C11	0.2981 (3)	0.2041 (2)	0.8102 (2)	0.056 (1)
C12	0.0060 (3)	0.2667 (2)	0.8044 (2)	0.059 (1)
C1	0.0171 (9)	0.1395 (8)	0.5228 (7)	0.042 (5)
C2	0.1346 (10)	0.1806 (8)	0.5079 (7)	0.047 (6)
C3	0.3567 (10)	0.2630 (8)	0.5915 (7)	0.046 (6)
C4	0.4024 (12)	0.3295 (9)	0.6589 (7)	0.052 (7)
C5	0.4930 (12)	0.3954 (10)	0.6429 (10)	0.054 (8)
C6	0.5324 (11)	0.3972 (10)	0.5680 (10)	0.074 (8)
C7	0.4855 (11)	0.3326 (10)	0.5056 (8)	0.061 (7)
C8	0.3966 (12)	0.2681 (9)	0.5187 (7)	0.055 (5)
C9	0.2873 (9)	0.0495 (8)	0.6173 (7)	0.045 (6)
C10	0.2465 (12)	−0.0124 (8)	0.6757 (8)	0.068 (7)
C11	0.2767 (13)	−0.1130 (10)	0.6793 (9)	0.074 (8)
C12	0.3508 (12)	−0.1514 (9)	0.6295 (9)	0.066 (8)
C13	0.3875 (15)	−0.0909 (11)	0.5708 (13)	0.102 (11)
C14	0.3533 (14)	0.0119 (10)	0.5658 (12)	0.102 (11)
C15	−0.0863 (9)	0.3299 (8)	0.5661 (7)	0.043 (5)
C16	−0.1414 (13)	0.3391 (8)	0.4836 (8)	0.057 (7)
C17	−0.1842 (14)	0.4323 (11)	0.4532 (9)	0.083 (9)
C18	−0.1792 (14)	0.5127 (10)	0.5040 (14)	0.093 (11)
C19	−0.1273 (14)	0.5065 (9)	0.5857 (10)	0.070 (8)
C20	−0.0781 (13)	0.4137 (8)	0.6154 (8)	0.069 (7)
C21	−0.1506 (9)	0.1410 (8)	0.6391 (8)	0.046 (6)
C22	−0.2615 (11)	0.1867 (9)	0.6427 (9)	0.061 (7)
C23	−0.3503 (12)	0.1332 (12)	0.6665 (11)	0.085 (9)
C24	−0.3341 (12)	0.0319 (12)	0.6893 (12)	0.094 (10)
C25	−0.2286 (15)	−0.0114 (10)	0.6848 (10)	0.088 (9)
C26	−0.1375 (11)	0.0431 (9)	0.6589 (9)	0.065 (7)

Table 2. *Selected geometric parameters (Å, °)*

Pd—C11	2.415 (3)	Pd—C12	2.394 (3)
Pd—P1	2.284 (3)	Pd—P2	2.264 (3)
P1—C1	1.85 (1)	P2—C2	1.87 (1)
C1—C2	1.56 (2)	P1—C15	1.81 (1)
P1—C21	1.85 (1)	P2—C3	1.89 (1)
P2—C9	1.84 (1)		
C12—Pd—C11	95.8 (1)	C15—P1—Pd	116.6 (3)
P1—Pd—C12	87.6 (1)	C15—P1—C1	107.5 (5)
P1—Pd—C11	172.4 (1)	C18—C19—C20	119 (1)
C2—P2—Pd	106.5 (4)	P1—C21—C22	123 (1)
C9—P2—Pd	113.0 (4)	C22—C21—C26	118 (1)
P2—Pd—C12	175.5 (1)	C22—C23—C24	119 (1)
P2—Pd—C11	88.5 (1)	C24—C25—C26	123 (1)
P2—Pd—P1	88.3 (1)	C9—P2—C3	107.0 (5)
C3—P2—Pd	120.2 (4)	C21—P1—Pd	114.9 (4)
C2—P2—C3	105.1 (5)	C21—P1—C1	106.4 (5)
C9—P2—C2	103.5 (5)	C15—P1—C21	106.5 (5)
C1—P1—Pd	104.3 (3)		

Data were corrected for Lorentz and polarization factors. The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1985). The structure was refined using *SHELX*76 (Sheldrick, 1976). H atoms were fixed geometrically. The perspective view of the title molecule was drawn using *ORTEP*II (Johnson, 1976) and geometrical analysis was performed using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Azidotetrakis(trimethylphosphine)nickel(II) Tetrafluoroborate

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Abstract

The title complex, $[Ni(N_3)(C_3H_9P)_4]BF_4$, is a nearly perfect trigonal bipyramid with the azide group at an apical position. The metal–azide bond angle, Ni1—N1—N2, of 138.6 (5)° is the largest observed for a terminal azide ligand.

