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Crystal and Molecular Structure of Bromotetrakis(trimethyl phosphito)nickel(II) Tetrafluoroborate, $\{Ni[P(OCH_3)_3]_4Br\}BF_4$

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The crystal and molecular structure of the five-coordinate nickel complex $\{NiBr[P(OCH_3)_3]_4\}BF_4$ has been determined from three-dimensional single-crystal X-ray data. The compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.333$ (4), $b = 18.195$ (5), $c = 11.731$ (2) Å, and $\beta = 93.61$ (2)°. The structure was determined by Patterson and conventional least-squares methods using 2894 independent nonzero reflections to give a final R factor of 0.060. The coordination geometry around Ni is essentially trigonal bipyramidal with Br in an equatorial position. Axial Ni–P distances are 2.181 (2) and 2.180 (2) Å while the equatorial Ni–P bonds are 2.187 (2) and 2.239 (2) Å and the Ni–Br distance is 2.456 (2) Å. The equatorial plane angles are Br–Ni–P = 123.44 (7) and 112.24 (7)°, and the P–Ni–P angle is 124.31 (9)°. The axial phosphorus ligands are bent toward the bromine with an average angle of 86.12°. Qualitative bonding considerations are used in comparing the present structure to others in the low-spin $NiL_5{}^{2+}$, NiL_4X^+, and NiL_3X_2 series.

Introduction

Few structural determinations of five-coordinate low-spin monodentate nickel(II) complexes in the series $NiL_5{}^{2+}$, NiL_4X, NiL_3X_2 (X = halogen or pseudohalogen) appear in the literature. The only $NiL_5{}^{2+}$ example for which structural data have been obtained is that in which L is the adamantane-like caged phosphite $P(OCH)_3(CH_2)_3$.[2] The relatively undistorted trigonal-bipyramidal geometry of this complex appears to persist in solution since the ^{31}P NMR spectrum for the close analog $Ni[P(OCH_2)_3CCH_3]_5{}^{2+}$ shows an A_3B_2 pattern at low temperature.[3] Earlier spectral assignments of trans cyano configurations in $Ni[P(OR)_3]_3(CN)_2$[4] and $Ni[P(OR)_2C_6H_5]_3(CN)_2$[5] were later supported by X-ray diffraction studies of $Ni[P(OC_2H_5)_2C_6H_5]_3(CN)_2$[6] and $Ni[P(CH_3)_2C_6H_5]_3(CN)_2$[7] although the geometries in both cases were somewhat distorted from trigonal bipyramidal. The conclusion drawn from one electronic study[8] that the halogens in $Ni[P(CH_3)_3]_3Br_2$ were trans was at variance with the suggestion based on a similar investigation in another laboratory[9] that they were cis. The question was resolved recently, however, by an X-ray diffraction study in which it was shown that the bromines lie in the equatorial plane of a trigonal bipyramid.[10] The same technique yielded similar geometries for $Ni[PH(C_6H_5)_2]_3I_2$[11] and $Ni[P(OCH_3)_3]_3I_2$[12] although both trigonal-bipyramidal and tetragonal-pyramidal coordination was observed in $NiL_3(CN)_2$ (L = 5-methyl-5*H*-dibenzophosphole), depending on the recrystallizing solvent.[13]

Aside from the distorted tetragonal-pyramidal structures found for some high-spin divalent iron, cobalt, and nickel complexes of the type $[ML_4X]^+$, where L = $OP(C_6H_5)_3$, $OAs(C_6H_5)_3$, $OP(C_6H_5)_2CH_3$, and $OAs(C_6H_5)_2CH_3$ and X = ClO_4,[14,15] no structures have been reported for low-spin members of this class. The low-spin cation in $Ni[PH(CH_2CH_3)_2]_4X[B(C_6H_5)_4]$ (X = Cl, Br, I, NCS)[16] and the isoelectronic complexes $\{Co[PF_2(C_6H_5)]_4X\}$, X = Cl, Br,[17] have been tentatively assigned tetragonal-pyramidal structures on the basis of electronic, infrared, and, additionally in the latter compound, ^{31}P and ^{19}F NMR spectral studies. The present ambiguity of such techniques for purposes of structural assignment in these systems coupled with the subtle forces which determine their stereochemistries prompted us to carry out an X-ray structural determination of $\{Ni[P(OCH_3)_3]_4Br\}BF_4$, a low-spin member of the ML_4X^+ class.

