Contribution No. 2714 from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

The Crystal and Molecular Structure of a Pentakis (Alkyl Phosphite) Nickel(II) Perchlorate, $Ni(P(OC_2H_3)_3)_5(ClO_4)_2$*

E. F. Riedel and R. A. Jacobson

Received April 10, 1970

The crystal and molecular structure of pentakis-2,8,9-trioxa-1-phosphaadamantane-nickel(II) perchlorate, $Ni(P(OC_2H_3)_3)_5(ClO_4)_2$, has been determined from three-dimensional X-ray data collected by counter techniques. Due to disorder in one of the perchlorate groups and the large number of parameters involved, only isotropic refinement was carried out, to a final R *factor of 0.15. The material crystallized in space group $P\bar{1}$ with lattice parameters* a = *11.53(5),* b = *18.92(7),* c = *12.61(5) Å,* α = *96.4(5),* β = *103.4(6), and* γ = *96.9(5)°. There are two molecules per unit cell and the calculated density is 1.67 g/cc. The inner coordination about the nickel atom is approximately trigonal bipyramidal. The average axial bond distance is somewhat shorter than the equitorial distance, 2.14(1) vs. 2.19(1) Å.*

Introduction

Recently the synthesis of a yellow diamagnetic complex $Ni(P(OCH_3)_3)_5(ClO_4)_2$ was reported,[1] and it was indicated on the basis of similar magnetic, spectral and conductivity properties that the complex containing the adamantane-like phosphite $Ni(P(OCH)_3(CH_2)_3)_5(ClO_4)_2$ [2] (hereafter referred to as $NiP_5(ClO_4)_2$) was probably also five-coordinate. We decided to carry out a single crystal X-ray investigation to firmly establish the coordination number of the nickel in this compound and to ascertain whether the cationic configuration was trigonal bipyramidal or tetragonal pyramidal in the event the nickel was five-coordinate. The number of such five-coordinate transition metal complexes containing monodentate ligands has multiplied rapidly in the past few years,[3-5] but it is still difficult to predict which of the two idealized geometries will be utilized in a given complex. The recent study on $Ni(CN)_5^{3-}$ illustrates that idealized geometries are not always utilized;[6] this anion exists in both trigonal bipyramidal and tetragonal pyramidal forms albeit distorted. It should also be noted that CN^- and $P(OR)_3$ have been shown to have very similar ligand field properties.[7]

Experimental Section

A sample of the compound was kindly supplied by J. G. Verkade. A number of solvents were tried in an attempt to obtain good single crystals for an X-ray analysis and finally a benzene-nitrobenzene mixture yielded untwinned yellow parallelipiped crystals. The crystals were mounted in glass capillaries to prevent decomposition in the atmosphere, and Weissenberg and precession photographs were taken. All photographs showed an absence of mirroring implying a triclinic space group. This space group was assumed to be $P\bar{1}$ on the basis of an analysis of the Patterson map and from the results of a statistical analysis,[8] and later confirmed by successful refinement in this space group. There are two molecules per unit cell giving a calculated density of 1.67 g/cc, in good agreement with the observed density of 1.65 g/cc which was determined by flotation techniques . The conventional reduced cell[9] lattice parameters are

$a = 11.53 \pm 0.05$ Å $\qquad \alpha = 96.4 \pm 0.5°$

$b = 18.92 \pm 0.07 \qquad \beta = 103.4 \pm 0.6$

$c = 12.61 \pm 0.05 \qquad \gamma = 96.9 \pm 0.5$

These parameters and their standard deviations were obtained from repeated film measurements.

For data collection, a crystal having the approximate dimensions 0.74×0.5×0.5 mm was selected and mounted on a General Electric single crystal orienter unit. Complete three-dimensional data were collected within a 2θ sphere of 50° in two octants and within 40° in the other two octants using Mo Kα radiation. Because of appreciable decomposition effects, data were collected using a 40-sec stationary crystal-stationary counter counting technique. A tabulation of background intensity *vs.* 2θ was made after the independence of the background on chi and phi was established.

The decomposition of the crystal in the X-ray beam was followed by measuring the peak height intensi-

---

(*) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(1) K. J. Coskran, J. J. Huttemann, and J. G. Verkade, *Advances in Chemistry*, 590 (1967).

(2) J. J. Huttemann, B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, *4*, 950 (1965).

