This discussion of the trichlorogermanyl groups shows that the chlorine atoms do not provide a source of steric repulsion in the cis isomer although the small deviation (1.1°) from 90° of the angles C(1)–Ru–C(2) and C(1)–Ru–C(2′) in the trans isomer may result from carbon–chlorine contacts. The major angular deformations from an octahedral geometry for the $RuGe_2C_4$ skeleton of the cis isomer appear to be due to the differences in carbon–carbon, carbon–germanium, and germanium–germanium repulsion within the immediate coordination sphere. The average ruthenium–carbon and ruthenium–germanium distances are collected in Table X, where a totally optimistic view has been taken with regard to the standard deviations of the averages concerned, $\sigma(\mathrm{av}) = (1/\Sigma_i 1/\sigma_i^2)^{1/2}$. While the cis isomer has its own internal calibration for ruthenium–carbon distances, it cannot provide the comparison for the ruthenium–germanium distances which might provide the more sensitive indicator of the trans ligand effects simply because these distances should be the most precise determined in each structure. However, in this respect it should be remembered that the manganese–manganese distances in $Mn_2(CO)_{10}$[23] and $Mn_2(CO)_8(P(C_2H_5)_3)_2$[24] are not significantly different despite the difference in trans ligand. The ruthenium–germanium distances are the same and are not significantly different from the value (2.47 Å) reported for $(Ru(CO)_3Ge(CH_3)_2)_2$.[25] The average ruthenium–carbon distances show no significant difference even when the totally optimistic view is taken in the calculation of their standard deviations. The values are higher than those previously[26–29] reported for ruthenium–carbon distances in carbonyl derivatives. This may be due to the corrections for thermal motion used in this structure and the proposed high π-bonding ability of the trichlorogermanyl groups in these compounds.

TABLE X

Atoms	Trans ligand	Isomer	Distance,[a] Å
Ru–Ge	$GeCl_3$	Trans	2.481 (1)
Ru–Ge	CO	Cis	2.481 (6)
Ru–C	CO	Trans	1.980 (4)
Ru–C	CO	Cis	2.00 (1)
Ru–C	$GeCl_3$	Cis	1.98 (1)

[a] Values with riding correction are used. Standard deviations are given in parentheses and refer to the last digit quoted.

Acknowledgment.—We thank the Research Council of Canada for its generous financial support.

(23) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).
(24) M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968).
(25) J. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J. Chem. Soc. D*, 1477 (1970).
(26) (a) E. R. Corey, Ph.D. Thesis, University of Wisconsin, 1963; (b) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).
(27) S. Merlino and G. Montagnoli, *Acta Crystallogr., Sect. B*, **24**, 424 (1968).
(28) M. Elder and D. Hall, *J. Chem. Soc. A*, 245 (1970).
(29) S. F. Watkins, *ibid.*, 1552 (1969).

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Structural Studies on Clathro Chelate Complexes. I. Trigonal-Prismatic Coordination of d^8 Nickel(II) in Crystalline [Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]nickel(II) Tetrafluoroborate

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Received December 27, 1971

[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]nickel(II) tetrafluoroborate, $[\{FB(ONCHC_5H_3N)_3P\}Ni^+][BF_4^-]$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with $a = 13.296$ (20), $b = 17.857$ (35), $c = 10.580$ (10) Å, $\beta = 108.68$ (5)°, and $Z = 4$. Observed and calculated densities are 1.65 (5) and 1.58 g cm^{-3}. The use of three-dimensional counter data ($\sin \theta_{\max} = 0.80$; Cu Kα radiation) has led to the location of all atoms (including hydrogens), the final discrepancy index being $R_F = 7.32\%$ for the 1781 symmetry-independent nonzero reflections. The cation is only slightly distorted from idealized C_{3v} symmetry. The central nickel(II) atom is coordinated to six nitrogen atoms, mean distances being Ni–N(aldoximo) = 2.030 (21) and Ni–N(pyridyl) = 2.043 (20) Å. The coordination sphere of the nickel atom defines a slightly tapered trigonal prism, in which N(aldoximo)···N(aldoximo) = 2.648 (11)–2.716 (12), N(pyridyl)···N(pyridyl) = 2.836 (11)–2.869 (11), and the aldoximo–pyridyl chelate "bite," N(aldoximo)···N(pyridyl), ranges from 2.521 (11) to 2.544 (12) Å. In addition, the triangle defined by the three aldoximo nitrogen atoms is rotated by ~1.6° relative to that defined by the three pyridyl nitrogens. However, deviations from an idealized trigonal-prismatic coordination of nickel(II) are relatively small.

Introduction

Trigonal-prismatic coordination of molybdenum(IV) and tungsten(IV) in the layer structures MoS_2 and WS_2 was reported by Dickinson and Pauling in 1923,[1] but more than 40 years was to elapse before this unusual coordination geometry was detected in a discrete molecular species.[2] Trigonal-prismatic coordination of transition metal ions by sulfur- and selenium-containing chelate ligands is now well established, as is exemplified by recent crystallographic studies on $Re(S_2C_2Ph_2)_3$,[2,3] $Mo(S_2C_2H_2)_3$,[4] $V(S_2C_2Ph_2)_3$,[5,6] and Mo-

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(1) R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, **45**, 1466 (1923).

(2) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965).

(3) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966).

(4) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **87**, 5798 (1965).

(5) R. Eisenberg, E. I. Stiefel, R. S. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).

(6) R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967).

$[Se_2C_2(CF_3)_2]_3$.[7] Other species in which trigonal-prismatic coordination is present include *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexanezinc(II)[8,9] and the central Co(II) ion in $[Co^{II}\{Co^{III}(OCH_2CH_2NH_2)_3\}_2{}^{2+}]$.[10]

Boston and Rose[11] were the first workers to prepare a "clathro chelate"[12] complex—*i.e.*, a species in which a metal atom is totally encapsulated by a bicyclic (or polycyclic) ligand system. It has subsequently been shown[13] that the Co(II) atom in $[Co(dmg)_3(BF)_2]$ has a coordination geometry in which the two triangles of nitrogen atoms are only 8.6° from an idealized trigonal-prismatic geometry, whereas in the Co(III) complex $[Co(dmg)_3(BF)_2{}^+]$ this angle is 45°. (Note that a rotation of 60° defines an *octahedral* coordination geometry.)

More recently, Holm and his coworkers[14,15] have synthesized Fe(II), Co(II), Ni(II), and Zn(II) derivatives (d^6, d^7, d^8, and d^{10} electronic configurations, respectively) of the bicyclic encapsulation ligand $[FB(O\ddot{N}CHC_5H_3\ddot{N})_3P^-]$, which is designed especially to impose a trigonal-prismatic geometry on a divalent first-row transition metal ion. We here report the results of a three-dimensional X-ray diffraction study of $[\{FB(ONCH\cdot C_5H_3N)_3P\}Ni^+][BF_4^-]$; the cation may be named as the [fluoroborotris(2-aldoximo-6-pyridyl)phosphine]nickel(II) monocation[14] or as {fluoro-[6,6′,6″-phosphinidynetris(α-picolinaldehyde oximato)-(3−)]borato(1−)} nickel(1+).[16] The former nomenclature is preferred by us and is used herein. A preliminary account of this study has appeared previously;[17] full details are to be found below.

Unit Cell and Space Group

A sample of the complex was supplied by Professor R. H. Holm of the Massachusetts Institute of Technology and was recrystallized from acetonitrile.

Optical examination and the observed reciprocal lattice symmetry (C_{2h}; $2/m$) indicated that the crystals belonged to the monoclinic system. Systematic examination of *h*(0–1)*l*, 0*kl*, and *hk*(0–1) Weissenberg and precession photographs revealed the systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, consistent only with the centrosymmetric space group $P2_1/c$ (C_{2h}^5; no. 14).