Collection and Reduction of X-Ray Data

The compound $\{NiBr(P(OCH_3)_3)_4\}BF_4$ was prepared by a procedure to be described elsewhere[18] and was recrystallized in a closed container by vapor diffusion of ether into a concentrated acetone solution. The deep red crystal selected for data collection was mounted in a 0.3-mm sealed Lindemann capillary to overcome the problem of sensitivity of the compound to prolonged exposure to atmospheric conditions. The crystal used was a rectangular column measuring 0.20 × 0.28 × 0.34 mm.

Data were collected at room temperature using a Syntex $P2_1$ automated four circle diffractometer operating with graphite-monochromated Cu Kα radiation (λ 1.5418 Å). The unit cell was determined to be monoclinic, $a = 13.333$ (4), $b = 18.195$ (5), $c = 11.731$ (2) Å, and $\beta = 93.61$ (2)°, using standard crystallographic techniques.

A density of 1.690 g/cm^3 was computed from the cell volume of 2840.2 Å^3 on the basis of four $\{NiBr[P(OCH_3)_3]_4\}BF_4$ ion pairs per unit cell. This agrees well with a density of 1.69 g/cm^3 measured by flotation using n-C_7H_{16}–$BrCH_2CH_2Br$ mixtures.

Data were taken with a variable ω-scan mode at a minimum scan rate of 3°/min within a 2θ sphere of 114° ($(\sin\theta)/\lambda = 0.544$ Å^{-1}). During data collection, intensities of three standards $(40\bar{4})$, $(52\bar{3})$, and $(60\bar{2})$ were monitored after every 50 reflections. The intensities of these standards decreased by 15% during the measurement of two octants (4434 reflections).

