Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br	0.40448 (3)	1.04636 (5)	0.08556 (3)	0.0396 (1)
Cu	1/4	3/4	0	0.0481 (3)
N1	0.3694 (2)	0.6134 (4)	0.0599 (2)	0.0351 (9)
N2	0.4560 (2)	0.4088 (4)	0.1050 (3)	0.042 (1)
N3	0.2643 (2)	0.7610 (4)	−0.1327 (2)	0.0360 (9)
N4	0.3189 (2)	0.8098 (4)	−0.2492 (3)	0.045 (1)
C1	0.3640 (3)	0.4703 (5)	0.0605 (3)	0.043 (1)
C2	0.5242 (3)	0.5217 (5)	0.1346 (4)	0.047 (1)
C3	0.4700 (3)	0.6474 (5)	0.1063 (4)	0.046 (1)
C4	0.3336 (3)	0.8294 (5)	−0.1507 (3)	0.043 (1)
C5	0.2340 (3)	0.7241 (6)	−0.2978 (3)	0.048 (1)
C6	0.2009 (3)	0.6948 (5)	−0.2248 (3)	0.042 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu···Br	3.3767 (4)	N3—C6	1.373 (6)
Cu—N1	2.008 (3)	N4—C4	1.336 (6)
Cu—N3	1.997 (4)	N4—C5	1.373 (6)
N1—C1	1.295 (7)	C2—C3	1.345 (6)
N1—C3	1.368 (6)	C5—C6	1.354 (7)
N2—C1	1.341 (6)	Br···N2^i	3.343 (4)
N2—C2	1.363 (6)	Br···N4^{ii}	3.383 (4)
N3—C4	1.312 (6)		
Br···Cu—N1	90.4 (1)	C4—N3—C6	106.2 (4)
Br—Cu—N3	88.2 (1)	C4—N4—C5	107.4 (4)
N1—Cu—N3	89.9 (1)	N1—C1—N2	111.4 (4)
Cu—N1—C1	124.8 (3)	N2—C2—C3	106.1 (4)
Cu—N1—C3	129.1 (3)	N1—C3—C2	109.4 (4)
C1—N1—C3	106.1 (4)	N3—C4—N4	111.2 (4)
C1—N2—C2	107.0 (4)	N4—C5—C6	106.1 (4)
Cu—N3—C4	128.6 (3)	N3—C6—C5	109.1 (4)
Cu—N3—C6	125.2 (3)		

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, 2 - y, \frac{1}{2} + z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *MolEN*.

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trans-Dichlorobis(7-thiabicyclo[2.2.1]-heptane)palladium(II) and *trans*-Dichlorobis(7-thiabicyclo[2.2.1]heptane)platinum(II)

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Abstract

The asymmetric unit of the title Pd complex, $[PdCl_2(C_6H_{10}S)_2]$, consists of two independent half molecules lying on inversion centres. The Pd atoms have square-planar coordination with Pd—S distances of 2.300 (2) and 2.313 (2) Å, Pd—Cl distances of 2.300 (2) and 2.307 (2) Å, and S—Pd—Cl angles of 88.21 (8) and 90.12 (8)°. The Pt complex, $[PtCl_2(C_6H_{10}S)_2]$, has the Pt atom lying on an inversion centre, also has square-planar coordination, and has a Pt—S distance of 2.286 (2), a Pt—Cl distance of 2.300 (2) Å and a S—Pt—Cl angle of 89.25 (8)°.

Comment

Platinum group metals occur in low amounts in association with other metal ores (*e.g.* Ni and Cu) (Hartley, 1973). One possible method for concentrating these metals is to take advantage of the ability of chloride derivatives to complex with thioether compounds to form hydrocarbon-soluble complexes. The base metals and

the thioether ligands can then be recovered by mild de-hydrogenation techniques (Clark, Kirk & Parvez, 1993). The Pd and Pt complexes of 7-thiabicyclo[2.2.1]heptane [(1) and (2), respectively] described here constitute two useful materials for this purpose.