Unit parameters, calculated from calibrated $[Pb(NO_3)_2$; $a_{25°} = 7.8571$ Å] zero-level precession photographs taken at 25° with Mo Kα radiation (λ 0.7107 Å) are as follows: $a = 13.296$ (20), $b = 17.857$ (35), $c = 10.580$ (10) Å, $\beta = 108.68$ (5)°. [Errors given are the "maximum possible errors" based on the sum of the inaccuracies involved in measuring (on precession photographs) the positions of diffraction rows from the crystal under investigation and from the $Pb(NO_3)_2$ calibrant.] The unit cell volume is 2380.5 Å^3.

The observed density ($\rho_{obsd} = 1.65$ (5) g cm^{-3}, by flotation in bromoform–carbon tetrachloride) is consistent with the value calculated from $M = 566.63$ and $Z = 4$ ($\rho_{calcd} = 1.58$ g cm^{-3}). No crystallographic symmetry is imposed upon either the cation or the anion.

Collection, Correction, and Unification of X-Ray Diffraction Data

The complex crystallizes as orange hexagonal plates. The crystals appear to be air stable and are not X-ray sensitive.

Intensity data were collected with a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer," using a "stationary-background, ω-scan, stationary-background" counting sequence. Both the apparatus and the experimental technique have previously been described at some length.[18] Details specific to the present structural analysis include the following: (i) Cu Kα radiation (λ 1.5418 Å) was used; (ii) $\omega(hkl) = [1.8 + \{0.6L^{-1}(hkl)\}]°$, where $L(hkl)$ is the Lorentz factor for the reflection *hkl;* the count associated with this scan is $C(hkl)$; (iii) $d\omega/dt = 2.0°$ min^{-1}; (iv) initial and final backgrounds, $B_i(hkl)$ and $B_f(hkl)$, were each measured for one-fourth the time of the ω scan; (v) the overall stability of the system—*i.e.*, crystal alignment, crystal stability, electronic stability—was monitored by remeasuring a carefully preselected strong reflection (within a given level) after each 40 reflections were collected; the maximum deviation from the mean was <2.5%; (vi) $I(hkl)$, the integrated intensity of the reflection *hkl*, was calculated as $I(hkl) = C(hkl) - 2[B_i(hkl) + B_f(hkl)]$.

Based on our previous experience with the ω-scan technique, data were assigned standard deviations according to the following scheme: $I(hkl) > 4900$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $4900 > I(hkl) > 3.0[C(hkl) + 4B_i(hkl) + 4B_f(hkl)]^{1/2}$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$; $3.0[C(hkl) + 4B_i(hkl) + 4B_f(hkl)]^{1/2} > I(hkl)$, reflection rejected as not significantly (3σ) above background.

Two crystals were used in the course of data collection. Crystal C (0.120 × 0.114 × 0.250 mm) was aligned along its elongated *c* axis, and crystal B (0.118 × 0.114 × 0.235 mm) was mounted on its *b* axis. Data were collected using equi-inclination Weissenberg geometry. A total of 1008 reflections from quadrants *hkl* and $\bar{h}kl$ of levels *hk*(0–7) were collected from crystal C; 1708 reflections from quadrants *hkl* and $\bar{h}kl$ of levels *h*(0–7)*l* were collected from crystal B. [Each level is complete to sin θ = 0.80, save for very low-angle data which are shielded from the counter by a Pb backstop; these data represent all reflections visible on long-exposure Weissenberg films.] All data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied[19] ($\mu = 25.76$ cm^{-1}). Transmission factors ranged from 0.73 to 0.77 for data from crystal C (volume 2.9 × 10^{-6} cm^3) and from 0.61 to 0.78 for crystal B (volume 2.9 × 10^{-6} cm^3).

All data were now merged to a common scale using a least-squares method which minimizes a set of residuals linear in the logarithms of the individual scale factors,[20] *viz.*

$$\sum_{\substack{hkl,\ ij \\ i \neq j}} w(hkl)_{ij}[\ln (S_iI(hkl)_i) - \ln (S_jI(hkl)_j)]^2$$

Here, S_i is the scale factor for the *i*th set, $I(hkl)_i$ is the intensity for the reflections *hkl* in set *i* (after correction for Lorentz, polarization, and absorption effects), and $[w(hkl)_{ij}]^{-1} = [\sigma^2\{I(hkl)_i\}/I^2(hkl)_i] + [\sigma^2\{I(hkl)_j\}/I^2(hkl)_j]$. The *R* factor for scaling

$$R(I) = \frac{\sum_{hkl,\ ij} |I(hkl)_i - I(hkl)_j|}{\sum_{hkl,\ ij} [I(hkl)_i + I(hkl)_j]}$$

was 4.7%. The resulting 1781 independent nonzero reflections were placed on an (approximate) absolute scale by means of a Wilson plot,[21] which also yielded the overall isotropic thermal parameter, $\bar{B} = 2.60$ Å^2.

Elucidation and Refinement of the Structure

All subsequent calculations were (unless otherwise indicated) performed on the now defunct (and lamented) Harvard Uni-

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[7] C. G. Pierpoint and R. Eisenberg, *J. Chem. Soc., A*, 2285 (1971).

[8] W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969).

[9] W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, **9**, 1825 (1970).

[10] J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, **91**, 2394 (1969).

[11] D. R. Boston and N. J. Rose, *ibid.*, **90**, 6859 (1968).

[12] D. H. Busch, *Rec. Chem. Progr.*, **25**, 107 (1964).

[13] G. A. Zakrewski, C. A. Ghilardi, and E. C. Lingafelter, *J. Amer. Chem. Soc.*, **93**, 4411 (1971).

[14] J. E. Parks, B. E. Wagner, and R. H. Holm, *ibid.*, **92**, 3500 (1970).

[15] J. E. Parks, B. E. Wagner, and R. H. Holm, *Inorg. Chem.*, **10**, 2472 (1971).

[16] M. R. Churchill and A. H. Reis, *Chem. Commun.*, 1307 (1971).

[17] M. R. Churchill and A. H. Reis, *ibid.*, 879 (1970).

[18] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

[19] Using a gaussian quadrature numerical integration method to determine absorption corrections for a crystal of essentially arbitrary shape (but having no reentrant angles): see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

[20] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[21] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

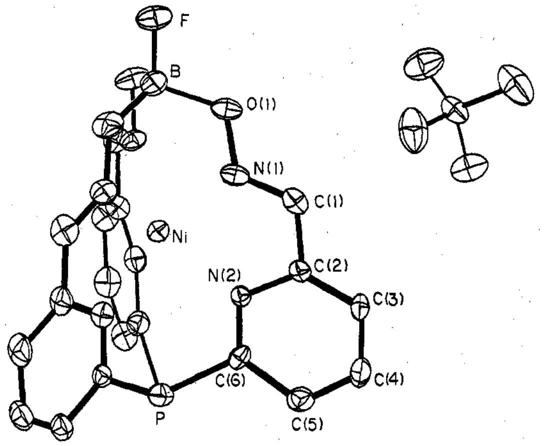

Figure 1.—Thermal vibration ellipsoids for nonhydrogen atoms in $[\{FB(ONCHC_5H_3N)_3P\}(Ni^{II})^+][BF_4^-]$.

versity IBM 7094 computer, using a locally modified version of the CRYRM system.[22] Scattering factors for neutral atoms (H, B, C, N, O, F, P) were taken from the compilation of Ibers;[23] the phosphorus form factors and the Thomas–Fermi–Dirac values for neutral nickel[24] were corrected for the real, but not the imaginary, component of dispersion [$\Delta f'(\mathrm{Ni}) = -3.1$ e, $\Delta f''(\mathrm{Ni}) = +0.6$ e; $\Delta f'(\mathrm{P}) = +0.2$ e, $\Delta f''(\mathrm{P}) = +0.5$ e].[25] The residual minimized during least-squares refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\}$ is derived from $\sigma\{I(hkl)\}$ by appropriate propagation of Lorentz, polarization, absorption, and scale factors.

