$\omega/2\theta$ scans
Absorption correction:
empirical *via* $\psi$ scan
(North *et al.*, 1968)
$T_{min} = 0.69$, $T_{max} = 0.87$
2192 measured reflections
2062 independent reflections

$R_{int} = 0.008$
$\theta_{max} = 26.97°$
$h = -21 \rightarrow 20$
$k = -15 \rightarrow 0$
$l = 0 \rightarrow 12$
1 standard reflection
frequency: 120 min
intensity decay: 1.5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.067$
$S = 1.08$
2062 reflections
175 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.4068P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å$^{-3}$
$\Delta\rho_{min} = -0.35$ e Å$^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Ni1—N1 | 2.063 (2) | P1—O2 | 1.581 (2) |
| Ni1—N2 | 2.079 (2) | O2—HO2 | 0.78 (4) |
| Ni1—O1 | 2.144 (2) | O3—HO3 | 0.76 (5) |
| P1—O1 | 1.486 (2) | N1—HN1 | 0.87 (4) |
| P1—O4 | 1.514 (2) | N2—HN2 | 0.83 (3) |
| P1—O3 | 1.571 (2) | | |
| N1$^{i}$—Ni1—N1 | 180.0 | O1$^{i}$—Ni1—O1 | 180.0 |
| N1—Ni1—N2$^{i}$ | 85.56 (9) | O1—P1—O4 | 116.2 (1) |
| N1—Ni1—N2 | 94.44 (9) | O1—P1—O3 | 112.4 (1) |
| N2$^{i}$—Ni1—N2 | 180.0 | O4—P1—O3 | 104.7 (1) |
| N1—Ni1—O1$^{i}$ | 90.87 (8) | O1—P1—O2 | 106.5 (1) |
| N2—Ni1—O1$^{i}$ | 90.16 (8) | O4—P1—O2 | 110.4 (1) |
| N1—Ni1—O1 | 89.13 (8) | O3—P1—O2 | 106.3 (1) |
| N2—Ni1—O1 | 89.84 (8) | P1—O1—Ni1 | 145.1 (1) |

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The $\theta$-scan width was $(0.6 + 0.6\tan\theta)°$. Data were corrected for Lorentz–polarization effects. The structure was solved by heavy-atom methods and refined by full-matrix least squares. The O atom of the water molecule is disordered. It was refined isotropically and the corresponding H atoms were not located. H atoms of the organic molecule and the phosphate group were located from difference Fourier syntheses and were refined isotropically. The C—H distances are in the range 0.91 (4)–0.99 (4) Å. The two N—H distances are 0.83 (3) and 0.87 (4) Å, and the two O—H distances are 0.76 (5) and 0.78 (4) Å. The $U_{iso}$ values of the H atoms vary from 0.03 (1) to 0.07 (1) Å$^2$.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992; Enraf-Nonius, 1994) . Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1417). Services for accessing these data are described at the back of the journal.

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# Chiral bisphosphanes. V.† Chloro{*rac*,*trans*-1-[chloro(piperidin-1-yl)phosphino]-2-[bis(piperidin-1-yl)phosphino]cyclopentane-*P*,*P*′}neopentylplatinum(II) acetone solvate

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## Abstract

In the title compound, $[PtCl(C_5H_{11})(C_{20}H_{38}ClN_3P_2)]\cdot(CH_3)_2CO$, coordination about the central metal deviates slightly from ideal square-planar geometry. The $-P(Cl)-NC_5H_{10}$ substituent resides in a *trans* position with respect to the neopentyl group, with the two remaining *trans* coordination sites being occupied by the chloro ligand and the $-P(NC_5H_{10})_2$ residue of the chelating bisphosphane ligand.

## Comment

The title complex, (I), was prepared as part of our continuing studies of Group 8 metal complexes derived

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† Part IV: Dahlenburg & Kaunert (1998).

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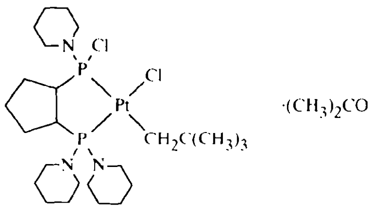
from racemic and optically pure bisphosphanes having chiral phosphorus centres supported on an asymmetric carbon backbone (Eckert *et al.*, 1995; Saare & Dahlenburg, 1995; Dahlenburg, 1997; Dahlenburg & Kurth, 1998; Dahlenburg & Kaunert, 1998). The crystal structure was determined in order to confirm the stereochemistry of the compound, since the *cis* or *trans* coordination of the chloro and neopentyl ligands with respect to the $-P(Cl)NC_5H_{10}$ residue and the $-P(NC_5H_{10})_2$ substituent of the chelating bisphosphane could not be established unequivocally on the basis of solution NMR data alone.



