Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

trans,trans-Bis[μ-1,5-bis(diisopropylphosphino)-pentane-$\kappa^2P:P'$]bis[dichloronickel(II)]

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Received 30 November 2006
Accepted 6 December 2006

In the title crystal structure, $[Ni_2Cl_4\{CH_2(CH_2CH_2PPr^i_2)_2\}_2]$, there are two independent molecules, one of which lies on a crystallographic inversion center. The Ni^{II} atoms in each dinuclear molecule are in slightly distorted square-planar geometries. The two independent molecules have markedly different conformations due to the relative orientations of the Cl/Ni/Cl groups with respect to the plane defined by the four P and the two Ni^{II} atoms.

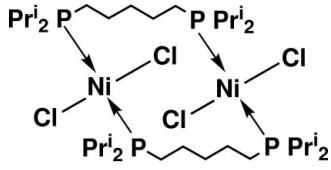
Key indicators

Single-crystal X-ray study
T = 220 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 21.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structures of many diphosphine-bridged dimeric complexes have been reported in the literature, but only a few nickel complexes of this type have been examined so far (Fontaine *et al.*, 1987; Manojlovic-Muir *et al.*, 1995; Vicic *et al.*, 2004; Xia *et al.*, 2002). During the course of our studies on the reactivity of diphosphine ligands with nickel(II), we isolated the title complex, (I), while attempting to prepare a PCsp^3P pincer complex.



(I)

The asymmetric unit of (I) contains one and a half molecules, the symmetry-complete molecule being generated by an inversion center. The two independent molecules are shown in Figs. 1 and 2 and selected bond lengths and angles are given in Table 1. The two molecules differ in the relative orientation of the Cl/Ni/Cl group with respect to the plane defined by the four P and the two Ni^{II} atoms. In the centrosymmetric molecule, these groups are both approximately perpendicular to the Ni_2P_4 plane, with a dihedral angle of 88.88 (2)° , whereas in the other molecule, the Cl3/Ni2/Cl4 group is approximately perpendicular to this plane [85.11 (2)°] but the Cl1/Ni1/Cl2 group makes an angle of 45.42 (2)° to the Ni_2P_4 plane. For each Ni^{II} atom, the coordination geometry is slightly distorted square-planar and the P atoms are in a *trans* arrangement. A search of the Cambridge Structural Database (Version 5.27 with updates up to August 2006; Allen, 2002) revealed 25 entries with a *trans* NiP_2Cl_2 molecular fragment. The mean values for the Ni—P and Ni—Cl bond lengths are 2.238 (3) and 2.173 (8) Å, respectively. The values for the same types of bonds in (I) are not significantly different from these mean values.

Experimental

$Pr^i_2P(CH_2)_5PPr^i_2$ (200 mg, 0.66 mmol) was added to a suspension of anhydrous $NiCl_2$ (86 mg, 0.66 mmol) in toluene (10 ml) and the mixture was heated to 353 K for 12 h. The title complex was obtained as a purple solid (237 mg, 83%) after evaporation of the solvent. Single crystals suitable for X-ray analysis were grown by the diffusion of hexanes into a saturated solution of the dimer in C_6D_6. Analysis calculated for $C_{34}H_{76}Cl_4Ni_2P_4$: C 47.04, H 8.82%; found: C 47.50, H 8.58%.

Crystal data

$[Ni_2Cl_4(C_{17}H_{38}P_2)_2]$	$Z = 6$
$M_r = 868.05$	$D_x = 1.257$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 21.1322$ (9) Å	$\mu = 4.63$ mm^{-1}
$b = 28.9229$ (10) Å	$T = 220$ (2) K
$c = 11.4019$ (4) Å	Block, purple
$\beta = 99.212$ (3)°	0.48 × 0.27 × 0.23 mm
$V = 6879.0$ (4) Å^3	