Discrepancy indices utilized are

$$R_F = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_{wF^2} = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$$

The position of the nickel atom ($x = 0.824$, $y = 0.104$, $z = 0.118$) was obtained from systematic examination of a three-dimensional Patterson synthesis. A three-dimensional Fourier synthesis, phased only by the nickel atom ($R_F = 54.2\%$), yielded unambiguously the positions of all 35 remaining nonhydrogen atoms. Four cycles of full-matrix least-squares refinement of atomic positional and isotropic thermal parameters led to convergence with reduction of the discrepancy index from $R_F = 36.1\%$ to $R_F = 11.06\%$. Refinement was now continued using anisotropic thermal parameters for all nonhydrogen atoms. Four cycles of least-squares refinement, with hydrogen atoms included in *calculated* positions with $d(\text{C–H}) = 1.08$ Å and in appropriate trigonal positions, led to convergence [$(\Delta/\sigma)_{\max} < 0.1$] at $R_F = 7.32\%$ and $R_{wF^2} = 3.26\%$. [During refinement processes the limited (32K words) storage capacity of the IBM 7094 computer necessitated the blocking of refined parameters into several submatrices, as follows: matrix 1, parameters for Ni, P, six N's, and the scale factor; matrix 2, parameters for F(1), B, three O's; matrices 3–5, parameters for C(1)–C(6), C(1′)–C(6′), C(1″)–C(6″), respectively; matrix 6, parameters for atoms of the BF_4^- anion.] A final difference-Fourier synthesis showed no significant features, thereby confirming the correctness of our structural analysis.

Observed and calculated structure factor amplitudes are listed elsewhere.[26] Final atomic coordinates are collected in Table I. Anisotropic thermal parameters are listed in Table II. Their associated atomic vibration ellipsoids are defined in Table III and illustrated in Figure 1.

TABLE I

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z
	(A) Atoms within the Clathro Chelate Cation		
Ni	0.82956 (12)	0.10395 (10)	0.11954 (14)
P	0.70570 (24)	0.03093 (18)	0.33341 (28)
N(1)	0.9748 (7)	0.1483 (5)	0.1550 (8)
N(1′)	0.8662 (6)	0.0545 (5)	−0.0333 (7)
N(1″)	0.7868 (7)	0.1922 (5)	−0.0107 (8)
N(2)	0.8906 (6)	0.0992 (4)	0.3217 (7)
N(2′)	0.7770 (6)	−0.0029 (5)	0.1209 (7)
N(2″)	0.6896 (6)	0.1416 (5)	0.1420 (7)
C(1)	1.0377 (8)	0.1558 (6)	0.2822 (10)
C(2)	0.9884 (7)	0.1249 (5)	0.3756 (10)
C(3)	1.0419 (8)	0.1293 (7)	0.5121 (10)
C(4)	0.9892 (10)	0.1001 (7)	0.5963 (10)
C(5)	0.8890 (10)	0.0720 (7)	0.5438 (11)
C(6)	0.8398 (8)	0.0703 (6)	0.4016 (9)
C(1′)	0.8436 (8)	−0.0134 (6)	−0.0569 (9)
C(2′)	0.7932 (8)	−0.0507 (7)	0.0283 (10)
C(3′)	0.7680 (9)	−0.1259 (7)	0.0231 (11)
C(4′)	0.7206 (9)	−0.1545 (7)	0.1127 (12)
C(5′)	0.7026 (8)	−0.1067 (8)	0.2068 (11)
C(6′)	0.7304 (8)	−0.0324 (7)	0.2110 (9)
C(1″)	0.7031 (10)	0.2319 (6)	−0.0143 (11)
C(2″)	0.6460 (9)	0.2005 (7)	0.0716 (10)
C(3″)	0.5518 (10)	0.2319 (8)	0.0729 (13)
C(4″)	0.5024 (9)	0.1995 (9)	0.1553 (14)
C(5″)	0.5469 (9)	0.1402 (8)	0.2329 (11)
C(6″)	0.6418 (7)	0.1107 (6)	0.2258 (9)
O(1)	1.1063 (6)	0.1764 (4)	0.0616 (7)
O(1′)	0.9149 (6)	0.0905 (5)	−0.1117 (7)
O(1″)	0.8450 (6)	0.2172 (5)	−0.0896 (7)
B(1)	0.9393 (11)	0.1681 (11)	−0.0739 (14)
F(1)	0.9901 (5)	0.1977 (4)	−0.1572 (6)
	(B) Atoms within the BF_4^- Anion		
B(2)	0.3209 (11)	0.1268 (11)	0.4015 (18)
F(2)	0.2946 (6)	0.1694 (5)	0.4960 (7)
F(3)	0.4210 (6)	0.1017 (5)	0.4582 (10)
F(4)	0.2507 (6)	0.0712 (5)	0.3654 (8)
F(5)	0.3159 (6)	0.1726 (5)	0.2999 (7)
	(C) Calculated Hydrogen Atom Positions[a]		
H(1)	1.1154	0.1815	0.3116
H(3)	1.1206	0.1523	0.5551
H(4)	1.0275	0.1005	0.7031
H(5)	0.8493	0.0508	0.6109
H(1′)	0.8609	−0.0426	−0.1369
H(3′)	0.7827	−0.1624	−0.0504
H(4′)	0.6989	−0.2129	0.1095
H(5′)	0.6669	−0.1288	0.2774
H(1″)	0.6788	0.2819	−0.0736
H(3″)	0.5163	0.2798	0.0126
H(4″)	0.4285	0.2224	0.1601
H(5″)	0.5071	0.1161	0.2975

[a] Hydrogen atoms are numbered similarly to their attached carbon atoms.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table IVA; average bond distances are collected in Table IVB. Individual and mean bond angles are listed in Tables VA and VB, respectively.

As anticipated,[14,15] the d^8 nickel(II) atom is totally encapsulated by the fluoroborotris(2-aldoximo-6-pyridyl)phosphine system and attains a configuration of 20 outer electrons by donation of electron pairs from the three aldoximo nitrogen atoms [N(1), N(1′), N(1″)]

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(22) CRYRM is an integrated sequence of crystallographic routines for the IBM 7094 computer, written under the direction of Dr. R. E. Marsh at the California Institute of Technology.

(23) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, pp 202–203.

(24) Reference 23, p 210.

(25) Reference 23, p 214.