Comment

Nickel(0) and nickel(I) reagents have significant utility in aryl-coupling reactions (Zembayashi, Tamao, Yoshida & Kumada, 1977; Semmelhack *et al.*, 1981; Rollin, Troupel, Tuck & Perichon, 1986; Amatore & Jutand, 1988; Zhou & Yamamoto, 1991). A potential source of such low-valency metal complexes are metal azides. This results from the ability of the azide to undergo photo-induced reductive elimination. As part of a study of nickel–azide–phosphine complexes, the azidotetrakis(trimethylphosphine)nickel(II) cation was synthesized as its BF_4^- salt, (1), and examined by X-ray crystallography. To our knowledge, this species is the only known five-coordinate nickel–azide complex.
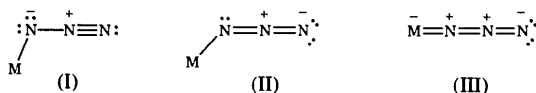

(1)
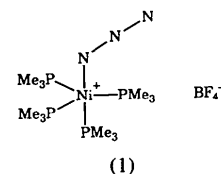
The title complex is a dark violet solid which is soluble in polar organic solvents, as well as in water. In solution the complex readily dissociates a phosphine ligand, as evidenced by changes in the electronic spectrum (391, 556 nm bands are replaced by one at 463 nm) and the IR spectrum (asymmetric azide stretch at $2062\ cm^{-1}$ is replaced by $2053\ cm^{-1}$). The solid may be stored in a sealed container below room temperature, but loses trimethylphosphine above 273 K over a period of several weeks.

Five-coordinate Ni complexes are not abundant, but most of those which are known exhibit approximate trigonal bipyramidal (tbp) geometry. Distortion from tbp geometry is very slight in the present case, as indicated by the N1—Ni1—P4 angle of 173.6 (2)°. The metal atom lies 0.183 (1) Å from the equatorial plane defined by P1, P2 and P3, displaced toward P4. The point group symmetry of the cation is reduced from C_s to C_1 since N2 and N3 of the azide ligand are neither eclipsed nor perfectly staggered with respect to the three equatorial P atoms. The P3—Ni1—N1—N2 dihedral angle is −34.6°. Comparison of the overall geometry of [Ni(N₃)(PMe₃)₄]BF₄ with those of the related complexes [NiBr(PMe₃)₄]BF₄ (Dartiguenave et al., 1978) and [NiBr{P(OMe)₃}₄]BF₄ (Milbrath, Springer, Clardy & Verkade, 1975) revealed that the bromide ligand in the previously reported nickel phosphine and phosphite structures assumes an equatorial position, while in the present case the azide ligand is axial. Bromide and azide ligands occupy similar positions in the spectrochemical series as a result of their similarity in electronegativity, nucleophilic constant and dipole moment (Patai &

Treinin, 1971). Theoretical calculations (Rossi & Hoffmann, 1975) suggest that π-donor ligands (such as Br and N₃) will prefer axial positions in d^8 tbp complexes. This is borne out only in the present case.

The azide group itself is nearly linear with N1—N2—N3 174.9 (8)°. The Ni1—N1 distance of 1.929 Å is somewhat short, but lies within the typical range of 1.93–2.12 Å (Dori & Ziolo, 1973). It should be noted that axial bond lengths in tbp nickel complexes are typically a little shortened. The N1—N2 and N2—N3 distances are also typical. However, the metal-azide bond angle, Ni1—N1—N2, of 138.6 (5)° is quite unusual. The generally accepted range is 117–128° (Dori & Ziolo, 1973), although at least one significant outlier to this range is known: [Cp₂Ti(N₃)₂] (de Gil, de Burguera, Rivera & Maxfield, 1977), where the Ti—N—N angle is 137°. In fact, the metal-azide bond angle in the present structure is, to our knowledge, the largest yet observed. This large metal-azide bond angle may be understood by examination of the contributing resonance structures (I)–(III):

$$\ddot{\underset{}{N}}-\overset{+}{N}\equiv N: \qquad \overset{\cdot\cdot}{N}=\overset{+}{N}=\overset{-}{N}\overset{\cdot\cdot}{\underset{}{}} \qquad \overset{-}{M}=\overset{+}{N}=\overset{+}{N}=\overset{-}{N}$$

