19 (5)	993 (6)	60
N(6)	5865 (13)	1515 (7)	5088 (7)	97
C(1)	−614 (12)	2493 (5)	1635 (8)	64
C(2)	91 (12)	2342 (6)	2669 (8)	68
C(3)	3739 (11)	2672 (5)	3127 (6)	55
C(4)	2804 (11)	1950 (5)	2620 (7)	61
C(5)	2595 (13)	554 (6)	3851 (8)	69
C(6)	1731 (14)	1384 (6)	3859 (7)	67
C(7)	−3101 (14)	1584 (8)	1060 (9)	84
C(8)	−1257 (17)	1761 (7)	94 (8)	83
C(9)	4102 (15)	4031 (6)	3204 (9)	81
C(10)	3624 (17)	3369 (8)	1689 (9)	106
C(11)	255 (11)	−358 (6)	3338 (7)	61
C(12)	2415 (15)	−450 (6)	2669 (10)	85
C(13)	−1701 (13)	−393 (6)	379 (7)	67
C(14)	6438 (11)	1309 (5)	4551 (7)	58

* The values given in this column are

$$U_{av} = \left(\frac{U_{11} + U_{22} + U_{33}}{3}\right) \text{Å}^2.$$

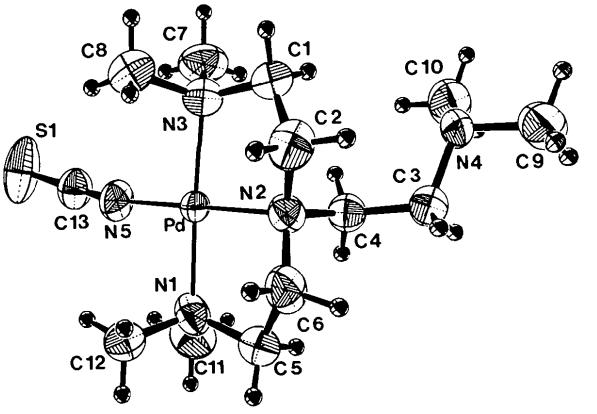


Fig. 1. The $[Pd(NCS)(Me_6tren)]^+$ cation showing the numbering scheme used.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Values in parentheses are the standard deviations in the last decimal place.

Pd—N(1)	2·054 (9)	N(3)—C(8)	1·45 (1)
Pd—N(2)	1·985 (8)	N(4)—C(3)	1·46 (1)
Pd—N(3)	2·055 (9)	N(4)—C(9)	1·51 (1)
Pd—N(5)	1·987 (8)	N(4)—C(10)	1·44 (1)
N(1)—C(5)	1·51 (1)	C(1)—C(2)	1·42 (1)
N(1)—C(11)	1·51 (1)	C(3)—C(4)	1·53 (1)
N(1)—C(12)	1·49 (1)	C(5)—C(6)	1·63 (1)
N(2)—C(2)	1·46 (1)	N(5)—C(13)	1·15 (1)
N(2)—C(4)	1·58 (1)	C(13)—S(1)	1·64 (1)
N(2)—C(6)	1·48 (1)	N(6)—C(14)	1·12 (1)
N(3)—C(1)	1·51 (1)	C(14)—S(2)	1·67 (1)
N(3)—C(7)	1·63 (1)		
Pd···S(1^{I})	3·640 (5)	Pd···S(2^{II})	4·271 (6)
N(1)—Pd—N(2)	87·3 (3)	Pd—N(3)—C(1)	107·3 (6)
N(1)—Pd—N(3)	167·6 (3)	Pd—N(3)—C(7)	105·7 (6)
N(1)—Pd—N(5)	92·6 (4)	Pd—N(3)—C(8)	112·4 (7)
N(2)—Pd—N(3)	84·1 (4)	C(1)—N(3)—C(7)	111·0 (9)
N(2)—Pd—N(5)	178·3 (4)	C(1)—N(3)—C(8)	111·4 (9)
N(3)—Pd—N(5)	96·3 (4)	C(7)—N(3)—C(8)	108·9 (9)
Pd—N(1)—C(5)	108·6 (5)	C(3)—N(4)—C(9)	105·8 (7)
Pd—N(1)—C(11)	108·6 (6)	C(3)—N(4)—C(10)	109·5 (9)
Pd—N(1)—C(12)	113·6 (7)	C(9)—N(4)—C(10)	106·8 (8)
C(5)—N(1)—C(11)	111·6 (8)	N(3)—C(1)—C(2)	109·2 (8)
C(5)—N(1)—C(12)	106·0 (9)	N(2)—C(2)—C(1)	110·0 (8)
C(11)—N(1)—C(12)	108·5 (8)	N(4)—C(3)—C(4)	113·1 (7)
Pd—N(2)—C(2)	106·4 (5)	N(2)—C(4)—C(3)	118·7 (7)
Pd—N(2)—C(4)	108·8 (5)	N(1)—C(5)—C(6)	105·8 (7)
Pd—N(2)—C(6)	106·5 (5)	N(2)—C(6)—C(5)	107·5 (7)
C(2)—N(2)—C(4)	111·8 (7)	Pd—N(5)—C(13)	170·7 (9)
C(2)—N(2)—C(6)	113·6 (8)	N(5)—C(13)—S(1)	176·7 (10)
C(4)—N(2)—C(6)	109·4 (7)	N(6)—C(14)—S(2)	174·9 (9)
N(1)—Pd···S(1^{I})	98·1 (2)	N(1)—Pd···S(2^{II})	83·1 (2)
N(2)—Pd···S(1^{I})	94·1 (2)	N(2)—Pd···S(2^{II})	80·6 (2)
N(3)—Pd···S(1^{I})	91·4 (2)	N(3)—Pd···S(2^{II})	86·7 (2)
N(5)—Pd···S(1^{I})	84·2 (2)	N(5)—Pd···S(2^{II})	101·1 (2)
S(1^{I})···Pd···S(2^{II})	174·5 (1)		