(26) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth N.W., Washington, D. C. 20036, by referring to code number INORG-72-1811. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	57.3 (1.3)	21.9 (0.8)	83.4 (1.9)	3.8 (1.6)	43.3 (2.4)	5.4 (1.9)
P	71.4 (2.3)	34.9 (1.6)	109.0 (3.5)	−4.7 (3.2)	74.4 (4.8)	−2.1 (3.7)
N(1)	77 (7)	29 (4)	140 (11)	4 (9)	126 (14)	−8 (11)
N(1′)	82 (7)	28 (4)	86 (9)	−20 (9)	85 (14)	12 (10)
N(1″)	84 (8)	33 (4)	126 (11)	−2 (10)	78 (16)	44 (11)
N(2)	44 (6)	22 (4)	76 (8)	3 (8)	34 (11)	−8 (9)
N(2′)	58 (6)	22 (4)	106 (10)	7 (8)	25 (14)	19 (10)
N(2″)	67 (6)	19 (4)	105 (10)	14 (9)	38 (13)	0 (11)
C(1)	59 (8)	22 (6)	162 (15)	0 (11)	71 (19)	−56 (16)
C(2)	50 (8)	18 (5)	93 (13)	15 (10)	49 (17)	−17 (13)
C(3)	51 (8)	53 (6)	86 (14)	4 (12)	−7 (18)	−13 (15)
C(4)	72 (11)	51 (7)	100 (14)	21 (15)	−10 (22)	−19 (16)
C(5)	88 (11)	43 (6)	122 (16)	33 (13)	88 (22)	6 (15)
C(6)	77 (9)	21 (6)	68 (13)	13 (11)	28 (18)	−11 (13)
C(1′)	84 (9)	24 (5)	105 (13)	4 (11)	61 (19)	−38 (14)
C(2′)	62 (9)	19 (6)	116 (13)	−8 (12)	60 (18)	−11 (15)
C(3′)	90 (11)	21 (6)	124 (16)	−35 (13)	63 (21)	−14 (15)
C(4′)	94 (10)	16 (6)	144 (16)	−19 (13)	38 (22)	−48 (17)
C(5′)	76 (10)	28 (6)	145 (17)	−5 (13)	55 (21)	58 (17)
C(6′)	63 (8)	34 (7)	93 (12)	−1 (12)	37 (16)	6 (15)
C(1″)	96 (9)	21 (7)	161 (18)	31 (13)	61 (22)	46 (18)
C(2″)	68 (10)	34 (6)	124 (14)	35 (12)	15 (19)	5 (15)
C(3″)	73 (12)	62 (8)	173 (20)	70 (16)	3 (26)	13 (19)
C(4″)	54 (10)	63 (8)	171 (20)	15 (15)	40 (24)	−20 (21)
C(5″)	57 (9)	38 (7)	119 (16)	12 (13)	35 (20)	−1 (17)
C(6″)	47 (9)	36 (6)	84 (12)	−11 (12)	22 (16)	−45 (14)
O(1)	93 (7)	36 (4)	157 (11)	−23 (8)	156 (16)	27 (10)
O(1′)	145 (8)	18 (4)	125 (10)	−19 (9)	169 (14)	2 (10)
O(1″)	123 (8)	41 (4)	132 (10)	6 (9)	117 (16)	77 (10)
B(1)	87 (12)	52 (11)	107 (19)	7 (20)	71 (25)	60 (23)
F(1)	146 (8)	41 (4)	169 (9)	−34 (9)	201 (15)	17 (9)
B(2)	59 (12)	41 (8)	184 (24)	12 (18)	81 (28)	17 (26)
F(2)	168 (8)	62 (5)	167 (10)	11 (10)	181 (15)	9 (12)
F(3)	91 (7)	79 (5)	389 (18)	22 (10)	124 (19)	97 (15)
F(4)	121 (8)	53 (4)	273 (14)	−50 (10)	−35 (17)	30 (12)
F(5)	192 (10)	53 (4)	178 (11)	34 (10)	191 (17)	44 (12)

[a] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

and the three nitrogen atoms of the pyridyl systems [*i.e.*, N(2), N(2′), N(2″)]. This is consistent with the observed magnetic moment of 3.11 BM,[15] indicating two unpaired electrons per nickel atom.

As shown clearly in Figure 2, the six nitrogen atoms are arranged around the nickel(II) center so as to define a slightly tapered trigonal prism. The Ni–N(aldoximo) distances [Ni–N(1), Ni–N(1′), Ni–N(1″)] range from 2.008 (8) to 2.050 (9) Å, averaging 2.030 (21) Å, while Ni–N(pyridyl) bond lengths [Ni–N(2), etc.] vary from 2.031 (7) to 2.066 (8) Å, with a mean value of 2.043 (20) Å. There is no appreciable interaction of the nickel atom with either the boron or the phosphorus "cap" of the clathrate ligand, since Ni···P = 3.452 (3) and Ni···B(1) = 3.089 (16) Å. Nitrogen···nitrogen distances within the N(1)···N(1′)···N(1″) triangle are 2.648 (11), 2.716 (12), and 2.669 (12) Å [average 2.678 (35) Å], while distances in the N(2)···N(2′)···N(2″) triangle are 2.839 (10), 2.869 (11), and 2.836 (11) Å [average 2.848 (18) Å]. The larger distances between nitrogen atoms of the pyridyl rings results from a combination of steric factors within the ligand including requirements for phosphorus–carbon bond distances, C—P—C angles, boron–oxygen bond distances, and O–B–O angles.

Individual "bites" of the three 2-aldoximo-6-pyridyl chelate systems are N(1)···N(2) = 2.529 (11), N(1′)···N(2′) = 2.521 (11), and N(1″)···N(2″) = 2.544 (12) Å, the mean value being 2.531 (12) Å.

Angles subtended at the nickel(II) center by adjacent pairs of nitrogen atoms define three distinct sets: those of the type N(1)–Ni–N(1′) range from 81.9 (3) to 83.4 (3)° [averaging 82.5 (8)°] and those of the type N(2)–Ni–N(2′) range from 87.6 (3) to 88.8 (3)° [averaging 88.3 (6)°], while the aldoximopyridyl chelate "bite" angles of the type N(1)–Ni–N(2) vary from 76.3 (3) to 77.5 (3)°, averaging 76.8 (6)°.

As well as being slightly tapered, the N_6 "trigonal prism" defining the nickel(II) coordination sphere is also subject to some slight rotational distortion, the mean torsional or "twist" angle [the ϕ of Holm, *et al.*[15]] being 1.6°. *Individual* values for dihedral angles of the kind N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2) are given in Table VI and shown diagramatically in Figure 3. [Here, ⟨N(1)⟩ and ⟨N(2)⟩ are the midpoints of the triangles defined by N(1), N(1′), N(1″) and N(2), N(2′), N(2″), respectively.]

The [fluoroborotris(2-aldoximo-6-pyridyl)phosphine]-nickel(II) cation has approximate, *but not exact*, C_{3v} symmetry, with F(1)–B(1)···Ni···P defining the pseudo-threefold axis. As shown in Table IVB, bond distances within the three arms of the ligand appear to be equivalent. [A possible exception is the trio defined by N(1)–C(1), N(1′)–C(1′), and N(1″)–C(1″), where individual values are 1.345 (13), 1.256 (13), and 1.308 (15) Å, respectively.]

Deviations from strict threefold symmetry manifest themselves principally in bond angle irregularities and in distortions from planarity of various portions of the aldoximopyridyl systems.