(3) J. A. Ibers, *Ann. Rev. Phys. Chem.*, *16*, 375 (1965).

(4) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), *20*, 245 (1966).

(5) J. S. Wood, *Coord. Chem. Rev.*, *2*, 403 (1967).

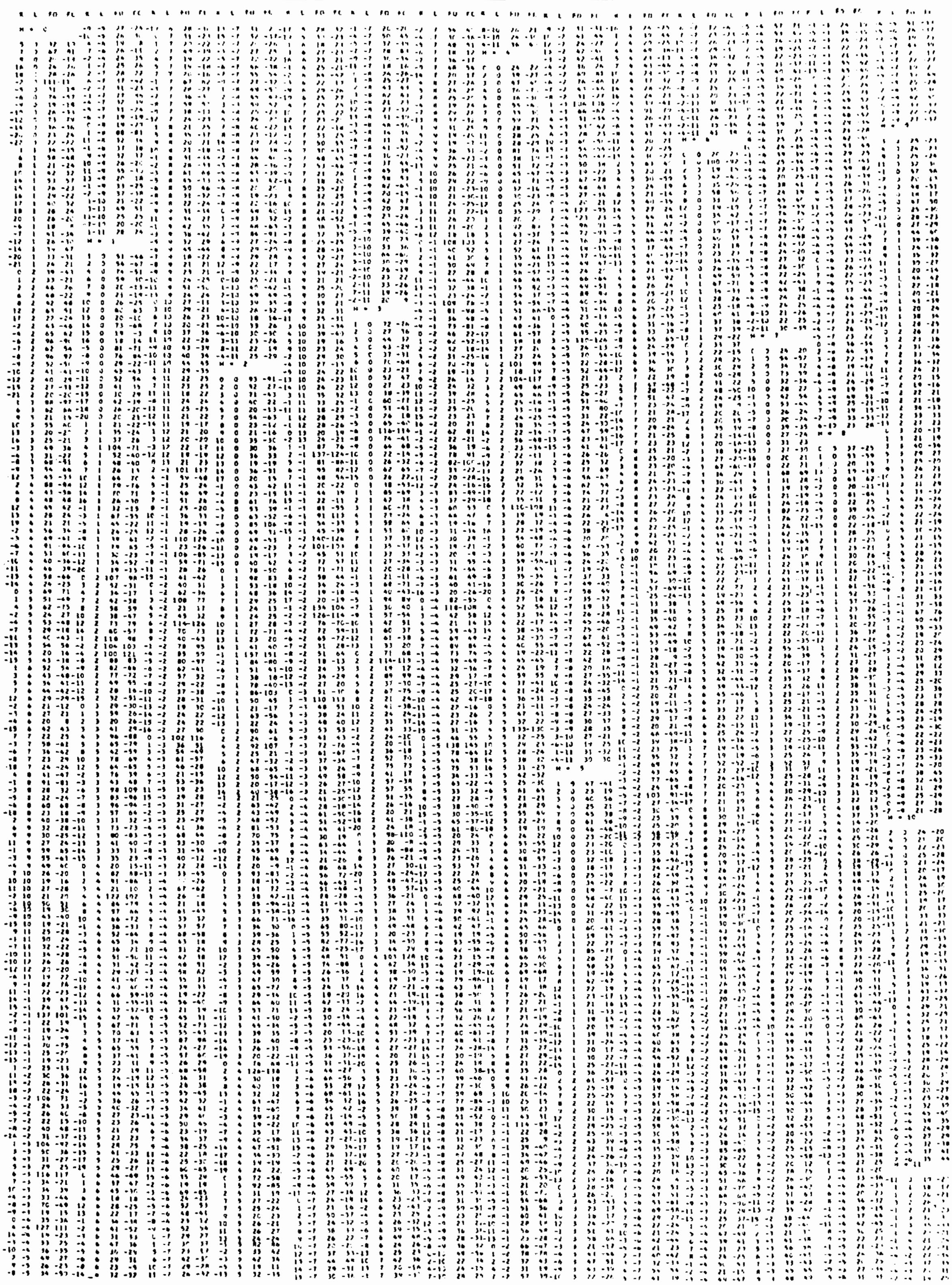
(6) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, *7*, 1362 (1968).

(7) J. G. Verkade, private communication.