(1)   (2)
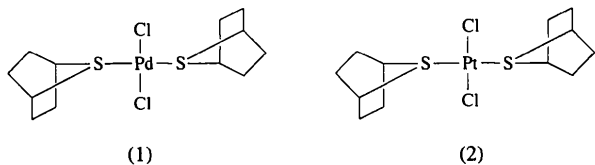
There are two independent centrosymmetric molecules of (1) and one of these is shown in Fig. 1; the other molecule has identical stereochemistry and conformation. Fig. 2 shows a view of the centrosymmetric molecule of (2).

A comparison of bond distances and angles around the square-planar Pd atoms in (1) with the data for corresponding trans-dichlorobis(S-ligand)palladium(II) complexes, where S-ligands are thiomorpholin-3-one (Fowler & Griffiths, 1978a), 1,4-thioxane (Fowler & Griffiths, 1978b), oxathia[4.3.3]propellene-S (Herb-stein et al., 1986), dimethyl sulfoxide (Bennett, Cotton, Weaver, Williams & Watson, 1967), 2,3-dihydrobenzo[b]thiophene-S (Clark, Fait, Jones & Kirk,

1991), and 2,3-dihydro-4-methylbenzo[b]thiophene and 2,3-dihydro-7-methylbenzo[b]thiophene (Clark, Kirk & Parvez, 1993), show no significant differences in the dimensions Pd—S, Pd—Cl and S—Pd—Cl which are 2.293–2.330 (3), 2.283–2.309 (3) Å and 84.1–95.9 (1)°, respectively, in the above mentioned complexes.

A similar comparison of (2) with the corresponding Pt^II complexes containing S-ligands, where S-ligands are 1,4-thioxane (Bugarcic, Louquist & Oskarsson, 1993), di-n-propyl sulfoxide (Melanson & Rochon, 1988) and 1,3-dihydrobenzo[c]thiophene-S (Parvez, Fait, Clark & Jones, 1993), reveals that there are no significant differences in the dimensions around the square-planar Pt atoms. The dimensions Pt—S, Pt—Cl and S—Pt—Cl in the above mentioned complexes are 2.292–2.313 (2), 2.293–2.300 (3) Å and 82.8–97.2 (1)°, respectively.

The S—C and C—C distances in the thiobicyclohep-tane ligands of (1) and (2) are normal with mean values of 1.833 (8) and 1.830 (8) Å for S—C and 1.54 (1) and 1.52 (1) Å for C—C in compounds (1) and (2), respectively, with the six-membered carbon rings adopting boat conformations in both structures.

Fig. 2. A perspective view of the Pt complex (2) with the atomic numbering scheme, plotted using ORTEPII (Johnson, 1976). Displacement ellipsoids are shown at 50% probability levels for non-H atoms and H atoms are assigned arbitrary radii.
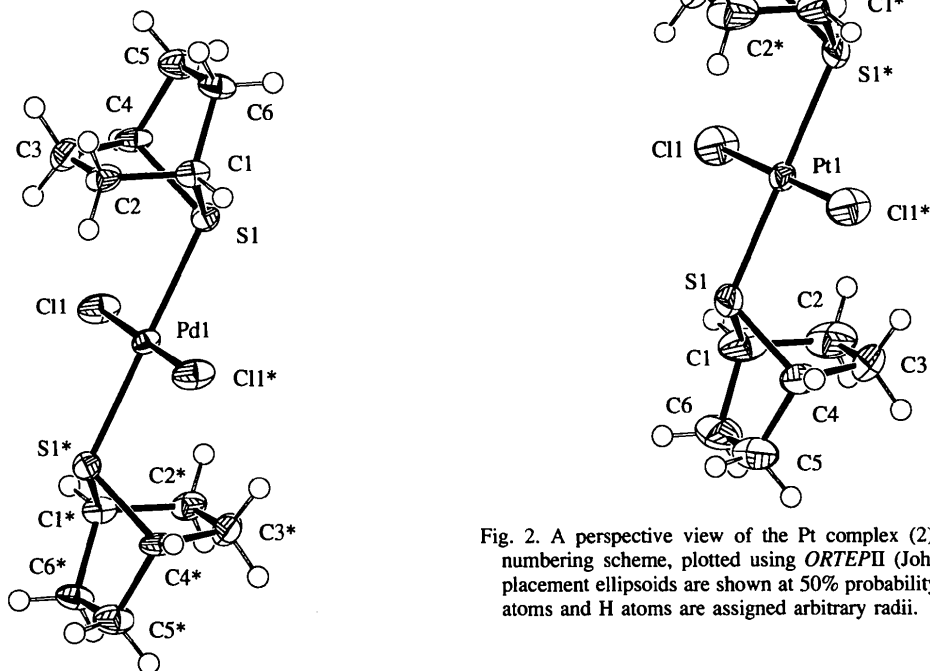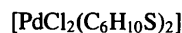