TABLE III

PRINCIPAL AXES OF ATOMIC VIBRATION ELLIPSOIDS[a–c]

Atom	B_{min} (dc's minor axis)	B_{med} (dc's median axis)	B_{max} (dc's major axes)
Ni	2.71 (111, −951, 237)	3.40 (198, −263, −957)	3.68 (−973, −162, 161)
P	3.77 (772, 158, −829)	4.38 (−138, −902, −341)	4.87 (−619, 399, −441)
N(1)	2.82 (774, −448, −671)	3.83 (−409, −893, 307)	6.44 (−481, 39, −675)
N(1′)	2.12 (−522, −591, 749)	3.90 (−19, −712, −658)	5.57 (−852, 379 , −68)
N(1″)	2.82 (292, 760, −643)	5.32 (−953, 181, 76)	6.29 (78, −624, −761)
N(2)	2.56 (485, −813, −460)	2.82 (−767, −219, −325)	3.41 (419, 539, −826)
N(2′)	2.39 (241, −876, 319)	3.70 (−749, −441, −227)	5.05 (617, −194, −920)
N(2″)	2.23 (288, −955, −35)	4.01 (−464, −194, −669)	4.93 (−837, −221, 742)
C(1)	1.74 (271, −892, −428)	3.66 (−951, −193, 79)	7.44 (143, 408, −900)
C(2)	1.55 (510, −825, −394)	3.44 (−762, −302, −297)	4.09 (398, 477, −869)
C(3)	2.39 (604, 409, 561)	4.98 (765, −309, −780)	6.88 (−223, −950, 278)
C(4)	3.01 (−522, 17, −641)	5.22 (578, −728, −534)	8.02 (−627, −685, 551)
C(5)	3.69 (−737, 598, 532)	4.85 (−46, 416, −845)	7.03 (−673, −684, −49)
C(6)	2.20 (175, −802, −598)	2.93 (−238, 528, −695)	5.45 (−955, −278, 399)
C(1′)	1.99 (201, −827, −501)	5.00 (−378, 428, −656)	5.50 (−904, −363, 504)
C(2′)	2.26 (−154, −975, −100)	3.87 (−986, 143, 392)	4.74 (−54, 168, −914)
C(3′)	2.00 (−367, −917, −25)	5.01 (180, 89, −985)	6.40 (−912, 387, 167)
C(4′)	1.26 (121, 919, 316)	5.79 (−637, 361, −439)	7.33 (760, 157, −841)
C(5′)	2.20 (199, 862, −505)	4.79 (−909, −14, −102)	7.38 (365, −507, −857)
C(6′)	3.56 (−361, 227, −740)	4.19 (−704, −701, 325)	4.56 (610, −675, −588)
C(1″)	1.84 (224, −909, 259)	6.55 (−910, −323, 49)	7.17 (346, −261, −964)
C(2″)	2.63 (−637, 662, −169)	4.86 (−141, −603, −697)	6.82 (757, 444, −696)
C(3″)	2.49 (754, −490, 171)	7.63 (−163, 503, 856)	10.64 (635, 711, −488)
C(4″)	3.33 (941, −148, −13)	6.63 (173, −559, −823)	8.75 (290, 815, −507)
C(5″)	3.40 (−849, 319, −125)	4.80 (58, −733, −659)	5.39 (524, 599, −740)
C(6″)	2.11 (−344, −508, −637)	3.42 (−928, 310, 491)	5.73 (141, 803, −593)
O(1)	2.04 (695, 553, −657)	5.72 (472, −832, −424)	7.62 (−542, −16, −622)
O(1′)	2.04 (−289, −911, 369)	3.52 (442, −389, −903)	9.60 (−848, 103, −219)
O(1″)	2.15 (260, 666, −745)	7.30 (−815, 541, 455)	8.35 (−513, −512, −487)
B(1)	2.88 (227, 497, −866)	5.47 (−973, 75, 103)	7.94 (45, −864, −489)
F(1)	2.83 (−591, −592, 707)	6.20 (260, −782, −619)	10.40 (−763, 193, −339)
B(2)	3.40 (−968, 220, 202)	5.18 (−241, −942, 297)	7.55 (56, −252, −933)
F(2)	5.13 (516, 26, −976)	7.81 (157, −985, 11)	11.00 (−842, −165, −216)
F(3)	5.52 (957, −154, −77)	8.59 (239, 894, −433)	17.59 (−158, 418, 898)
F(4)	4.84 (632, 686, 139)	7.25 (362, −672, 495)	16.08 (−685, 277, 857)
F(5)	5.13 (−248, −576, 816)	6.97 (−487, 768, 548)	12.78 (837, 276, 179)

[a] Direction cosines (dc's) are referred to the monoclinic axis system; they are multiplied by 10^3. [b] The minor, median, and major axes of the ellipsoids are defined in terms of B (the isotropic thermal parameter, having units of Å^2). The transformation to root-mean-square displacement is $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$. [c] The vibration ellipsoids are illustrated in Figure 1.

Thus, there are some slight, but, nevertheless, statistically significant, irregularities in bond angles about the boron cap of the clathro chelate ligands: the angle O(1′)–B(1)–F(1) = 110.9 (11)°, whereas the angles O(1)–B(1)–F(1) and O(1″)–B(1)–F(1) are significantly smaller, having values of 103.0 (11) and 102.7 (12)°, respectively; similarly, the angle O(1″)–B(1)–O(1) is 105.6 (11)°, whereas O(1)–B(1)–O(1′) = 116.7 (12) and O(1′)–B(1)–O(1″) = 116.4 (12)°. [These distortions may very well arise as a result of the central nickel(II) ion not being the ideal size to fit exactly the cavity within the bicyclic encapsulation ligand; *vide infra.*]

Angles about the capping phosphorus atom are equivalent within the limits of experimental error, individual values being C(6)–P–C(6′) = 97.3 (5), C(6′)–P–C(6″) = 98.8 (5), and C(6″)–P–C(6) = 98.1 (5)°, with a mean of 98.1 (8)°.

Each of the pyridyl rings is planar within the limits of experimental error; root-mean-square deviations from planarity are 0.011 Å (plane A, Table VII), 0.008 Å (plane B), and 0.005 Å (plane C). However, the three FB–($ONCHC_5H_3N$)–P arms of the fluoroborotris(2-aldoximo-6-pyridyl)phosphine anion are *not* each planar. Thus, the dihedral angles B(1)–O(1)–N(1)–C(1), O(1)–N(1)–C(1)–C(2), and N(1)–C(1)–C(2)–N(2) [and their primed counterparts] are, respectively, 177.5, 179.1, 2.3° in the unprimed aldoximopyridyl system, 177.3, 179.9, 1.0° in the singly primed system, and 176.1, 177.9, 1.5° in the doubly primed system [*cf.* Table VI].

Distortions of the entire ligand from C_{3v} symmetry are therefore principally reflected in the geometry of the O(1)–N(1)–C(1) portions of the three aldoximo moieties (which are probably the most "flexible" portions of the clathro chelate cage). Atoms in the unprimed system FB···(C_5H_3N)···P [*i.e.*, plane D of Table VII] have a root-mean-square (rms) deviation from planarity of 0.023 Å; O(1), N(1), and C(1) are coplanar with this, having individual deviations of only 0.000, −0.007, and −0.015 Å, respectively. For the analogous singly primed system [plane E of Table VII] the rms deviation of atoms is 0.028 Å, while O(1′), N(1′), and C(1′) lie −0.077, −0.056, and −0.075 Å (respectively) from this plane. Similarly, for the (doubly primed) plane F, the rms deviation of its component atoms is 0.040 Å, with O(1″), N(1″), and C(1″) lying +0.101, +0.077, and +0.070 Å, respectively, from this least-squares plane. Clearly, in these latter two cases the aldoximo (O–N–C) moiety appears to be buckled away from the plane of the remaining atoms in the pertinent arm of the cation.