The superscripts refer to the following equivalent positions
(I) $\bar{x},\bar{y},\bar{z}$ (II) $-1+x,y,z$.

Discussion. The cation (Fig. 1) has slightly distorted square-planar geometry similar to that found for the protonated complex $[PdCl(Me_6trenH)]^{2+}$; the fourth N atom, N(4), of the Me_6tren ligand is not involved in any coordination. The Pd—N(isothiocyanato) bond length [1·987 (8) Å] is not significantly longer than the Pd—N distance [1·969 (3) Å] in *trans*-$[Pd(NCS)_2(PPh_3)_2]$ (Carty, Chieh, Taylor & Wong, 1976) but is shorter than the Pd—N distance [2·055 (3) Å] in $\{Pd(NCS)_2[Ph_2P(CH_2)_3PPh_2]\}$ (Palenik, Mathew, Steffen & Beran, 1975) where the N atoms are *trans* to the P atom. The Pd—N distances with the (Me_6tren) ligand are of two types: that *trans* to isothiocyanate is 1·985 (8) Å, whereas those *trans* to $(CH_3)_2N$— are much longer, 2·054 (9) and 2·055 (9) Å. In $[PdCl(Me_6trenH)]^+$ the corresponding distances are 2·039 (6) (*trans* to Cl) and 2·071 (9) Å (*trans* to N). The *cis*-(Me_6tren)N—Pd—N(Me_6tren) angles are less than 90° (84·1 and 87·3°) as a consequence of the steric bite of the ligand and the (isothiocyanato)N—Pd—N(Me_6tren) angles are greater than 90° (92·6 and 96·3°). The Pd and N(1), N(2), N(3) and N(5) atoms are almost coplanar with a r.m.s. deviation of 0·09 Å from the best plane through them.

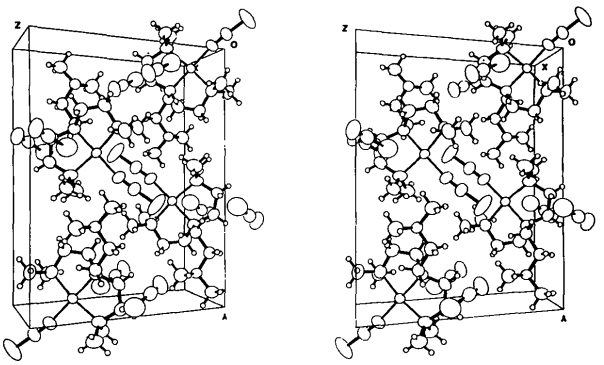


Fig. 2. A stereoscopic view of the crystal packing of $[Pd(NCS)(Me_6tren)]^+.NCS^-$.

The poor quality of the data leads to a considerable variation in C—C and C—N distances (averaging 1·53 and 1·50 Å respectively) in the Me_6tren ligand; the angles around the C and N atoms are in the range 105·8 (7) to 113·6 (8)° except for N(2)—C(4)—C(3) 118·7 (7)° which is enlarged presumably to relieve intramolecular H···H interactions between protons on C(3) and C(6). [The relevant H···H separation is 2·30 Å and if the N(2)—C(4)—C(3) angle had not enlarged, the separation would have been considerably smaller.]

