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cis-Di(nitrato-*O*,*O'*)bis(tricyclohexylphosphine oxide-*O*)nickel(II)

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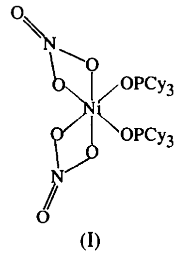
Abstract

The formal pseudo-octahedral coordination around the Ni^{II} atom in the title complex, [Ni(NO_3)$_2$($OPCy_3$)$_2$], places the $OPCy_3$ ligands ($C_{18}H_{33}OP$; Cy is cyclohexyl, C_6H_{11}) in an unusual mutually *cis* conformation. This may be rationalized by viewing each bidentate NO_3 group as occupying only one site of a tetrahedral coordination shell.

Comment

The ability of stereochemically demanding ligands to stabilize unusual coordination geometries and electronic states has been well documented (Brown & Lee, 1993; Murray, Hope, Hvoslef & Power, 1984). *cis*-[Ni(η^2-NO_3)$_2$($OPCy_3$)$_2$], (I), was obtained during our studies of a series of tricyclohexylphosphine complexes, prepared to help elucidate the nature of this stabilization process.



(I)

The coordination geometry about nickel would be conventionally described as octahedral, with six O atoms bound to the metal. Distortion of the octahedron is caused by the intrinsically small bite angles of the bidentate nitrate groups [61.2 (1) and 61.6 (1)° for O(3)—Ni(1)—O(4) and O(6)—Ni(1)—O(7), respectively]. It has been noted, however, by Cotton & Bergman (1964), that such bidentate ligands may be viewed as occupying one coordination site of a metal. Thus, compound (I) could be described alternatively as having a distorted tetrahedral structure about the Ni(1) atom. This alternative description is supported by the N(1)···Ni(1)···N(2) angle of 108.6 (1)° and by consideration of the relative stereochemistry of the $OPCy_3$ ligands [O(1)—Ni(1)—O(2) 95.3 (1) and P(1)···Ni(1)···P(2) 115.92 (3)°]. In an octahedral arrangement, these ligands must be viewed as being mutually *cis*. Such a relationship between bulky groups is unexpected. For example, PCy_3 ligands are normally situated *trans* with respect to one another, the *cis* geometry being a rarity (Watson, Woodward, Conole, Kessler & Sykara, 1994; Clark & Hampden-Smith, 1987). Although sterically less demanding than PCy_3, as defined by the classic cone angle (Tolman, 1977), $OPCy_3$ is nevertheless a large ligand and it is unusual for such ligands to preferentially adopt a *cis* arrangement. A similar conformation is found in the related complex [Ni(η^2-NO_3)$_2$($OAsPh_3$)$_2$] (Marques & Tomita, 1990) and comparable geometric parameters are in good agreement between the complexes.

The NO_3 ligands are symmetrically bidentate, as classified by Kleywegt *et al.* (1985). The P—O distances of 1.505 (3) and 1.502 (3) Å are slightly shorter than

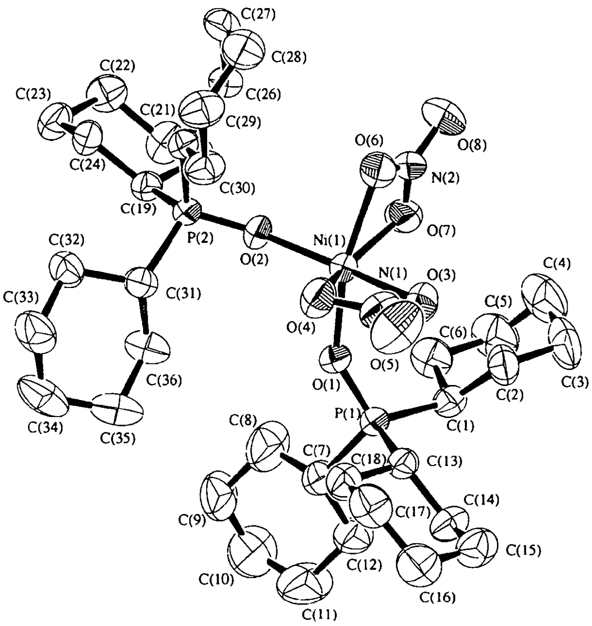


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I) with 50% probability ellipsoids. H atoms have been omitted for clarity.

that of 1.52 (1) Å found in *cis*-[$Rh(CO)_2Cl(OPCy_3)$], the only other known crystal structure containing coordinated $OPCy_3$ (Bandoli *et al.*, 1974), and slightly longer than those found in free $OPCy_3$ [P—O range 1.487 (2)–1.490 (2) Å; Davies, Dutremez & Pinkerton, 1991]. Neither the P—C bond lengths [1.813 (4)–1.831 (4) Å] nor the O—P—C bond angles deviate significantly from those in $OPCy_3$, indicating the absence of severe steric strain.