Probably the most definitive measure of the distortion of the cation from strict C_{3v} symmetry comes from

TABLE IVA

INTERATOMIC DISTANCES (Å)

Atoms	Dist	Atoms	Dist
(a) Distances from Nickel Atom			
Ni–N(1)	2.008 (8)	Ni–N(2)	2.031 (7)
Ni–N(1′)	2.033 (8)	Ni–N(2′)	2.033 (8)
Ni–N(1″)	2.050 (9)	Ni–N(2″)	2.066 (8)
(b) Distances within Nonprimed Aldoximopyridyl Ligand			
B(1)–O(1)	1.478 (18)	C(4)–C(5)	1.363 (17)
O(1)–N(1)	1.372 (11)	C(5)–C(6)	1.435 (16)
N(1)–C(1)	1.345 (13)	C(6)–N(2)	1.342 (12)
C(1)–C(2)	1.457 (14)	N(2)–C(2)	1.324 (12)
C(2)–C(3)	1.392 (15)	C(6)–P	1.836 (10)
C(3)–C(4)	1.398 (16)		
(c) Distances within Singly Primed Ligand			
B(1)–O(1′)	1.449 (18)	C(4′)–C(5′)	1.389 (17)
O(1′)–N(1′)	1.364 (11)	C(5′)–C(6′)	1.374 (16)
N(1′)–C(1′)	1.256 (13)	C(6′)–N(2′)	1.395 (13)
C(1′)–C(2′)	1.445 (15)	N(2′)–C(2′)	1.367 (13)
C(2′)–C(3′)	1.380 (16)	C(6′)–P	1.826 (11)
C(3′)–C(4′)	1.391 (17)		
(d) Distances within Doubly Primed Ligand			
B(1)–O(1″)	1.494 (18)	C(4″)–C(5″)	1.353 (19)
O(1″)–N(1″)	1.381 (11)	C(5″)–C(6″)	1.391 (15)
N(1″)–C(1″)	1.308 (15)	C(6″)–N(2″)	1.355 (12)
C(1″)–C(2″)	1.469 (16)	N(2″)–C(2″)	1.315 (14)
C(2″)–C(3″)	1.377 (18)	C(6″)–P	1.850 (10)
C(3″)–C(4″)	1.375 (20)		
(e) Boron–Fluorine Distance within Cation			
B(1)–F(1)	1.376 (17)		
(f) Boron–Fluorine Distance within Anion			
B(2)–F(2)	1.386 (19)	B(2)–F(4)	1.332 (19)
B(2)–F(3)	1.349 (20)	B(2)–F(5)	1.334 (19)
(g) Nonbonded Contacts within Nickel Coordination Environment			
Ni···P	3.452 (3)	N(2′)···N(2″)	2.869 (11)
Ni···B(1)	3.089 (11)	N(2″)···N(2)	2.836 (11)
N(1)···N(1′)	2.648 (11)	N(1)···N(2)	2.529 (11)
N(1′)···N(1″)	2.716 (12)	N(1′)···N(2′)	2.521 (11)
N(1″)···N(1)	2.669 (12)	N(1″)···N(2″)	2.544 (12)
N(2)···N(2′)	2.839 (10)		

TABLE IVB

AVERAGE BOND LENGTHS (Å) IN THE MOLECULE

Atoms	No. of observns	Range	Av[a]
Ni–N(1)	3	2.008–2.050	2.030 (21)
Ni–N(2)	3	2.031–2.066	2.043 (20)
F(1)–B	1	1.376	1.376 (17)[b]
B–O(1)	3	1.449–1.494	1.473 (23)
O(1)–N(1)	3	1.364–1.381	1.372 (09)
N(1)–C(1)	3	1.256–1.345	1.303 (44)
C(1)–C(2)	3	1.445–1.469	1.457 (12)
C(2)–C(3)	3	1.377–1.392	1.383 (09)
C(3)–C(4)	3	1.375–1.398	1.388 (10)
C(4)–C(5)	3	1.353–1.389	1.368 (21)
C(5)–C(6)	3	1.374–1.435	1.400 (30)
C(6)–N(2)	3	1.342–1.395	1.364 (27)
N(2)–C(2)	3	1.315–1.367	1.335 (27)
C(6)–P	3	1.826–1.850	1.837 (12)
B(2)–F(anion)	4	1.332–1.386	1.350 (27)
N(1)···N(1′)	3	2.648–2.716	2.678 (35)
N(2)···N(2′)	3	2.836–2.869	2.848 (18)
N(1)···N(2)	3	2.521–2.544	2.531 (12)

[a] Estimated standard deviations (esd's) for average bond lengths are obtained from the expression

$$\sigma = \left[\left\{\sum_{i=1}^{i=N}(X_i - \bar{X})^2\right\}\Big/(N-1)\right]^{1/2}$$

where X_i is the ith bond length and $\bar{X}$ is the mean of the N equivalent values. [b] Individual esd (see Table IVA).

TABLE VA

INDIVIDUAL INTERATOMIC ANGLES (DEG)

(a) Angles about Nickel Atom			
N(1)–Ni–N(2)	77.5 (3)	N(2″)–Ni–N(2)	87.6 (3)
N(1′)–Ni–N(2′)	76.6 (3)	N(1)–Ni–N(2″)	134.2 (3)
N(1″)–Ni–N(2″)	76.3 (3)	N(1)–Ni–N(2′)	132.9 (3)
N(1)–Ni–N(1′)	81.9 (3)	N(1′)–Ni–N(2″)	133.7 (3)
N(1′)–Ni–N(1″)	83.4 (3)	N(1′)–Ni–N(2)	134.6 (3)
N(1″)–Ni–N(1)	82.3 (4)	N(1″)–Ni–N(2)	132.1 (3)
N(2)–Ni–N(2′)	88.6 (3)	N(1″)–Ni–N(2′)	134.7 (3)
N(2′)–Ni–N(2″)	88.8 (3)		
(b) Angles about the Boron Atom of the Cation			
O(1)–B(1)–F(1)	103.0 (11)	O(1)–B(1)–O(1′)	116.7 (12)
O(1′)–B(1)–F(1)	110.9 (11)	O(1′)–B(1)–O(1″)	116.4 (12)
O(1″)–B(1)–F(1)	102.7 (12)	O(1″)–B(1)–O(1)	105.6 (11)
(c) Angles about the Phosphorus Atom			
C(6)–P–C(6′)	97.3 (5)	C(6″)–P–C(6)	98.1 (5)
C(6′)–P–C(6″)	98.8 (5)		
(d) Angles within the Nonprimed Aldoximopyridyl Ligand			
B(1)–O(1)–N(1)	111.1 (9)	C(3)–C(4)–C(5)	119.6 (10)
O(1)–N(1)–C(1)	116.0 (9)	C(4)–C(5)–C(6)	118.1 (11)
N(1)–C(1)–C(2)	112.8 (9)	C(5)–C(6)–N(2)	120.9 (10)
C(1)–C(2)–N(2)	114.9 (8)	C(6)–N(2)–C(2)	119.4 (8)
C(1)–C(2)–C(3)	120.6 (9)	N(2)–C(6)–P	122.1 (7)
N(2)–C(2)–C(3)	124.3 (9)	C(5)–C(6)–P	116.9 (8)
C(2)–C(3)–C(4)	117.6 (10)		
(e) Angles within the Singly Primed Ligand			
B(1)–O(1′)–N(1′)	113.2 (9)	C(3′)–C(4′)–C(5′)	118.2 (11)
O(1′)–N(1′)–C(1′)	116.6 (8)	C(4′)–C(5′)–C(6′)	119.8 (10)
N(1′)–C(1′)–C(2′)	114.9 (9)	C(5′)–C(6′)–N(2′)	120.3 (10)
C(1′)–C(2′)–N(2′)	112.3 (10)	C(6′)–N(2′)–C(2′)	117.8 (10)
C(1′)–C(2′)–C(3′)	124.2 (10)	N(2′)–C(6′)–P	120.0 (9)
N(2′)–C(2′)–C(3′)	123.5 (10)	C(5′)–C(6′)–P	119.6 (8)
C(2′)–C(3′)–C(4′)	120.4 (10)		
(f) Angles within the Doubly Primed Ligand			
B(1)–O(1″)–N(1″)	111.6 (9)	C(3″)–C(4″)–C(5″)	119.5 (12)
O(1″)–N(1″)–C(1″)	117.7 (9)	C(4″)–C(5″)–C(6″)	120.4 (11)
N(1″)–C(1″)–C(2″)	113.4 (10)	C(5″)–C(6″)–N(2″)	121.0 (10)
C(1″)–C(2″)–N(2″)	116.2 (10)	C(6″)–N(2″)–C(2″)	120.2 (9)
C(1″)–C(2″)–C(3″)	123.0 (11)	N(2″)–C(6″)–P	119.9 (8)
N(2″)–C(2″)–C(3″)	120.8 (11)	C(5″)–C(6″)–P	118.9 (8)
C(2″)–C(3″)–C(4″)	118.0 (12)		
(g) Angles in the BF_4^- Anion			
F(2)–B(2)–F(3)	108.1 (13)	F(3)–B(2)–F(4)	110.2 (14)
F(2)–B(2)–F(4)	105.6 (12)	F(3)–B(2)–F(5)	111.0 (13)
F(2)–B(2)–F(5)	109.1 (14)	F(4)–B(2)–F(5)	112.6 (13)