Fig. 1. A perspective view of one of the two independent molecules of the Pd complex (1) with the atomic numbering scheme, plotted using ORTEPII (Johnson, 1976). Displacement ellipsoids are shown at 50% probability levels for non-H atoms and H atoms are assigned arbitrary radii.

Experimental

7-Thiabicyclo[2.2.1]heptane (Johnson, Keiser & Sharp, 1969) (2 mol equiv.) was added to a suspension of palladium(II) chloride for (1) and platinum(II) chloride for (2) (1 mol

equiv.) in ethanol and the mixture heated under reflux for 30 min. The mixture was cooled and the ethanol solvent removed by rotary evaporation. Crystallization of the residues from dichloromethane–ethanol solution gave crystals melting at >573 K with decomposition.

Compound (1)

Crystal data

$[PdCl_2(C_6H_{10}S)_2]$	Mo $K\alpha$ radiation
$M_r = 405.72$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 6.815 (1)$ Å	$\theta = 15–20°$
$b = 17.967 (2)$ Å	$\mu = 1.866$ mm^{-1}
$c = 6.223 (1)$ Å	$T = 295 (1)$ K
$\alpha = 98.52 (1)°$	Prismatic
$\beta = 98.69 (1)°$	$0.30 \times 0.20 \times 0.14$ mm
$\gamma = 84.52 (1)°$	Orange
$V = 742.9 (2)$ Å^3	
$Z = 2$	
$D_x = 1.814$ Mg m^{-3}	