The collected data were scaled for decomposition using the al-

Table I. Final Positional and Anisotropic Temperature Factors for $\{Ni[P(OCH_3)_3]_4Br\}BF_4$[a-c]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.40160 (9)	0.19071 (6)	0.25273 (9)	6.61 (8)	3.02 (4)	8.46 (9)	−0.02 (4)	0.11 (6)	0.01 (4)
Br	0.24819 (7)	0.25410 (5)	0.30422 (8)	5.41 (6)	3.29 (3)	10.69 (8)	0.91 (3)	1.49 (5)	−0.20 (3)
P(1)	0.31737 (16)	0.08857 (10)	0.26513 (17)	4.41 (13)	2.25 (6)	7.05 (17)	−0.46 (7)	−0.30 (12)	0.31 (8)
P(2)	0.46712 (16)	0.30026 (9)	0.24583 (16)	5.05 (14)	1.85 (6)	5.98 (15)	−0.04 (7)	0.02 (11)	−0.29 (7)
P(3)	0.50030 (17)	0.15918 (11)	0.40644 (17)	5.46 (15)	2.52 (6)	6.09 (16)	−0.19 (8)	−1.16 (12)	0.25 (8)
P(4)	0.43598 (16)	0.16731 (10)	0.07653 (15)	4.24 (13)	2.08 (6)	5.26 (14)	0.24 (7)	0.07 (10)	−0.32 (7)
O(1)	0.21163 (50)	0.07741 (34)	0.20255 (58)	6.55 (45)	3.80 (22)	12.52 (62)	−1.32 (26)	−2.77 (43)	0.99 (29)
O(2)	0.38164 (47)	0.02172 (28)	0.22589 (53)	6.74 (44)	2.12 (16)	12.93 (60)	−0.21 (22)	0.82 (40)	−0.44 (25)
O(3)	0.29485 (48)	0.06481 (34)	0.39095 (50)	6.59 (44)	4.32 (21)	8.69 (50)	−0.98 (26)	1.15 (38)	1.41 (27)
O(4)	0.40324 (48)	0.35271 (29)	0.16358 (47)	8.18 (46)	2.47 (17)	8.54 (46)	0.26 (23)	−0.60 (37)	1.11 (23)
O(5)	0.57688 (44)	0.30134 (29)	0.20325 (47)	5.97 (40)	3.18 (19)	9.24 (48)	−0.74 (23)	0.88 (34)	−0.90 (24)
O(6)	0.47708 (48)	0.34014 (28)	0.36478 (46)	7.91 (45)	2.56 (17)	8.19 (45)	0.64 (23)	−1.08 (36)	−1.01 (23)
O(7)	0.46008 (63)	0.16849 (42)	0.53146 (54)	11.38 (65)	5.62 (30)	8.13 (53)	−0.16 (35)	−0.55 (46)	1.04 (31)
O(8)	0.52508 (51)	0.07532 (33)	0.43115 (57)	7.49 (49)	3.34 (20)	12.42 (61)	0.19 (26)	−0.60 (45)	1.74 (29)
O(9)	0.60538 (46)	0.19956 (31)	0.40357 (50)	5.99 (40)	3.28 (20)	10.71 (53)	−0.70 (24)	−2.87 (37)	0.81 (26)
O(10)	0.35545 (45)	0.11862 (32)	0.00554 (48)	6.13 (42)	3.81 (21)	8.65 (49)	−0.75 (24)	−0.84 (37)	−2.38 (25)
O(11)	0.53397 (43)	0.12102 (29)	0.05901 (48)	5.02 (38)	3.33 (19)	9.09 (48)	0.59 (21)	0.14 (35)	−0.94 (23)
O(12)	0.44610 (46)	0.23924 (28)	0.00288 (42)	7.73 (43)	2.88 (17)	6.28 (42)	0.36 (23)	0.60 (34)	0.52 (21)
C(1)	0.15530 (80)	0.11606 (62)	0.11452 (91)	6.77 (73)	5.57 (44)	10.76 (91)	−0.23 (46)	−2.64 (68)	1.80 (50)
C(2)	0.3490 (11)	−0.05433 (50)	0.2398 (14)	12.2 (11)	1.68 (27)	25.5 (18)	−1.03 (44)	2.1 (11)	0.43 (53)
C(3)	0.2071 (10)	0.08682 (66)	0.4498 (10)	11.0 (10)	5.16 (45)	14.4 (12)	−0.48 (54)	5.59 (92)	1.60 (57)
C(4)	0.66343 (86)	0.33977 (65)	0.2585 (11)	6.37 (72)	5.37 (44)	17.3 (12)	−2.87 (49)	−0.64 (77)	−0.81 (60)
C(5)	0.4450 (11)	0.40745 (63)	0.0890 (11)	13.6 (12)	4.25 (40)	14.6 (12)	−1.18 (56)	−0.95 (96)	4.01 (57)
C(6)	0.4297 (11)	0.40870 (60)	0.3961 (10)	12.8 (11)	4.07 (37)	13.0 (11)	2.82 (53)	−1.20 (86)	−3.02 (50)
C(7)	0.4165 (12)	0.23446 (76)	0.57345 (95)	15.8 (14)	6.50 (56)	8.80 (88)	1.40 (70)	3.28 (88)	−1.09 (55)
C(8)	0.58886 (95)	0.03476 (65)	0.3570 (12)	8.58 (88)	4.43 (40)	18.0 (14)	1.18 (50)	1.31 (89)	−1.82 (60)
C(9)	0.68669 (91)	0.18597 (65)	0.49234 (99)	8.28 (80)	5.44 (42)	13.1 (10)	−0.06 (51)	−6.20 (76)	−0.26 (53)
C(10)	0.46855 (97)	0.23943 (62)	−0.11452 (81)	11.58 (97)	5.46 (43)	7.26 (76)	0.31 (53)	2.12 (68)	0.99 (44)
C(11)	0.63477 (71)	0.14770 (54)	0.09371 (87)	5.12 (60)	3.92 (33)	12.76 (95)	0.22 (38)	−0.33 (61)	−0.67 (45)
C(12)	0.37359 (96)	0.05842 (68)	−0.0693 (11)	9.70 (91)	5.40 (45)	14.6 (12)	0.51 (53)	−1.84 (84)	−5.57 (61)
B	0.37259 (90)	0.43308 (61)	0.74518 (88)	7.40 (88)	3.84 (38)	7.32 (84)	−0.35 (46)	0.84 (68)	−1.56 (47)
F(1)	0.33660 (93)	0.36616 (42)	0.7354 (12)	19.9 (11)	4.32 (28)	38.7 (18)	−1.27 (44)	−14.6 (12)	0.50 (54)
F(2)	0.3253 (10)	0.47309 (71)	0.8160 (12)	18.4 (11)	10.60 (56)	32.2 (17)	0.01 (66)	13.4 (12)	−5.86 (81)
F(3)	0.35563 (11)	0.46959 (61)	0.64522 (75)	27.8 (15)	9.18 (47)	13.78 (84)	1.10 (67)	−0.58 (82)	2.62 (49)
F(4)	0.47009 (63)	0.43200 (61)	0.7827 (10)	7.84 (57)	9.90 (49)	30.4 (14)	−1.39 (43)	−2.81 (72)	0.01 (66)