(I) (II) (III)

Since most metal-azide bond angles are around 120°, it is reasonable that form (II) (having sp^2 hybridization at the bound N atom) is usually dominant. On the other hand, the large metal-azide bond angle found in the title compound corresponds to a resonance hybrid between (II) and (III). Resonance form (III) results from nitrogen-to-nickel π donation. The conclusion that the azide behaves as a strong π donor in [Ni(PMe₃)₄(N₃)]⁺ is reasonable given the acceptor character of the phosphine ligands. The Ni1—N1—N2 bond angle may also be influenced by crowding from the phosphine ligands. Each of the three P4—Ni1—PX (X = 1, 2, 3) angles is approximately 94–95°.

Experimental

Nickel tetrafluoroborate was prepared from nickel carbonate and HBF₄. Ni(BF₄)₂ and NaN₃ (1 mmol of each) were dissolved in about 10 ml of H₂O. To this lime-green solution, 4 ml of 1 M PMe₃ in tetrahydrofuran was added. Dark violet crystals precipitated and were collected after cooling the solution to 258 K. Suitable single crystals were grown over several weeks at room temperature from a concentrated CH₂Cl₂ solution layered with hexanes in a 3 mm i.d. tube.
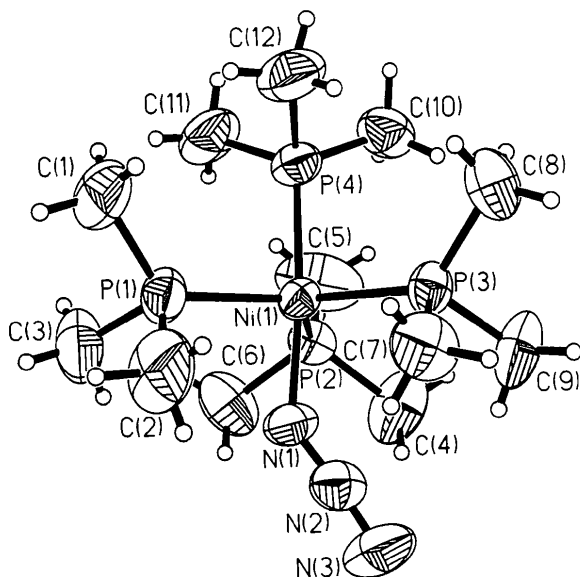

Fig. 1. View of the azidotetrakis(trimethylphosphine)nickel(II) cation. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown with arbitrary radii.

Crystal data

[Ni(N₃)(C₃H₉P)₄]BF₄

$M_r = 491.84$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Orthorhombic
Pbca
$a = 13.778\,(2)$ Å
$b = 13.2816\,(13)$ Å
$c = 26.188\,(3)$ Å
$V = 4792.1\,(9)$ Å^3
$Z = 8$
$D_x = 1.363$ Mg m^{-3}

Cell parameters from 39
reflections
$\theta = 2.15$–$25.0°$
$\mu = 1.109$ mm^{-1}
$T = 298\,(2)$ K
Prism
$0.54 \times 0.38 \times 0.20$ mm
Dark violet

Data collection

Siemens *P*4 diffractometer
Profile-fitted ω scans
Absorption correction:
empirical
$T_{min} = 0.524$, $T_{max} = 0.609$
5242 measured reflections
4220 independent reflections
2018 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0426$
$\theta_{max} = 25.00°$
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 15$
$l = -31 \rightarrow 1$
3 standard reflections
frequency: 97 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0577$
$wR(F^2) = 0.1337$
$S = 1.106$
4220 reflections
232 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.052$
$\Delta\rho_{max} = 0.657$ e Å^{-3}
$\Delta\rho_{min} = -0.633$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
from *International Tables*
for Crystallography (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

U_{iso} for disordered BF$_4$; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for remainder.