(I)

The structure determination proves the neopentyl group is *trans* with respect to the $-P(Cl)NC_5H_{10}$ residue, with the $-P(NC_5H_{10})_2$ substituent and the chloro ligand occupying the two remaining sites of the four-coordinated Pt atom. The X-ray structure analysis also revealed the presence of molecules showing slight tetrahedral distortion from square-planar coordination geometry; although the sum of the four inter-ligand *cis* angles (359.8°) is as required for a planar coordination of the central metal, the *trans* angles P1—Pt—C1 [178.6 (3)°] and Cl1—Pt—P2 [170.37 (11)°] deviate considerably from linearity. Consistently, the angle between the normals to the two planes defined by the *cis*-C1—Pt—Cl1 and *cis*-P1—Pt—P2 fragments, the limiting value of which is 0° for square-planar coordination and 90° for tetrahedral, amounts to 9.2°. The P1—Pt—P2 bite angle of 85.39 (11)° is smaller than that of 87.7 (1)° reported earlier for the structurally related complex $[(1S,2S)\text{-}C_5H_8\{P(CH_3)C_8H_{15}\text{-cyclo-}(R)\}_2PtI_2]$, bearing a bis[(cyclooctyl)methylphosphino]-substituted cyclopentane-based chelate ligand (Dahlenburg & Kurth, 1998). The significant difference in metal–phosphorus bond lengths observed for Pt—P1 [2.289 (3) Å] and Pt—P2 [2.213 (3) Å] is as expected, because a chloro ligand is at the *trans* position for the shorter one and is known to be a much weaker *trans*-influencing group than the neopentyl residue which is *trans* to the longer platinum-to-phosphorus bond.

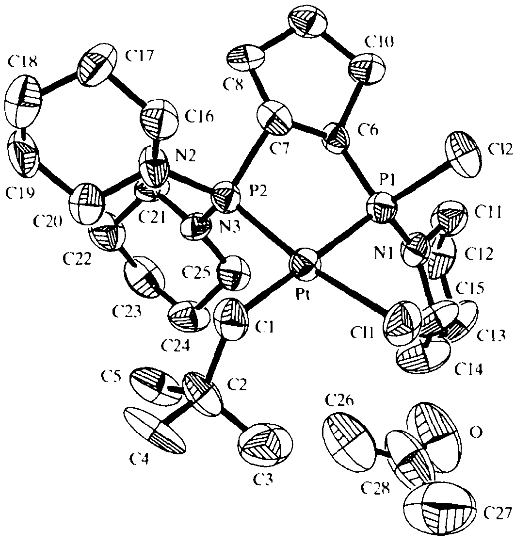


Fig. 1. The structure of the title complex, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

## Experimental

An ethereal solution containing *rac,trans*-$C_5H_8[P(Cl)NC_5H_{10}]$-$[P(NC_5H_{10})_2]$ and *rac,trans*-$C_5H_8[P(NC_5H_{10})_2]_2$ in approximately equimolar quantities was prepared from a 1:4:4 reaction between *rac,trans*-$C_5H_8(PCl_2)_2$ (Allen *et al.*, 1983; Green, 1983), piperidine and triethylamine, and subsequently treated with a slight deficiency of $[(1,5\text{-}C_8H_{12})Pt(Cl)CH_2\text{-}C(CH_3)_3]$ in dichloromethane. After stirring for 24 h, the reaction mixture exhibited $^{31}P$ NMR resonances at $\delta$ = 79.7 [$^2J$(P,P) = 18, $^1J$(Pt,P) = 5211 Hz] and $\delta$ = 102.4 [$^2J$(P,P) = 18, $^1J$(Pt,P) = 2007 Hz], as well as at $\delta$ = 79.5 [$^2J$(P,P) = 16, $^1J$(Pt,P) = 4973 Hz] and $\delta$ = 138.0 [$^2J$(P,P) = 16, $^1J$(Pt,P) = 1711 Hz] (downfield from an external $H_3PO_4$ standard), indicating the presence in solution of [*rac,trans*-$C_5H_8\{P(NC_5H_{10})_2\}_2Pt(Cl)CH_2C(CH_3)_3$] and [*rac,trans*-$C_5H_8\{P(Cl)NC_5H_{10}\}\{P(NC_5H_{10})_2\}Pt(Cl)CH_2\text{-}C(CH_3)_3$], (I), in nearly equal proportions. The two compounds were separated by crystallization from acetone, which gave (I) as single crystals containing one solvent molecule of crystallization.