Data collection

Rigaku AFC-5S diffracto-meter	2240 observed reflections $[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.026$
Absorption correction: empirical via 3 ψ scans (North, Phillips & Mathews, 1968)	$\theta_{max} = 25°$ $h = 0 \rightarrow 8$ $k = -21 \rightarrow 21$ $l = -7 \rightarrow 7$
$T_{min} = 0.948$, $T_{max} = 1.000$	3 standard reflections frequency: 180 min intensity decay: 1.05%
2879 measured reflections	
2633 independent reflections	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.74$ e Å^{-3}
$R = 0.044$	$\Delta\rho_{min} = -1.07$ e Å^{-3}
$wR = 0.059$	Extinction correction:
$S = 2.81$	secondary
2240 reflections	Extinction coefficient:
157 parameters	3.765×10^{-7}
H atoms riding with C—H = 0.95 Å	Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)
$w = 1/\sigma^2(F)$	
$(\Delta/\sigma)_{max} = 0.01$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Pd(1)	0	0	0	1.61 (2)
Pd(2)	-1/2	-1/2	-1/2	1.61 (2)
Cl(1)	0.2435 (3)	0.0835 (1)	0.1170 (4)	2.85 (5)
Cl(2)	-0.3327 (3)	-0.5739 (1)	-0.2490 (4)	3.07 (5)
S(1)	-0.2294 (3)	0.1028 (1)	-0.0309 (3)	1.89 (4)
S(2)	-0.7818 (3)	-0.5623 (1)	-0.5121 (4)	1.86 (4)
C(1)	-0.4049 (12)	0.0863 (5)	-0.2837 (13)	1.9 (2)
C(2)	-0.2699 (13)	0.0652 (5)	-0.4633 (13)	2.4 (2)
C(3)	-0.0999 (13)	0.1209 (5)	-0.4000 (14)	2.7 (2)
C(4)	-0.1436 (12)	0.1693 (4)	-0.1890 (14)	2.1 (2)
C(5)	-0.3342 (13)	0.2209 (5)	-0.2343 (15)	2.8 (2)
C(6)	-0.5036 (12)	0.1673 (5)	-0.2944 (14)	2.3 (2)
C(7)	-0.7289 (12)	-0.6641 (4)	-0.5395 (14)	1.9 (2)
C(8)	-0.6218 (14)	-0.6822 (5)	-0.7417 (17)	3.1 (2)
C(9)	-0.7346 (16)	-0.6350 (6)	-0.9071 (16)	3.5 (2)
C(10)	-0.9034 (14)	-0.5886 (5)	-0.7948 (15)	2.8 (2)
C(11)	-1.0509 (14)	-0.6401 (5)	-0.7582 (16)	3.1 (2)
C(12)	-0.9388 (14)	-0.6929 (5)	-0.5957 (16)	3.2 (2)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Pd(1)—Cl(1)	2.307 (2)	Pd(2)—Cl(2)	2.300 (2)
Pd(1)—S(1)	2.313 (2)	Pd(2)—S(2)	2.300 (2)
S(1)—C(1)	1.832 (8)	S(1)—C(4)	1.842 (8)
S(2)—C(7)	1.817 (8)	S(2)—C(10)	1.842 (9)
Cl(1)—Pd(1)—Cl(1^i)	180.0	S(1)—Pd(1)—S(1^i)	180.0
Cl(2)—Pd(2)—Cl(2^{ii})	180.0	S(2)—Pd(2)—S(2^{ii})	180.0
Cl(1)—Pd(1)—S(1)	88.21 (8)	Cl(2)—Pd(2)—S(2)	90.12 (8)
Pd(1)—S(1)—C(1)	110.4 (3)	Pd(1)—S(1)—C(4)	110.5 (3)
C(1)—S(1)—C(4)	80.8 (4)	Pd(2)—S(2)—C(7)	112.1 (3)
Pd(2)—S(2)—C(10)	112.3 (3)	C(7)—S(2)—C(10)	80.0 (4)
S(1)—C(1)—C(2)	103.7 (5)	S(1)—C(1)—C(6)	100.0 (5)
S(1)—C(4)—C(5)	101.1 (6)	S(1)—C(4)—C(3)	104.1 (6)
S(2)—C(7)—C(8)	104.0 (5)	S(2)—C(7)—C(12)	102.3 (6)
S(2)—C(10)—C(11)	101.0 (6)	S(2)—C(10)—C(9)	102.9 (6)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-1 - x, -1 - y, -1 - z$.

Compound (2)

