Tetraethylammonium trichloro(triphenylphosphine)nickelate(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.177
Data-to-parameter ratio = 13.1

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

The ions of the title compound, $(C_8H_{20}N)[NiCl_3(C_{18}H_{15}P)]$, both lie on the threefold rotation axes along the body diagonal vectors of a cubic unit cell in the space group $Pb\bar{3}$ (equivalent to $Pa\bar{3}$, No. 205, with h and k indices interchanged). The Ni atom within the anion is tetrahedrally coordinated to three symmetry-related Cl atoms and the P atom. The cation is disordered.

Comment

The title compound, (I), was isolated as a secondary product in an alternative preparation of $[Ni\{Fe(\{SCH_2CH_2\}_3N)(CO)\}_2]$ (Smith *et al.*, 2001) from $[NEt_4][Fe(\{SCH_2CH_2\}_3N)(CO)]$ and $[NiCl_2(PPh_3)_2]$ under a carbon monoxide atmosphere. Related compounds containing the same anion have been previously prepared (Yamamoto, 1954; Smith, 1982; Brenndörfer *et al.*, 1985) and the crystal structure of $[PH(C_6H_{11})_3][NiCl_3(PPh_3)]$ has been reported (Brenndörfer *et al.*, 1985).

(I)
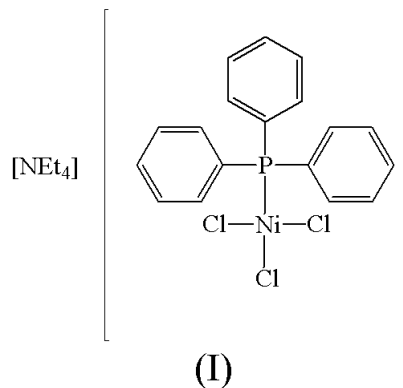
The X-ray analysis of (I) shows that both ions lie on the threefold rotation axis along the body-diagonal vectors of the unit cell. The anion (Fig. 1) lies with the Ni—P bond coincidental with the axis; the cation N atom lies on the rotation axis and the cation is disordered with each carbon having one-third occupancy (*i.e.* there are three discrete orientations possible for each cation). The Ni atom is tetrahedrally coordinated by the three symmetry-related Cl atoms and the P atom, with Cl—Ni—Cl and Cl—Ni—P angles of 114.61 (6) and 103.65 (8)°, respectively, and Ni—P and Ni—Cl bond lengths of 2.322 (4) and 2.233 (2) Å, respectively. Torsion angles Cl1—Ni—P1—C11 about the Ni—P1 axis are −69.7 (3), 50.3 (3) and 170.3 (3)° for the three symmetry-related C atoms, showing a staggered conformation about the Ni—P bond. The cation shows an apparently distorted tetrahedral arrangement about the N atom, with poorly determined C—N—C angles ranging from 90 (3) to 124 (2)° and N—C bond lengths
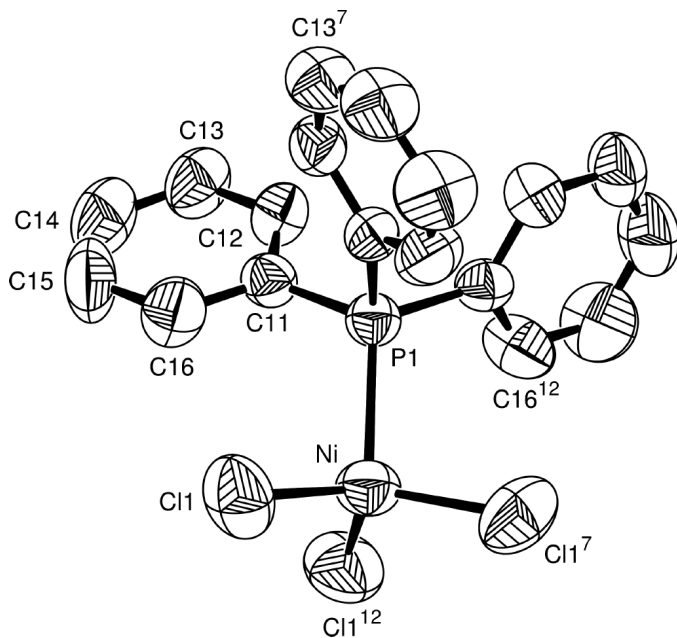
Figure 1
The structure of the title anion, with 50% probability displacement ellipsoids.

ranging from 1.44 (4) to 1.61 (3) Å. Normal van der Waals contacts bind the ions in a three-dimensional network. The structure of the related monoclinic crystals of $[PH(C_6H_{11})_3]$-$[NiCl_3(PPh_3)]$ (Brenndörfer *et al.*, 1985) has the space group $P2_1/n$, but shows the anion to be essentially identical to that of compound (I).