[a] Standard deviations are given in parentheses here and in subsequent tables. [b] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] All β values are $\times 10^3$.

gorithm: corrected intensity = (observed intensity)/(1 − fraction of decay). The data were also corrected for Lorentz and polarization effects during reduction of 2894 reflections whose intensities were greater than 3σ above background. Calculation of the linear absorption coefficient (56.17) and transmission factors indicated that no absorption correction was necessary.

Investigation of the systematic extinctions in the reflection data of $h + l = 2n$ for $h0l$ and $k = 2n$ for $0k0$ uniquely established the space group as $P2_1/n$ and this choice was confirmed by the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure

The positions of the nickel and bromine atoms were determined from a three-dimensional Patterson function. After three cycles of least-squares refinement of the positional parameters with isotropic thermal parameters held at 3.0 and a single scale factor, the conventional unweighted and weighted discrepancy factors were 0.467 and 0.490, respectively. The heavy-atom phased electron density synthesis[19] revealed the positions of the four phosphorus atoms. After three more cycles of refinement[20] on the positional parameters with the isotropic thermal parameters for the phosphorus atoms also held at 3.0, the agreement factors were 0.341 and 0.363, respectively. The locations of all of the oxygen, carbon, fluorine, and boron atoms were established from difference Fourier maps. Refinement of all positional isotropic thermal parameters in the model produced R and R_w values of 0.107 and 0.118, respectively.

Further refinement using anisotropic thermal parameters for all atoms and weights, assigned as $1/\sigma(F^2)$, resulted in final discrepancy factors of $R = 0.060$ and $R_w = 0.064$. The ratio of the largest shift in the last refinement to the standard deviation of the coordinate was 0.01. Final difference Fourier maps showed no peaks larger than 0.5 e/Å^3. The hydrogen atoms were not located.

The atomic scattering factors used in the refinement were those of Hanson et al.[21] and the real and imaginary corrections[22] for anomalous dispersion for bromine and nickel were also included in the calculations. The final positional and anisotropic thermal parameters of the atoms are shown in Table I. The final observed and calculated structure factor amplitudes (in electrons ×10) for the 2894 reflections have been tabulated.[23]

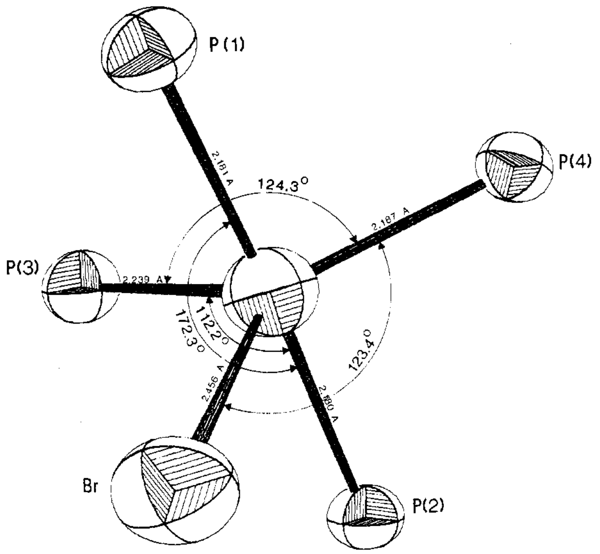

Figure 1. Computer drawing of the NiP_4Br portion of $\{Ni[P(OCH_3)_3]Br\}BF_4$ showing the angles and distances within the inner coordination sphere.