	x	y	z	U_{iso}/U_{eq}
Ni1	0.0554 (1)	0.1954 (1)	0.1057 (1)	0.045 (1)
P1	−0.0521 (1)	0.0847 (2)	0.1435 (1)	0.064 (1)
P2	0.0447 (1)	0.2476 (1)	0.0221 (1)	0.054 (1)
P3	0.2006 (1)	0.2210 (1)	0.1483 (1)	0.053 (1)
P4	−0.0137 (1)	0.3283 (1)	0.1353 (1)	0.061 (1)
N1	0.1045 (4)	0.0742 (4)	0.0744 (2)	0.064 (2)
N2	0.1775 (5)	0.0430 (5)	0.0588 (2)	0.066 (2)
N3	0.2459 (5)	0.0070 (6)	0.0414 (3)	0.135 (3)
C1	−0.1307 (6)	0.1079 (7)	0.1977 (3)	0.104 (3)
C2	0.0090 (6)	−0.0275 (6)	0.1652 (4)	0.117 (3)
C3	−0.1370 (5)	0.0334 (7)	0.0972 (3)	0.105 (3)
C4	0.1597 (5)	0.2487 (7)	−0.0110 (2)	0.104 (3)
C5	−0.0031 (7)	0.3651 (6)	−0.0028 (3)	0.127 (4)
C6	−0.0250 (6)	0.1607 (6)	−0.0140 (3)	0.094 (3)
C7	0.2418 (5)	0.1089 (5)	0.1797 (3)	0.087 (2)
C8	0.2271 (6)	0.3115 (5)	0.1980 (3)	0.085 (2)
C9	0.2988 (5)	0.2474 (7)	0.1035 (3)	0.094 (3)
C10	0.0457 (5)	0.4435 (5)	0.1184 (3)	0.078 (2)
C11	−0.1383 (5)	0.3483 (7)	0.1138 (3)	0.097 (3)
C12	−0.0239 (6)	0.3390 (7)	0.2042 (3)	0.098 (3)
B1*A*	0.5877 (13)	0.1762 (14)	0.1749 (7)	0.091 (3)
F1*A*	0.6431 (9)	0.2511 (9)	0.1930 (5)	0.125 (5)
F2*A*	0.6170 (9)	0.0885 (9)	0.1978 (5)	0.143 (4)
F3*A*	0.5931 (11)	0.1587 (11)	0.1241 (4)	0.164 (5)
F4*A*	0.4943 (7)	0.1954 (8)	0.1857 (4)	0.122 (4)
B1*B*	0.5961 (14)	0.1787 (14)	0.1687 (7)	0.091 (3)
F1*B*	0.6541 (8)	0.2595 (8)	0.1723 (4)	0.104 (4)
F2*B*	0.6433 (8)	0.1076 (9)	0.1402 (5)	0.134 (4)
F3*B*	0.5189 (9)	0.2053 (9)	0.1390 (5)	0.141 (4)
F4*B*	0.5706 (10)	0.1377 (11)	0.2148 (4)	0.161 (5)

Table 2. *Selected geometric parameters* (Å, °)

Ni1—N1	1.929 (6)	P2—C5	1.815 (7)
Ni1—P4	2.152 (2)	P3—C7	1.793 (7)
Ni1—P2	2.301 (2)	P3—C8	1.809 (7)
Ni1—P1	2.309 (2)	P3—C9	1.825 (6)
Ni1—P3	2.316 (2)	P4—C10	1.791 (7)
P1—C2	1.804 (8)	P4—C12	1.815 (7)
P1—C1	1.812 (7)	P4—C11	1.826 (7)
P1—C3	1.817 (7)	N1—N2	1.162 (7)
P2—C6	1.773 (7)	N2—N3	1.150 (8)
P2—C4	1.806 (7)		
N1—Ni1—P4	173.6 (2)	N1—Ni1—P3	91.4 (2)
N1—Ni1—P2	82.6 (2)	P4—Ni1—P3	95.03 (7)
P4—Ni1—P2	93.89 (7)	P2—Ni1—P3	118.02 (7)
N1—Ni1—P1	82.9 (2)	P1—Ni1—P3	116.15 (7)
P4—Ni1—P1	94.80 (8)	N2—N1—Ni1	138.6 (5)
P2—Ni1—P1	123.95 (7)	N3—N2—N1	174.9 (8)