Experimental

To a solution of $[NEt_4][Fe(\{SCH_2CH_2\}_3N)(CO)]$ (0.59 g, 1.44 mmol) in MeCN (25 ml) was added a solution of $[NiCl_2(PPh_3)_2]$ (1.17 g, 1.79 mmol) in MeCN (100 ml). The dark-red solution that immediately formed was stirred for 90 min under an atmosphere of CO. Upon standing overnight, dark crystals of $[Ni\{Fe(\{SCH_2CH_2\}_3N)$-$(CO)\}_2]$ (0.25 g, 56%) formed. These were collected by filtration, washed repeatedly with diethyl ether and dried *in vacuo*. Over a period of 3 d, the retained filtrate, under a dinitrogen atmosphere, slowly changed to a dark-blue colour whilst giving a crystalline precipitate of PPh_3. The solution was evaporated to ~15 ml under vacuum and then filtered to remove PPh_3. Diethyl ether (5 ml) was added to the blue filtrate, leading to the formation of large royal blue crystals of $[NEt_4][NiCl_3(PPh_3)]$ and white crystals of $[NEt_4]Cl$. These were collected by filtration, washed with diethyl ether and dried *in vacuo*. A crystal of $[NEt_4][NiCl_3(PPh_3)]$ was selected for the X-ray study.

Crystal data

$C_8H_{20}N^+ \cdot C_{18}H_{15}Cl_3NiP^-$	Cell parameters from 25
$M_r = 557.58$	reflections
Cubic, $Pb\bar{3}$	$\theta = 10\text{–}11°$
$a = 17.6676\,(7)$ Å	$\mu = 1.07$ mm^{-1}
$V = 5514.8\,(4)$ Å^3	$T = 293\,(2)$ K
$Z = 8$	Octahedral, translucent intense blue
$D_x = 1.343$ Mg m^{-3}	$0.36 \times 0.29 \times 0.24$ mm
Mo–Kα radiation	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.022$
	$\theta_{max} = 24.0°$
ω scans	$h = -4 \rightarrow 13$
Absorption correction: ψ scan	$k = -4 \rightarrow 14$
(*EMPABS*; Sheldrick *et al.*, 1977)	$l = -1 \rightarrow 20$
$T_{min} = 0.728$, $T_{max} = 0.774$	3 standard reflections
1750 measured reflections	every 400 reflections
1445 independent reflections	frequency: 167 min
497 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	Only H-atom U's refined
$R[F^2 > 2\sigma(F^2)] = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2]$
$wR(F^2) = 0.177$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	$(\Delta/\sigma)_{max} = 0.002$
1445 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—Cl1	2.233 (2)	P1—C11	1.809 (7)
Ni—P1	2.322 (4)		
Cl1—Ni—Cl1^i	114.61 (6)	C11—P1—C11^i	104.7 (3)
Cl1—Ni—P1	103.65 (8)	C11—P1—Ni	113.9 (2)
Cl1—Ni—P1—C11	−69.7 (3)	Cl1—Ni—P1—C11^i	170.3 (3)
Cl1—Ni—P1—C11^{ii}	50.3 (3)		

Symmetry codes: (i) $\frac{3}{2} - y, \frac{1}{2} + z, 1 - x$; (ii) $1 - z, \frac{3}{2} - x, y - \frac{1}{2}$.

Data were collected and the structure determined in a space group setting involving exchange of h and k indices, and of x and y coordinates relative to the standard setting of $Pa\bar{3}$; we have denoted this as $Pb\bar{3}$. Data above $\theta = 24°$ were weak, as a consequence of the disorder, and were not used. H atoms were subject to riding-model constraints; isotropic displacement parameters were freely refined for those of the anion.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *CAD*-4 (Hursthouse, 1976); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1971); software used to prepare material for publication: *SHELXL*93.

References

Brenndörfer, M., Brune, H. A., Debaerdemaeker, T. & Hemmer, R. (1985). *Z. Naturforsch. Teil B*, **40**, 357–362.
Enraf–Nonius (1992). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Hursthouse, M. B. (1976). *CAD*-4 *Processing program*. Queen Mary College, London.
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Sheldrick, G. M., Orpen, A. G., Reichert, B. E. & Raithby, P. R. (1977). 4th European Crystallographic Meeting, Oxford, Abstracts, p. 147.
Smith, M. C., Longhurst, S., Barclay, J. E., Cramer, S. P., Davies, S. C., Hughes, D. L., Gu, W. & Evans, D. J. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1387–1388.
Smith, W. E. (1982). *Spectrochim. Acta*, pp. 1063–1068.
Yamamoto, K. (1954). *Bull. Chem. Soc. Jpn*, **27**, 501–505.