Discussion

The unit cell contains four unique molecules with evidence for some cation–anion interactions. The closest intermolecular contacts of 3.083 (12) Å between anion fluorines and surrounding cation methyl groups are significantly shorter than the sum of the van der Waals radii[24] (3.35 Å) of a methyl group (2.0 Å) and fluorine (1.35 Å). As shown in Figure 1,[25]

Table II. Intramolecular Bond Distances and Angles in $\{Ni[P(OCH_3)_3]_4Br\}BF_4$

	Distances, Å		
Ni-Br	2.456 (1)	Ni-P(3)	2.239 (2)
Ni-P(1)	2.181 (2)	Ni-P(4)	2.187 (2)
Ni-P(2)	2.180 (2)		
	Angles, Deg		
Br-Ni-P(1)	86.76 (7)	P(1)-Ni-P(3)	90.40 (8)
Br-Ni-P(2)	85.50 (6)	P(1)-Ni-P(4)	92.10 (8)
Br-Ni-P(3)	112.24 (7)	P(2)-Ni-P(3)	92.73 (8)
Br-Ni-P(4)	123.44 (7)	P(2)-Ni-P(4)	91.98 (8)
P(1)-Ni-P(2)	172.26 (10)	P(3)-Ni-P(4)	124.31 (9)

Table III. Intramolecular Nonbonded Distances (Å) among the $Ni[P(OMe)_3]_4Br^+$ Cations

Br-P(1)	3.192 (2)	P(1)-P(2)	4.351 (2)	P(2)-P(3)	3.198 (2)
Br-P(2)	3.154 (2)	P(1)-P(3)	3.137 (3)	P(2)-P(4)	3.141 (2)
Br-P(3)	3.900 (2)	P(1)-P(4)	3.145 (3)	P(3)-P(4)	3.914 (2)
Br-P(4)	4.091 (8)				

the inner coordination sphere around the nickel atom is slightly distorted from trigonal bipyramidal with bromine in an equatorial position. In Table II the immediate distances and angles around the nickel atom are tabulated. These parameters and their deviations are computed from the final parameters and the correlation matrix.[26]

The trigonal-bipyramidal geometry of the complex is somewhat distorted with the axial $P(OCH_3)_3$ ligands forced toward the bromine atom and away from both equatorial $P(OCH_3)_3$ groups resulting in a P(1)–Ni–P(2) angle of 172.26 (10)° rather than the ideal 180°. The Br–Ni–P(3) angle in the equatorial plane is closed to 112.24 (1)° while the other angles in the plane are opened accordingly to 123.44 (7) and 124.31 (9)° with the latter angle P(3)–Ni–P(4) reflecting the steric size of the phosphorus ligands. From Table III which lists the intramolecular nonbonding contacts it can be seen that the P(1)–Br and P(2)–Br distances 3.192 (2) and 3.154 (2) Å are considerably shorter than the van der Waals distance (3.95 Å).[24] Interestingly this crowding does not cause a distortion toward tetragonal pyramidal as in other nickel complexes.[6,7,10–12] Thus the axial ligands in the present complex are forced toward the equatorial bromine rather than between a pair of equatorial ligands. The least squares plane calculated (which includes Ni, Br, P(1), and P(2)) with the equation $0.242X - 0.070Y + 0.968Z = 3.871$ shows only small deviations of these atoms from this plane (0.002, 0.000, −0.002, and −0.002 Å, respectively). Moreover, deviations from the least-squares plane which can be fitted to include the three equatorial atoms as well as the nickel using the equation $0.476X + 0.878Y - 0.042Z = 5.381$ are also quite small (Ni (0.004 Å), Br (−0.001 Å), P(3) (−0.003 Å), and P(4) (−0.004 Å)) further attesting to the trigonal-bipyramidal nature of the coordination geometry.

Bond lengths and angles of the trimethyl phosphite ligands are tabulated in Table IV, and Figure 2 shows the spatial orientation of the methoxy groups relative to the overall geometry. The average P–O and O–C bond distances, 1.579 (7) and 1.45 (2) Å, and the average P–O–C and O–P–O angles, 124.9 (7) and 103.2 (4)°, compare favorably with those reported for other structural determinations involving this ligand.[12,27,28] The orientation of the methoxy groups in relation to one another is only partially in the expected "head-to-tail" fashion, deviations from this pattern probably being due to crystal packing forces.