*Crystal data*

$[PtCl(C_5H_{11})(C_{20}H_{38}Cl\text{-}N_3P_2)]\cdot C_3H_6O$
$M_r$ = 777.68
Monoclinic
$P2_1/n$
$a$ = 9.830 (3) Å
$b$ = 23.121 (2) Å
$c$ = 15.701 (1) Å
$\beta$ = 105.95 (1)°
$V$ = 3431 (1) Å$^3$
$Z$ = 4
$D_x$ = 1.505 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.7107 Å
Cell parameters from 25 reflections
$\theta$ = 9–14°
$\mu$ = 4.363 mm$^{-1}$
$T$ = 293 (2) K
Block
0.20 × 0.15 × 0.15 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer

3241 reflections with $I > 2\sigma(I)$

$\omega$ scans
Absorption correction:
empirical *via* $\psi$ scans
(North *et al.*, 1968)
$T_{\min} = 0.463$, $T_{\max} = 0.520$
7090 measured reflections
6024 independent reflections

$R_{\rm int} = 0.081$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = -1 \rightarrow 27$
$l = -1 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: <2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.100$
$S = 1.015$
5938 reflections
339 parameters
H-atom parameters
constrained

$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.811$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.744$ e Å$^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Pt—C1 | 2.106 (10) | P1—N1 | 1.632 (9) |
| Pt—P2 | 2.213 (3) | P1—C6 | 1.827 (10) |
| Pt—P1 | 2.289 (3) | P2—N3 | 1.648 (9) |
| Pt—Cl1 | 2.391 (3) | P2—N2 | 1.667 (9) |
| Cl2—P1 | 2.088 (4) | P2—C7 | 1.840 (10) |
| C1—Pt—P2 | 95.2 (3) | N1—P1—Pt | 118.6 (4) |
| C1—Pt—P1 | 178.6 (3) | C6—P1—Pt | 108.1 (3) |
| P2—Pt—P1 | 85.39 (11) | Cl2—P1—Pt | 113.7 (2) |
| C1—Pt—Cl1 | 87.7 (3) | N3—P2—N2 | 102.4 (5) |
| P2—Pt—Cl1 | 170.37 (11) | N3—P2—C7 | 109.8 (5) |
| P1—Pt—Cl1 | 91.51 (11) | N2—P2—C7 | 102.9 (5) |
| N1—P1—C6 | 105.5 (5) | N3—P2—Pt | 116.2 (3) |
| N1—P1—Cl2 | 107.2 (3) | N2—P2—Pt | 122.4 (4) |
| C6—P1—Cl2 | 102.2 (4) | C7—P2—Pt | 102.1 (4) |

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The resulting structural model was refined to convergence with allowance for anisotropic thermal motion of the non-H atoms. H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to 1.3 times the $U_{\rm eq}$ of their carrier atoms. According to some of the $U^{ij}$ values of the tertiary butyl C atoms, rotational disorder about the C1—C2 bond was suggested for this substituent, but was not accounted for during refinement. The highest peaks in the final difference map were located less than 1.0 Å from the Pt atom.

Data collection: *CAD*-4-*PC* (Enraf-Nonius, 1995). Cell refinement: *CAD*-4-*PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1171). Services for accessing these data are described at the back of the journal.

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# A monohelical cobalt(II) complex of a quinquepyridine ligand

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## Abstract

The monohelical mononuclear title complex, (6,6''''-dimethyl-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine-$\kappa^5N$)-bis(nitrato)cobalt(II), $[Co(NO_3)_2(C_{27}H_{21}N_5)]$, was obtained by the reaction of the quinquepyridine ligand (dmqpy) with hydrated cobalt nitrate, $Co(NO_3)_2(H_2O)_4$. In the complex, the coordination geometry of the Co$^{II}$ atom is a distorted pentagonal bipyramid, with the dmqpy ligand twisted about the equatorial plane and the two $NO_3^-$ ions occupying the apical positions.