Data collection

Bruker SMART 2000 diffractometer	55920 measured reflections
	13507 independent reflections
ω scans	9282 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$R_{int} = 0.038$
	$\theta_{max} = 72.9°$
$T_{min} = 0.238$, $T_{max} = 0.345$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.110$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
$S = 0.91$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
13507 reflections	Extinction correction: *SHELXL97*
620 parameters	Extinction coefficient: 0.000034 (10)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—Cl2	2.1613 (9)	Ni2—P3	2.2535 (9)
Ni1—Cl1	2.1627 (9)	Ni2—P2	2.2595 (9)
Ni1—P4	2.2440 (9)	Ni3—Cl6	2.1629 (9)
Ni1—P1	2.2508 (9)	Ni3—Cl5	2.1670 (9)
Ni2—Cl3	2.1524 (9)	Ni3—P6^i	2.2468 (9)
Ni2—Cl4	2.1782 (9)	Ni3—P5	2.2535 (9)
Cl2—Ni1—Cl1	167.87 (5)	Cl3—Ni2—P2	92.16 (3)
Cl2—Ni1—P4	89.60 (3)	Cl4—Ni2—P2	88.24 (3)
Cl1—Ni1—P4	90.97 (3)	P3—Ni2—P2	176.46 (4)
Cl2—Ni1—P1	90.82 (3)	Cl6—Ni3—Cl5	175.36 (4)
Cl1—Ni1—P1	90.31 (3)	Cl6—Ni3—P6^i	87.26 (3)
P4—Ni1—P1	171.91 (4)	Cl5—Ni3—P6^i	92.48 (3)
Cl3—Ni2—Cl4	170.36 (4)	Cl6—Ni3—P5	93.09 (4)
Cl3—Ni2—P3	91.39 (3)	Cl5—Ni3—P5	87.13 (4)
Cl4—Ni2—P3	88.26 (3)	P6^i—Ni3—P5	179.37 (4)

Symmetry code: (i) $-x+1, -y+1, -z+2$.

H atoms were placed in calculated positions (C—H = 0.97–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (Maris, 2004).

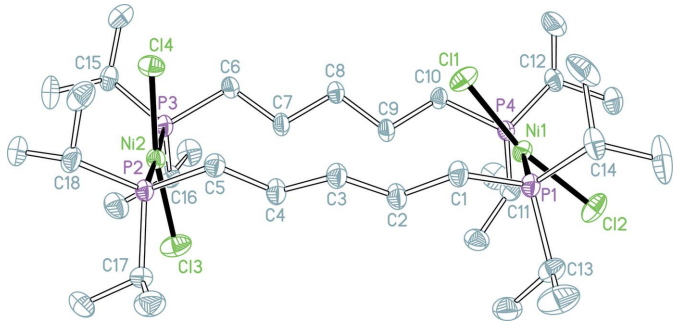


Figure 1
The structure of one of the independent molecules in (I), showing displacement ellipsoids at the 30% probability level.

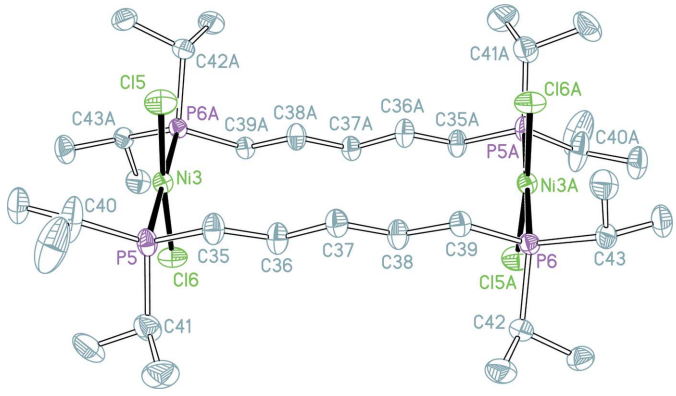


Figure 2
The structure of the centrosymmetric molecule in (I) showing displacement ellipsoids at the 30% probability level. Atoms labeled with the suffix A are related by the symmetry operator $(1-x, 1-y, 2-z)$

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada, the Fonds Québécois de la Recherche sur la Nature et les Technologies and the Université de Montréal for financial support.

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