The Ni–Br distance of 2.456 (1) Å compares favorably with the equatorial Ni–Br distances of 2.451 and 2.553 Å for trigonal-bipyramidal $Ni[P(CH_3)_3]_3Br_2$.[10] This distance is intermediate between the apical Ni–Br separation in tetragonal-pyramidal $Ni\{HN[CH_2CH_2CH_2P(C_6H_5)_2]_2\}Br_2$[29] and $Ni[(CH_3)_2As(CH_2)_3As(CH_3)(CH_2)_3As(CH_3)_2]Br_2$[30] (2.698 and 2.69 Å, respectively) and the basal Ni–Br distances (2.333 and 2.37 Å, respectively). The difference in Ni(II) radius for the equatorial plane of the trigonal bipyramid of the present compound and the basal plane of the tetragonal pyramid of the above compounds is somewhat larger (0.11 Å) than that previously reported by others (0.08 Å)[31,32] but the same as noted for $Ni[P(OCH_3)_3]_3I_2$ (0.12 Å).[12] The Ni–Br bond length in $\{Ni[P(OCH_3)_3]_4Br\}BF_4$ is only slightly shorter than the sum of the covalent radii (2.50 Å).[24]

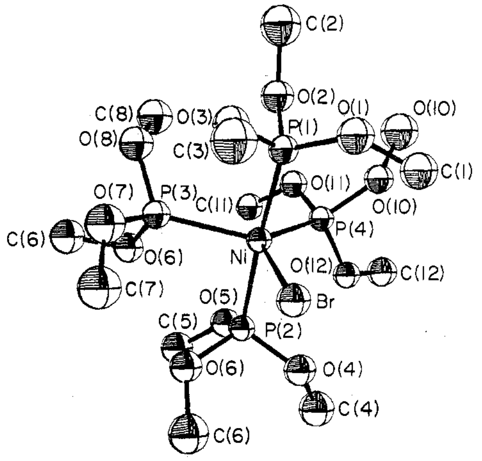

Figure 2. Computer drawing of $\{Ni[P(OCH_3)_3]_4Br\}BF_4$ showing the conformations of the methoxy groups in the $P(OCH_3)_3$ ligands.

Table IV. Intramolecular Distances and Angles among the Trimethyl Phosphite Ligands and the Tetrafluoroborate Anion

	Distances, Å		
P(1)-O(1)	1.561 (6)	O(3)-C(3)	1.45 (1)
P(1)-O(2)	1.573 (6)	O(4)-C(4)	1.46 (1)
P(1)-O(3)	1.585 (6)	O(5)-C(5)	1.46 (1)
P(2)-O(4)	1.570 (5)	O(6)-C(6)	1.46 (1)
P(2)-O(5)	1.576 (6)	O(7)-C(7)	1.43 (1)
P(2)-O(6)	1.571 (5)	O(8)-C(8)	1.46 (1)
P(3)-O(7)	1.602 (7)	O(9)-C(9)	1.48 (1)
P(3)-O(8)	1.584 (6)	O(10)-C(10)	1.43 (1)
P(3)-O(9)	1.584 (6)	O(11)-C(11)	1.46 (1)
P(4)-O(10)	1.587 (5)	O(12)-C(12)	1.43 (2)
P(4)-O(11)	1.579 (5)	B-F(1)	1.31 (1)
P(4)-O(12)	1.579 (5)	B-F(2)	1.35 (1)
O(1)-C(1)	1.41 (1)	B-F(3)	1.30 (1)
O(2)-C(2)	1.46 (1)	B-F(4)	1.35 (1)
	Angles, Deg		
P(1)-O(1)-C(1)	124.1 (6)	O(10)-P(4)-O(11)	99.9 (3)
P(1)-O(2)-C(2)	121.8 (7)	O(10)-P(4)-O(12)	104.7 (3)
P(1)-O(3)-C(3)	125.0 (6)	O(11)-P(4)-O(12)	105.7 (3)
P(2)-O(4)-C(4)	124.8 (7)	Ni-P(1)-O(1)	122.2 (2)
P(2)-O(5)-C(5)	125.9 (6)	Ni-P(1)-O(2)	110.3 (2)
P(2)-O(6)-C(6)	127.3 (5)	Ni-P(1)-O(3)	115.0 (2)
P(3)-O(7)-C(7)	124.7 (6)	Ni-P(2)-O(4)	112.1 (2)
P(3)-O(8)-C(8)	120.1 (6)	Ni-P(2)-O(5)	113.9 (2)
P(3)-O(9)-C(9)	121.2 (6)	Ni-P(2)-O(6)	113.6 (2)
P(4)-O(10)-C(10)	127.8 (6)	Ni-P(3)-O(7)	119.7 (3)
P(4)-O(11)-C(11)	122.7 (5)	Ni-P(3)-O(8)	120.0 (2)
P(4)-O(12)-C(12)	124.1 (5)	Ni-P(3)-O(9)	109.9 (2)
O(1)-P(1)-O(2)	104.7 (3)	Ni-P(4)-O(10)	115.4 (2)
O(1)-P(1)-O(3)	100.6 (3)	Ni-P(4)-O(11)	116.8 (2)
O(2)-P(1)-O(3)	101.6 (3)	Ni-P(4)-O(12)	112.7 (2)
O(4)-P(2)-O(5)	106.0 (3)	F(1)-B-F(2)	109.9 (9)
O(4)-P(2)-O(6)	106.1 (3)	F(1)-B-F(3)	112.8 (12)
O(5)-P(2)-O(6)	104.3 (3)	F(1)-B-F(4)	110.8 (10)
O(7)-P(3)-O(8)	90.7 (4)	F(2)-B-F(3)	102.6 (11)
O(7)-P(3)-O(9)	108.5 (4)	F(2)-B-F(4)	113.3 (10)
O(8)-P(3)-O(9)	106.0 (3)	F(3)-B-F(4)	107.3 (10)