TABLE VB

AVERAGE BOND ANGLES (DEG)

Atoms	No. of observns	Range	Av[a]
N(1)–Ni–N(2)	3	76.3–77.5	76.8 (6)
N(1)–Ni–N(1′)	3	81.9–83.4	82.5 (8)
N(2)–Ni–N(2′)	3	87.6–88.8	88.3 (6)
F(1)–B(1)–O(1)	3	102.7–110.9	105.5 (43)
O(1)–B(1)–O(1′)	3	105.6–116.7	112.9 (65)
B(1)–O(1)–N(1)	3	111.1–113.2	112.0 (11)
O(1)–N(1)–C(1)	3	116.0–117.7	116.8 (9)
N(1)–C(1)–C(2)	3	112.8–114.9	113.7 (11)
C(1)–C(2)–N(2)	3	112.3–116.2	114.5 (20)
C(1)–C(2)–C(3)	3	120.6–124.2	122.6 (16)
N(2)–C(2)–C(3)	3	120.8–124.3	122.9 (18)
C(2)–C(3)–C(4)	3	117.6–120.4	118.7 (15)
C(3)–C(4)–C(5)	3	118.2–119.6	119.1 (8)
C(4)–C(5)–C(6)	3	118.1–120.4	119.4 (14)
C(5)–C(6)–N(2)	3	120.3–121.0	120.7 (4)
C(6)–N(2)–C(2)	3	117.8–120.2	119.1 (12)
N(2)–C(6)–P	3	119.9–122.1	120.7 (13)
C(5)–C(6)–P	3	116.9–119.6	118.5 (14)
C(6)–P–C(6′)	3	97.3–98.8	98.1 (8)
F–B(2)–F(anion)	6	105.6–112.6	109.4 (24)

[a] See footnote *a* to Table IVB.

consideration of the dihedral angles O(1)–B(1)···P–C(6), O(1′)–B(1)···P–C(6′), and O(1″)–B(1)···P–C(6″). These should be strictly zero for true C_{3v} symmetry but are, in fact, 2.0, 2.9, and 6.4°, respectively—see Table VI.

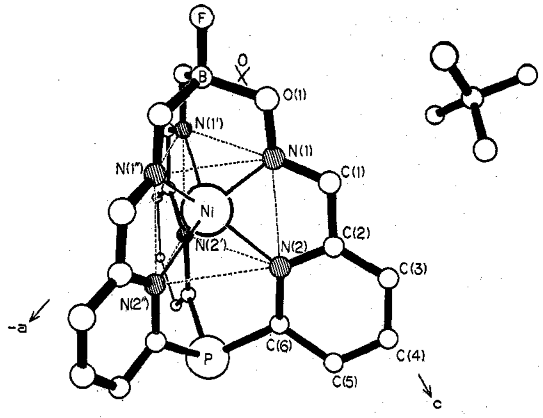

Figure 2.—The molecule, viewed down "*b*" showing the essential trigonal-prismatic coordination of Ni(II) by six nitrogen atoms.

TABLE VI

DIHEDRAL ANGLES WITHIN THE MOLECULE (DEG)

O(1)–B(1)···P–C(6)	2.0
O(1′)–B(1)···P–C(6′)	2.9
O(1″)–B(1)···P–C(6″)	6.4
B(1)–O(1)–N(1)–C(1)	177.5
B(1)–O(1′)–N(1′)–C(1′)	177.3
B(1)–O(1″)–N(1″)–C(1″)	176.1
O(1)–N(1)–C(1)–C(2)	179.1
O(1′)–N(1′)–C(1′)–C(2′)	179.9
O(1″)–N(1″)–C(1″)–C(2″)	177.9
N(1)–C(1)–C(2)–N(2)	2.3
N(1′)–C(1′)–C(2′)–N(2′)	1.0
N(1″)–C(1″)–C(2″)–N(2″)	1.5
N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2)	1.83[a]
N(1′)–⟨N(1)⟩–⟨N(2)⟩–N(2′)	1.10[a]
N(1″)–⟨N(1)⟩–⟨N(2)⟩–N(2″)	1.82[a]

[a] ⟨N(1)⟩ and ⟨N(2)⟩ are defined as the centers of the triangles N(1), N(1′), N(1″) and N(2), N(2′), N(2″), respectively.

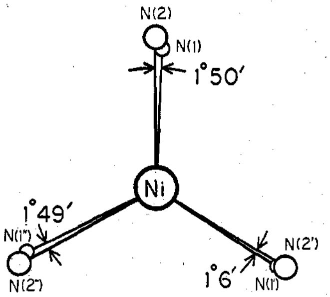

Figure 3.—The NiN_6 core of the molecule, showing the slight deviations from true D_{3h} geometry.

While details of the distortion from C_{3v} symmetry of the $[\{FB(ONCHC_5H_3N)_3P\}(Ni^{II})^+]$ ion are well-defined (*vide supra*), there is no unique explanation. Four principal factors may be mentioned. These are the following (not necessarily in order of priority, nor necessarily mutually exclusive).

(i) **Relative Sizes of the Ni^{2+} Ion and the Cavity within the Encapsulation Ligand.**—Any lack of precise match will prevent perfect trigonal-prismatic coordination of the enclosed metal ion. Wagner[27] has derived the geometric relationships among the rotational

TABLE VII

LEAST-SQUARES PLANES[a,b] WITHIN THE $[\{FB(ONCHC_5H_3N)_3P\}Ni^+]$ CATION

Atom	Dev, Å	Atom	Dev, Å
(A) Unprimed Pyridyl Group: $0.4252X - 0.9037Y - 0.1834Z = 2.834$			
C(2)	+0.016	C(5)	+0.007
C(3)	−0.006	C(6)	+0.003
C(4)	−0.005	N(2)	−0.014
(B) Singly Primed Pyridyl Group: $0.7373X - 0.2110Y + 0.3715Z = 8.095$			
C(2′)	−0.011	C(5′)	0.000
C(3′)	+0.005	C(6′)	−0.006
C(4′)	+0.001	N(2′)	+0.012
(C) Doubly Primed Pyridyl Group: $0.2806X - 0.6090Y + 0.6128Z = 5.046$			
C(2″)	+0.005	C(5″)	+0.003
C(3″)	−0.007	C(6″)	−0.005
C(4″)	+0.003	N(2″)	+0.001
(D) $0.4312X - 0.9004Y - 0.1932Z = 2.867$			
P(1)	−0.004	N(2)	−0.003
C(2)	+0.031	C(1)*	0.000
C(3)	−0.001	N(1)*	−0.007
C(4)	−0.014	O(1)*	−0.015
C(5)	−0.007	B(1)	0.039
C(6)	0.000	F(1)	−0.041
(E) $0.7207X - 0.2353Y + 0.3867Z = 7.987$			
P(1)	+0.006	N(2′)	−0.032
C(2′)	−0.052	C(1′)*	−0.077
C(3′)	0.000	N(1′)*	−0.056
C(4′)	+0.033	O(1′)*	−0.075
C(5′)	+0.032	B(1)	+0.009
C(6′)	−0.014	F(1)	+0.018
(F) $0.3087X - 0.6228Y + 0.5820Z = 5.261$			
P(1)	+0.035	N(2″)	+0.030
C(2″)	+0.058	C(1″)*	+0.101
C(3″)	+0.018	N(1″)*	+0.077
C(4″)	−0.028	O(1″)*	+0.070
C(5″)	−0.049	B(1)	−0.056
C(6″)	−0.026	F(1)	+0.019

[a] Equations to planes are given in cartesian coordinates (X, Y, Z) which are related to the fractional cell coordinates (x, y, z) by the transformation $[X, Y, Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [b] Atoms marked with an asterisk were given zero weight in the least-squares plane calulation; all other atoms entered below the equation to a specific plane were given unit weight.