The structure was determined by Patterson methods and refined initially by use of programs in the *SHELXTL/PC* (Sheldrick, 1990) package, which was also used for the figure. The quality of the solution was compromised somewhat by disorder in the BF$_4^-$ ion. This disorder was modeled as two half-occupancy ions with individual isotropic displacement parameters, except for the parameters for the two B half-atoms which were constrained to be equal. All B—F distances were restrained to be similar with a standard deviation of 0.03 Å, as were all F$\cdots$F distances within each ion. Only nine of the H atoms appeared in a difference map. Each H atom was introduced in an ideal position, riding on the atom to which it is bonded and refined with an isotropic temperature factor 20% greater than that of the parent atom. All other atoms were refined with anisotropic displacement parameters. The 12 methyl groups were allowed to rotate about their P—C bonds. Final refinement on F^2 was carried out using *SHELXL93* (Sheldrick, 1993).

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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two S atoms in the equatorial plane. Two axial isoquinoline ligands are coordinated to the metal atom through their N atoms. The Ni—S and Ni—N bond distances are 2.507 (2)–2.518 (1) Å and 2.118 (3) Å, respectively.

Comment

The structures of the triphenylphosphine and pyridine adducts of (diethyl dithiophosphato)nickel(II) have been reported (Liu, Lin, Yu, Zhu, Xu, Gou & You, 1991; Ooi & Fernando, 1967). In [Ni{(C₂H₅O)₂PS₂}₂{P(C₆H₅)₃}], the Ni atom displays square-pyramidal coordination (Liu *et al.*, 1991), whereas octahedral metal coordination was found in [Ni{(C₂H₅O)₂PS₂}₂(C₅H₅N)₂] (Ooi & Fernando, 1967). Crystals of the title compound, (I), are composed of discrete molecules (Fig. 1) and each Ni atom lies on a crystallographic centre of symmetry. Two dtp ligands are bonded to nickel by their two S atoms, forming four-membered chelate rings in the equatorial plane; the octahedral coordination is completed by the N atoms of two isoquinoline ligands.

trans-Bis(*O,O'*-diethyl dithiophosphato-κ²*S*, *S'*)bis(isoquinoline-κ*N*)nickel(II)

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Abstract

In (*OC*-6-12)-bis(*O,O'*-diethyl dithiophosphato-κ²*S*, *S'*)-bis(isoquinoline-κ*N*)nickel(II), [Ni(C₄H₁₀O₂PS₂)₂(C₉H₇N)₂], a distorted N₂S₄ octahedron is formed around the central Ni atom. Two *O,O'*-diethyl dithiophosphate (dtp) ions act as bidentate ligands, each forming a four-membered chelate ring by coordination of its

(I)

The Ni—S distances [2.507 (2) and 2.518 (1) Å] are slightly longer than those in [Ni{(C₂H₅O)₂PS₂}₂{P(C₆H₅)₃}] and [Ni(dtp)₂] [2.43 (3) and 2.21 Å, re-
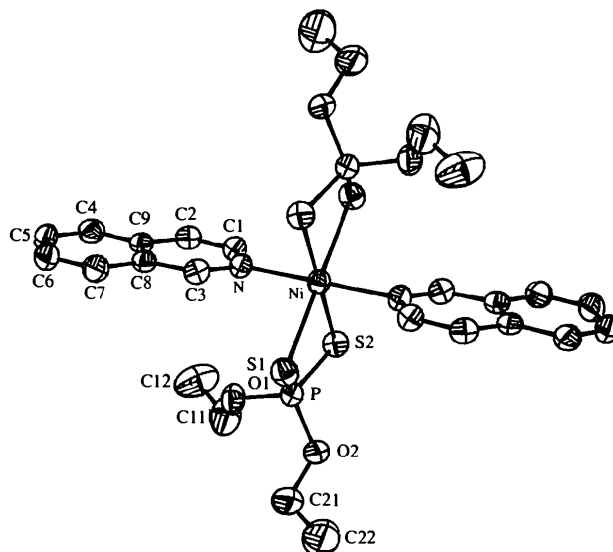

Fig. 1. Molecular structure (*ORTEP*II; Johnson, 1976) of the title complex showing 40% probability displacement ellipsoids. H atoms are omitted for clarity.