Experimental

Compound (I) was obtained in good yield by refluxing $Ni(NO_3)_2.6H_2O$ and PCy_3 (1:2 molar ratio) in ethanol. Orange prisms were obtained on recrystallizing the crude product from hot toluene.

Crystal data

[$Ni(NO_3)_2(C_{18}H_{33}OP)_2$]
M_r = 775.57
Monoclinic
$P2_1/c$
a = 9.573 (4) Å
b = 20.857 (6) Å
c = 20.467 (7) Å
β = 95.86 (3)°
V = 4065 (2) Å^3
Z = 4
D_x = 1.267 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.2–16.1°
μ = 0.605 mm^{-1}
T = 295 K
Prism
0.5 × 0.2 × 0.2 mm
Orange

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.802, T_{max} = 0.886
8719 measured reflections
8218 independent reflections

4260 reflections with $I > 2\sigma(I)$
R_{int} = 0.0468
θ_{max} = 26.01°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 25$
$l = -25 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: <1.5%

Refinement

Refinement on F
R = 0.0416
wR = 0.0463
S = 1.452
4260 reflections
442 parameters
H atoms not refined; C—H 0.96 Å and U(H) = $1.2U_{eq}$(C)

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = <0.001
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Ni(1)—O(1)	1.998 (2)	P(2)—O(2)	1.502 (3)
Ni(1)—O(2)	1.970 (3)	O(3)—N(1)	1.262 (4)
Ni(1)—O(3)	2.132 (3)	O(4)—N(1)	1.280 (4)
Ni(1)—O(4)	2.091 (3)	O(5)—N(1)	1.209 (4)
Ni(1)—O(6)	2.134 (3)	O(6)—N(2)	1.268 (5)
Ni(1)—O(7)	2.065 (3)	O(7)—N(2)	1.276 (4)
P(1)—O(1)	1.505 (3)	O(8)—N(2)	1.208 (4)
O(1)—Ni(1)—O(2)	95.3 (1)	O(6)—Ni(1)—O(7)	61.6 (1)
O(1)—Ni(1)—O(3)	93.5 (1)	Ni(1)—O(1)—P(1)	142.5 (2)
O(1)—Ni(1)—O(4)	99.7 (1)	Ni(1)—O(2)—P(2)	148.6 (2)
O(1)—Ni(1)—O(6)	161.4 (1)	Ni(1)—O(3)—N(1)	91.0 (2)
O(1)—Ni(1)—O(7)	100.5 (1)	Ni(1)—O(4)—N(1)	92.3 (2)
O(2)—Ni(1)—O(3)	161.6 (1)	Ni(1)—O(6)—N(2)	90.0 (2)
O(2)—Ni(1)—O(4)	101.3 (1)	Ni(1)—O(7)—N(2)	93.0 (2)
O(2)—Ni(1)—O(6)	92.0 (1)	O(3)—N(1)—O(4)	115.4 (4)
O(2)—Ni(1)—O(7)	96.6 (1)	O(3)—N(1)—O(5)	122.2 (4)
O(3)—Ni(1)—O(4)	61.2 (1)	O(4)—N(1)—O(5)	122.4 (4)
O(3)—Ni(1)—O(6)	84.7 (1)	O(6)—N(2)—O(7)	115.4 (3)
O(3)—Ni(1)—O(7)	97.7 (1)	O(6)—N(2)—O(8)	123.1 (4)
O(4)—Ni(1)—O(6)	95.6 (1)	O(7)—N(2)—O(8)	121.5 (5)
O(4)—Ni(1)—O(7)	151.5 (1)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992), from the Patterson function. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*, including anisotropic displacement parameters of all non-H atoms.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1297). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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