The small deviations of the Pd—N(5)—C and N—C—S angles from linearity (Table 2) lie within normal values and may be attributed to packing effects. The C—N and S—C bond distances in both the free and coordinated NCS groups are comparable with those found, for example, in $[Pd(NCS)_2(PPh_3)_2]$ [N—C 1·138 (6) and C—S 1·621 (5) Å].

The crystal structure (Fig. 2) contains discrete $[Pd(NCS)(Me_6tren)]^+$ cations and SCN^- thiocyanate anions. The S atoms of the thiocyanate ion and of a neighbouring isothiocyanato (—NCS) group are situated above and below the palladium coordination plane at Pd···S distances 4·27 Å (thiocyanate ion) and 3·64 Å (isothiocyanate) with N—Pd···S angles in the range 80·6 to 101·1° for the SCN^- thiocyanate ion and 84·2 to 98·1° for the —NCS isothiocyanato moiety. All other inter-ion contacts correspond to normal van der Waals distances.

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Nonacarbonyl-di-μ-hydrido-(triphenylphosphine)-*triangulo*-triosmium

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Abstract. $C_{27}H_{17}O_9Os_3P$, $Os_3(C_{18}H_{15}P)(CO)_9H_2$, monoclinic, $P2_1/n$, $a = 8{\cdot}756$ (3), $b = 16{\cdot}899$ (7), $c = 20{\cdot}142$ (9) Å, $\beta = 98{\cdot}31$ (2)°, $U = 2949{\cdot}1$ Å^3, $Z = 4$, $D_c = 2{\cdot}45$ Mg m^{-3}, μ(Mo $K\alpha$) = 12·98 mm^{-1}. The structure was refined to an R of 0·035 for 4078 unique diffractometer data. The three Os atoms define an isosceles triangle. The triphenylphosphine group bonds in an equatorial site on one of the Os atoms associated with the short Os—Os bond. The carbonyl ligands are all terminal, and their distribution suggests that both hydride ligands bridge the short Os—Os edge.

Introduction. $H_2Os_3(CO)_{10}$ is of interest because it is a particularly reactive molecule and has been used as a starting material in many reactions leading to the formation of complex cluster species (Bryan, Johnson & Lewis, 1977). Its reactivity is thought to be due to the unsaturation of one Os—Os bond. The nature of the bonding in this system is not well understood. Recent X-ray (Churchill, Hollander & Hutchinson, 1977) and combined X-ray/neutron (Orpen, Rivera, Bryan, Pippard, Sheldrick & Rouse, 1978) studies have shown that both hydrides bridge the short unsaturated Os—Os edge. An X-ray analysis of the title compound was undertaken to investigate the influence of the presence of a phosphine ligand on the Os—Os bonding and on the cluster geometry as a whole.

The title compound was prepared by reacting triphenylphosphine with $H_2Os_3(CO)_{10}$ in hexane, and refluxing the product, $H_2Os_3(CO)_{10}P(C_6H_5)_3$, to remove a carbonyl group (Zuccaro, 1979). Recrystallization from hexane yielded dark-purple, rectangular blocks. 4240 intensities were recorded ($1{\cdot}5 < \theta < 25{\cdot}0°$) on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, a θ–2θ scan, and a crystal 0·288 × 0·272 × 0·224 mm. Lp corrections, and semi-empirical absorption corrections based on a pseudo-ellipsoid model and 372 azimuthal scan data from 14 independent reflections were applied; transmission factors ranged from 0·539 to 0·678 for the full data set. Equivalent reflections were averaged to give 4078 unique observed intensities [$F > 4\sigma(F)$]. Cell dimensions were derived from the angular measurements of 25 strong reflections ($10{\cdot}0 < \theta < 15{\cdot}0°$).

The Os atoms were located by multisolution $\sum_2$ sign expansion; positions of all the other non-hydrogen atoms were found from a subsequent difference synthesis. The structure was refined by full-matrix least squares with complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and weights $w = 0{\cdot}4991/[\sigma^2(F) + 0{\cdot}0002|F_o|^2]$. The refined parameters included anisotropic thermal parameters for Os, P, and the carbonyl C and O atoms, a common isotropic temperature factor for the phenyl H atoms, and an empirical extinction parameter x, which refined to 0·00071 (2); F_c is multiplied by $(1 - 0{\cdot}0001xF_c^2/\sin\theta)$. The phenyl rings were refined as rigid groups with the constraints: C—C 1·395 Å,

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