The average axial Ni–P bond length (2.180 (2) Å) is 0.033 Å shorter than the average equatorial bond (2.213 (2) Å). In previously reported structures of phosphite nickel(II) complexes this difference has been found to be 0.05 and 0.013 Å in $N[P(OCH)_3(CH_2)_3]_5^{2+}$ [2] and $Ni[P(OCH_3)_3]_3I_2$,[12] respectively. Although these results are consistent with Gillespie's prediction[33] of shorter axial bonds for d^8 or d^9 complexes when the d_{z^2} orbital is empty or half-filled, it is difficult to decide whether the present structure conforms to such an oblate ellipsoid model since one of the differences for the dissimilar equatorial Ni–P bonds (0.007 and 0.059 Å) is barely significant. Other Ni–P distances are 2.18 Å in $Ni[PH(C_6H_5)_2]_3I_2$[11] and $Ni[P(OCH_3)_3]_3I_2$,[12] 2.19 Å in $\{Ni[P(OCH_2)_3CCH_3]_3NO\}BF_4$,[34] 2.20 Å in $Ni[P(CH_3)_3]_3Br_2$,[10] 2.21 Å in $[Ni(TAP)CN]ClO_4$ (TAP = $P[CH_2CH_2CH_2As(CH_3)_2]_3$,[35] and 2.23 Å in $Ni[P(OCH_2CH_3)_2C_6H_5]_3(CN)_2$.[6]

The general rule[36] that the more electronegative substituent of a trigonal-bipyramidal structure prefers axial positions is violated by the present structure as well as by $Ni[P(OCH_3)_3]_3I_2$,[12] $Ni[P(CH_3)_3]_3Br_2$,[10] and $Ni[PH(C_6H_5)_2]_3I_2$[11] whereas the cyano groups of $Ni[P(OCH_2CH_3)_2C_6H_5]_3(CN)_2$[6] and $Ni[P(CH_3)_3C_6H_5]_3(CN)_2$[7] appear to conform. In the case of d^8 complexes, metal d orbital repulsions by the ligand as well as ligand–ligand repulsions would be minimized by placing negatively charged ligands on the axis facing the empty d_{z^2} orbital. Although cyanide ions appear to follow this prediction, halogens do not. Recently a unified MO treatment revealed that the stronger cylindrical π acceptor favors the equatorial positions while the stronger σ and cylindrical π donor is directed to the axis in d^8 trigonal bipyramids.[39] While the structural results for $[NiL_4Br]^+$, $[NiL_3I_2]$, and $[NiL_3(CN)_2]$ contradict these predictions, steric effects may well be dominant. Thus the smaller of the two ligating atoms in each case would tend to occupy the more sterically restrictive axial position. Others have recently rationalized these structural results on the basis of a second-order Jahn–Teller effect resulting in an axial preference trend reflecting the spectral order cyanide > phosphorus ligands > halide.[10]

While the small difference in energy between the square-pyramidal and trigonal-bipyramidal geometries for low-spin d^8 systems[37,38] makes structural prediction difficult, it is interesting that, thus far, the predominant configuration for monodentate systems is trigonal bipyramidal, particularly where symmetrical phosphorus ligands are involved.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50167V-11-75.

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