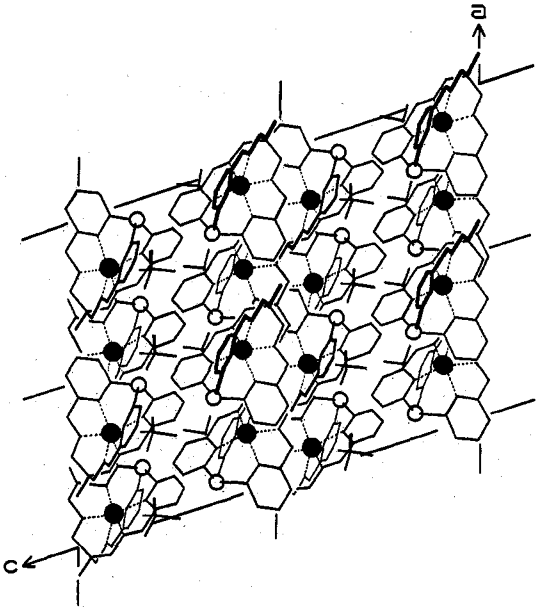

Figure 4.—Packing of ions within the unit cell.

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[27] B. E. Wagner, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

distortion (ϕ) from a regular trigonal-prismatic coordination geometry, the metal–ligand bond distances (Ni–N in the present case), the bite distance of the chelate system (N(1)···N(2), etc., here), and the mean distance between metal-bonded atoms within the two triangular ends of the trigonal prism (*i.e.*, the mean of N(1)···N(1′) and N(2)···N(2′) distances in the present molecule). Based on the *distances* derived from the present structural analysis, the twist angle is calculated as 2° 12′ (found 1° 35′).

(ii) **Ligand Field Effects.**—Wentworth, *et al.*,[28] suggested that the tendency toward an octahedral (rather than trigonal-prismatic) geometry should decrease in the order: d^6 (low-spin) > d^8 > d^7 > d^{10} = d^5 (high-spin). That the present d^8 Ni(II) complex adopts a geometry very close to trigonal prismatic is indicative either of a very rigid cage or of the fulfillment of conditions outlined under (i).

(iii) **General Strain Effects.**—The simultaneous requirements for metal–ligand interactions coupled with retention of the total ligand geometry will almost certainly cause strain somewhere in the species. It is probably this net effect that causes the slight buckling of two of the three aldoximo moieties from their respective FB···(C_5H_3N)···P planes.

(iv) **Interionic Repulsion.**—We may note that there are some close contacts between the doubly primed aldoximopyridyl system and a BF_4^- anion. Thus H(5″)···F(3) = 2.348 Å, H(4″)···F(5) = 2.577 Å, and H(5″)···F(5) = 2.743 Å. [Accepted van der Waals radii for hydrogen and fluorine are ~1.2 and ~1.35 Å.[29]] Effects of this kind will not, of course, be maintained in solution.

The packing of ions within the unit cell is shown in Figure 4.

Further crystallographic studies on these systems, presently in progress, should help to clarify these findings. It should be noted that preliminary data on the d^6 iron(II) species $[\{FB(ONCHC_5H_3N)_3P\}(Fe^{II})^+]$ show the mean twist angle, ϕ, to be 21° 32′.[16] Details of this structure, and of others in this series, will be published at a later date.

Acknowledgments.—We thank Professor R. H. Holm and Drs. J. E. Parks and B. E. Wagner for providing samples of the complex studied and for many informative conversations. This work was supported, in part, by National Science Foundation Grant No. GP-26293 (awarded to M. R. C.).

[28] W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, **9**, 1825 (1970).

[29] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 115.

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Synthesis and Molecular Geometry of Hexameric Triphenylphosphinocopper(I) Hydride and the Crystal Structure of $H_6Cu_6(PPh_3)_6 \cdot HCONMe_2$

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Received March 9, 1972

The thermally stable phosphinocopper(I) hydride cluster $H_6Cu_6(PPh_3)_6$ has been prepared from the reaction of $(PPh_3CuCl)_4$ and sodium trimethoxyborohydride in dimethylformamide (DMF). It crystallizes from DMF as $H_6Cu_6(PPh_3)_6 \cdot$DMF in the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}; No. 61) with $a = 40.10 \pm 0.04$, $b = 22.46 \pm 0.02$, $c = 21.86 \pm 0.02$ Å, and $Z = 8$. Observed and calculated densities are 1.367 ± 0.005 and 1.368 g cm^{-3}, respectively. A single-crystal X-ray diffraction study based on counter data ($\sin \theta_{max} = 0.65$, Cu Kα radiation) has led to the location of all 125 nonhydrogen atoms, the final discrepancy index being $R_F = 9.2\%$ for 3180 independent nonzero reflections. The crystal consists of discrete molecular units of $H_6Cu_6(PPh_3)_6$ and DMF, mutually separated by normal van der Waals distances. The $H_6Cu_6(PPh_3)_6$ molecule contains a (slightly distorted) octahedral cluster of copper atoms. Two mutually trans faces of this octahedron are enlarged with their copper–copper distances ranging from 2.632 (6) to 2.674 (5) and averaging 2.655 ± 0.017 Å, while the remaining six copper–copper bond lengths range from 2.494 (6) to 2.595 (5), averaging 2.542 ± 0.044 Å. Each copper atom is apically bonded to a triphenylphosphine ligand with copper–phosphorus distances varying from 2.217 (7) to 2.262 (7), averaging 2.240 ± 0.017 Å. Decomposition of the complex with $C_6H_5CO_2D$ yields H_2 and HD (but no D_2) in varying proportions. An assay of liberated [^{1}H]hydrogen indicates that the cluster is associated with *six* hydride ligands. Possible sites for these ligands (which were not located from the diffraction study) are discussed.

Introduction

Although Würtz prepared a "copper(I) hydride" rather more than a century ago,[3] no truly *stoichiometric* hydridocopper species has yet been isolated although indirect evidence has indicated that thermally unstable phosphine adducts of copper hydride [such as R_3P-$(CuH)_2$,[4] (diphos)$(CuH)_2$,[4] and (n-Bu_3P)CuH[5]] exist in solution.

We have now found that the reaction of tetrameric triphenylphosphinocopper chloride (also the corresponding bromide, iodide, cyanide, thiocyanate) with sodium trimethoxyborohydride in dimethylformamide (DMF) under an inert atmosphere yields hexameric

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[3] A. Würtz, *Ann. Chim. Phys.*, [3] **11**, 250 (1844).

[4] J. S. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, **91**, 4088 (1969).

[5] G. M. Whitesides, J. San Filippo, E. R. Stredronsky, and C. P. Casey, *ibid.*, **91**, 6542 (1969).