Crystal data
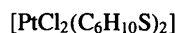
$[PtCl_2(C_6H_{10}S)_2]$	Mo $K\alpha$ radiation
$M_r = 494.41$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 7.934 (3)$ Å	$\theta = 10–15°$
$b = 11.759 (3)$ Å	$\mu = 9.703$ mm^{-1}
$c = 8.256 (2)$ Å	$T = 295 (1)$ K
$\beta = 94.94 (1)°$	Prismatic
$V = 767.4 (3)$ Å^3	$0.20 \times 0.16 \times 0.13$ mm
$Z = 2$	Lemon yellow
$D_x = 2.140$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	1351 observed reflections $[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.013$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$\theta_{max} = 27°$ $h = 0 \rightarrow 10$ $k = 0 \rightarrow 14$ $l = -10 \rightarrow 10$
1880 measured reflections	3 standard reflections frequency: 120 min intensity decay: none
1759 independent reflections	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.80$ e Å^{-3}
$R = 0.035$	$\Delta\rho_{min} = -1.45$ e Å^{-3}
$wR = 0.050$	Extinction correction:
$S = 3.63$	secondary
1351 reflections	Extinction coefficient:
80 parameters	2.574×10^{-6}
H atoms riding with C—H = 0.95 Å	Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)
$w = 1/\sigma^2(F)$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B$_{eq}$
Pt(1)	0	0	0	1.96 (1)
Cl(1)	0.2563 (3)	0.0228 (2)	0.1491 (3)	3.82 (5)
S(1)	0.1400 (3)	−0.0297 (2)	−0.2270 (2)	2.86 (4)
C(1)	0.3077 (9)	−0.1367 (7)	−0.1855 (10)	3.9 (2)
C(2)	0.2128 (13)	−0.2371 (7)	−0.1270 (10)	4.4 (2)
C(3)	0.0483 (11)	−0.2442 (6)	−0.2345 (11)	3.7 (2)
C(4)	0.0508 (9)	−0.1458 (6)	−0.3523 (9)	3.0 (2)
C(5)	0.1873 (11)	−0.1635 (7)	−0.4675 (10)	4.0 (2)
C(6)	0.3542 (12)	−0.1572 (9)	−0.3607 (13)	5.4 (3)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Pt(1)—Cl(1)	2.300 (2)	Pt(1)—S(1)	2.286 (2)
S(1)—C(1)	1.841 (8)	S(1)—C(4)	1.819 (7)
Cl(1)—Pt(1)—Cl(1^i)	180.0	C(1)—S(1)—C(4)	80.4 (3)
Cl(1)—Pt(1)—S(1)	89.25 (8)	S(1)—Pt(1)—S(1^i)	180.0
Pt(1)—S(1)—C(1)	110.3 (3)	Pt(1)—S(1)—C(4)	112.9 (2)

Symmetry code: (i) −x, −y, −z.

The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations with non-H atoms anisotropic. Allowance was made for anomalous dispersion (Ibers & Hamilton, 1964).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (1) and *Enraf–Nonius CAD-4 Diffractometer Controlling Software* (Schagen, Straver, van Meurs & Williams, 1988) for (2). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Structure solution: *DIRDIF PATTY* (Beurskens et al., 1992). Structure refinement: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Preparation of material for publication: *TEXSAN*.

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[*M*(CNMe)$_4$](PF$_6$)$_2$ (*M* = Pt, Pd)

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Abstract

The compounds tetrakis(methyl isocyanide)platinum bis(hexafluorophosphate), [Pt(CNMe)$_4$](PF$_6$)$_2$, and tetrakis(methyl isocyanide)palladium bis(hexafluorophosphate), [Pd(CNMe)$_4$](PF$_6$)$_2$, are isostructural; both crystallize with a tetragonal unit cell with a simple ionic packing arrangement related to that of NaCl.

Comment

No simple salts of tetrakis(methyl isocyanide)-transition metal complexes have been structurally characterized, apart from [Cu(CNMe)$_4$]BF$_4$, in which the Cu atom has a tetrahedral arrangement of CNMe ligands (Spek, 1982). The structures of [*M*(CNMe)$_4$](PF$_6$)$_2$ [*M* = Pt (1) and Pd (2)] were determined to allow a comparison of the cation geometry with that previously found in complex salts of general formula [*M*(CNMe)$_4$][*M'*(mnt)$_2$]$_n$ {mnt = [S$_2$C$_2$(CN)$_2$]$^{2-}$; *M*, *M'* = Pt, Pd; *n* = 1 or 2} (Connelly, Crossley, Orpen & Salter, 1992). Both compounds (1) and (2) crystallize in the tetragonal space group *P4/mbm* and have essentially identical structures.