

Dichlorobis(triphenylphosphine oxide- κ O)nickel(II)Rodolfo Moreno-Fuquen,^{a*} Olga Cifuentes,^a Jaime Valderrama Naranjo,^b Luis Manuel Serratto^a and Alan R. Kennedy^c^aDepartamento de Química, Facultad de Ciencias, Universidad del Valle, Apartado 25360, Santiago de Cali, Colombia,^bDepartamento de Física, Facultad de Ciencias, Universidad del Valle, Apartado 25360, Santiago de Cali, Colombia, and ^cDepartment of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

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Key indicators

Single-crystal X-ray study

T = 123 K

Mean σ (C–C) = 0.003 Å

R factor = 0.026

wR factor = 0.063

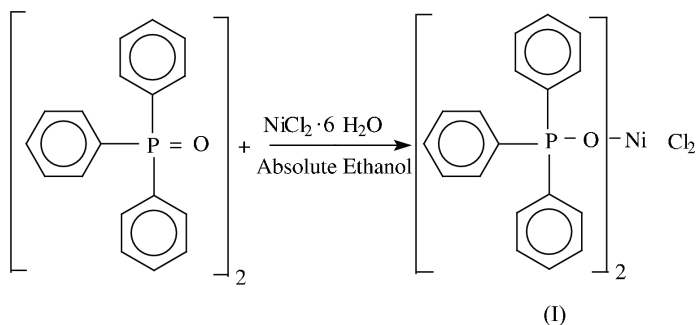
Data-to-parameter ratio = 18.9

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

The title nickel(II) complex, $[\text{NiCl}_2(\text{C}_{18}\text{H}_{15}\text{OP})_2]$, was prepared in order to determine the coordination of the Ni atom. The Ni atom lies on a twofold axis and is four-coordinated by two Cl atoms and two O atoms in a distorted tetrahedral coordination geometry. The Ni–Cl and Ni–O distances are 2.2151 (6) and 1.9662 (16) Å, respectively. The title compound is compared with the four-coordinated copper(II) analog; the two systems are isostructural.

Comment

In the period 1950–1960, there was a suggestion, based on the valence-bond theory, that paramagnetic nickel(II) complexes should be planar (Ballhausen & Liehr, 1959). This suggestion was difficult to verify due to the rather rare occurrence of tetrahedrally coordinated nickel(II) ions. Later, during the 1960s, some $[(\text{C}_6\text{H}_5)_3\text{PO}]_2\text{NiX}_2$ complexes ($X = \text{Cl}, \text{Br}, \text{I}$) were prepared (Cotton & Goodgame, 1960). Their electronic spectra, IR spectra and magnetic moments were recorded and analyzed in order to demonstrate that the nickel ion, in each case, was tetrahedrally coordinated (Cotton & Goodgame, 1960). Unfortunately, the purity of the $[(\text{C}_6\text{H}_5)_3\text{PO}]_2\text{NiCl}_2$ complex system was questioned and doubt of a tetrahedral array persisted. In order to elucidate the coordination of the nickel(II) ion in the $[(\text{C}_6\text{H}_5)_3\text{PO}]_2\text{NiCl}_2$ system, its crystal structure determination was undertaken.



A perspective view of the title molecule, (I), showing the atomic numbering scheme is given in Fig. 1. The Ni^{II} ion has C_2 site symmetry; C_2 is parallel to the c axis. The analogous dichlorobis(triphenylphosphine oxide)copper(II) system, (II) (Bertrand & Kalyanaraman, 1971), was taken as a reference and its internal parameters were compared to the parameters of the title complex. Within the tetrahedral geometry around the central Ni atom, complex (II) shows Cu–Cl and Cu–O bond lengths of 2.170 (2) and 1.958 (4) Å, respectively, while (I) shows Ni–Cl and Ni–O bond lengths of 2.2151 (6) and 1.9662 (16) Å, respectively. The Cl–Cu–Cl and O–Cu–O

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bond angles in (II) are 102.2 (1) and 93.0 (1)°, while in (I) the Cl—Ni—Cl and O—Ni—O bond angles are 116.17 (3) and 95.91 (10)°, respectively. The two systems are isostructural. The triphenylphosphine portion of the complex does not show any unusual features and the other bond lengths and angles of these systems are within expected ranges.

Experimental

Reagents and solvents for the synthesis were purchased from the Aldrich Chemical Co. and were used without additional purification. Crystals of (I) were obtained following the synthesis previously reported by Cotton & Goodgame (1960). The product of this synthesis was recrystallized by slow evaporation of an acetonitrile solution at room temperature, in contact with oxygen. The pale-blue crystals had a melting point of 463 (1) K.

Crystal data

[NiCl ₂ (C ₁₈ H ₁₅ OP) ₂]	Mo K α radiation
$M_r = 686.15$	Cell parameters from 3709 reflections
Orthorhombic, <i>Fdd2</i>	$\theta = 1.0\text{--}27.5^\circ$
$a = 20.6356$ (3) Å	$\mu = 0.89$ mm ⁻¹
$b = 32.5388$ (6) Å	$T = 123$ (2) K
$c = 9.7240$ (1) Å	Prism, pale blue
$V = 6529.25$ (17) Å ³	$0.35 \times 0.30 \times 0.15$ mm
$Z = 8$	
$D_x = 1.396$ Mg m ⁻³	

Data collection

Nonius KappaCCD diffractometer	3686 independent reflections
ω scans	3468 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>DENZO</i> ; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.802$, $T_{\text{max}} = 0.868$	$\theta_{\text{max}} = 27.5^\circ$
7169 measured reflections	$h = -26 \rightarrow 26$
	$k = -42 \rightarrow 42$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\text{max}} = 0.45$ e Å ⁻³
$wR(F^2) = 0.063$	$\Delta\rho_{\text{min}} = -0.29$ e Å ⁻³
$S = 1.07$	Extinction correction: <i>SHELXL97</i>
3686 reflections	Extinction coefficient: 0.00057 (6)
195 parameters	Absolute structure: Flack (1983), 1705 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.001 (1)
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 7.7683P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

All H atoms were placed at geometrically idealized positions and were treated as riding atoms, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

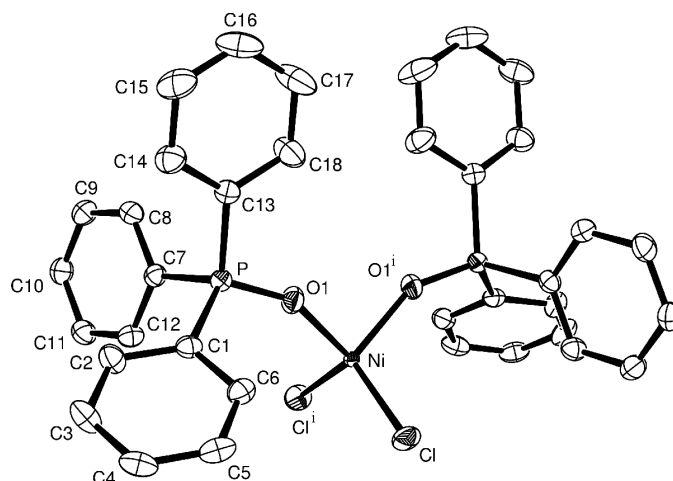


Figure 1

An ORTEP-3 plot (Farrugia, 1997) of the title compound, with the atomic labeling scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.]

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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