(8) E. R. Howells, D. C. Philips, and D. Rogers, *Acta Cryst.*, *3*, 210 (1950).

(9) S. L Lawton and R. A. Jacobson, « The Reduced Cell and Its Crystallographic Applications », USAEC Rept. IS-1141 (1965).

Table I. Observed and Calculated Structure Factors (Columns are *h, k, F_o* and F_o).



ties of four standard reflections. Decomposition, even with the use of peak height methods, amounted to 30% over the data collection period. The intensity data were also corrected for Lorentz-polarization effects and for streak effects.[10] Because of the small absorption coefficient, $\mu = 11.62$ cm^{-1}, and especially the small difference between the maximum and minimum transmission factors, no correction for

---

[10] D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, *86*, 1660 (1954).

absorption was applied.

A theoretical curve was used to correct the peak height data to integrated intensity data. This was done following the method of Alexander and Smith[11] using the experimental values determined by Furnas.[12]

Errors in the intensities were estimated and weights assigned using the method described by Hoard and Jacobson,[13] and a total of 2300 structure factors were found to be greater than or equal to three times their standard errors and were considered to be observed.

Solution and Refinement of the Structure. A Patterson map was computed from sharpened data[14] and the nickel-nickel vector was readily found. Three superpositions were carried out using this nickel-nickel vector and two nickel-phosphorus vectors, and resulted in a recognizable image of most of the molecule. By a combination of structure factor and electron density map calculations, all the atoms were located with the exception of some of the oxygen atoms in one of the perchlorate ions. It was found that this one perchlorate ion was disordered, and although one of its oxygens was readily located, only small peaks for two of the other oxygens were found, and no clear evidence for the third was present. These two oxygens were included in the refinement as whole atoms with large temperature factors·

A full-matrix least-squares refinement[15] was carried out with all atoms isotropic. Scattering factors of Hanson, Herman, Lea and Skillman[16] were used, with the scattering factor for nickel corrected for anomalous dispersion.[17] It was observed on a difference electron density map that there was appreciable anisotropic motion of the nickel, chlorine and phosphorus atoms. An attempt was made to refine these atoms anisotropically, but due to the large number of atoms in the asymmetric unit, only half of the parameters could be varied in one cycle. The results did indicate that there is appreciable anisotropic motion of these atoms, but the splitting of the variables used was found to be unsatisfactory. For this reason and because of the long cycle time, it was decided to discontinue the anisotropic refinement. The results did indicate that the conventional discrepency factor ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$) would drop approximately five percent below that for the isotropic discrepancy factor. Isotropic least-squares refinement and a final weighting scheme adjustment on the 2300 observed reflections gave a final R of 15.0%.

A list of the calculated and observed structure factors is given in Table I and the final positional and thermal parameters are given in Table II. The interatomic distances and their errors were computed using the program of Busing, Martin ana Levy[18] and are given in Table III.

Table II. Final Parameters and Standard Errors for Ni-$(PO_3C_6H_9)_5(ClO_4)_2$

Atom	x	y	z	B
Ni	0.0294(4) [a]	0.2533(2)	0.4657(4)	3.2(1)
P_1	0.1733(8)	0.3055(5)	0.6015(8)	3.1(2)
P_2	0.8875(8)	0.2034(5)	0.3255(8)	3.6(2)
P_3	0.9019(8)	0.2531(5)	0.5675(7)	3.0(2)
P_4	0.0579(8)	0.3456(5)	0.3772(8)	3.5(2)
P_5	0.1251(8)	0.1600(5)	0.4564(8)	3.2(2)
O_{11}	0.1762(9)	0.2719(11)	0.7081(18)	4.0(5)
O_{12}	0.2988(21)	0.3078(13)	0.5812(20)	4.9(5)
O_{13}	0.1654(20)	0.3899(12)	0.6387(19)	4.6(5)
O_{21}	0.7991(21)	0.2540(13)	0.2866(20)	5.0(5)
O_{22}	0.8011(21)	0.1371(12)	0.3506(20)	4.9(5)
O_{23}	0.9309(21)	0.1712(13)	0.2258(20)	5.0(6)
O_{31}	0.8936(19)	0.1845(12)	0.6241(19)	4.4(5)
O_{32}	0.9305(19)	0.3191(12)	0.6731(18)	4.4(5)
O_{33}	0.7630(19)	0.2562(12)	0.5085(19)	4.3(5)
O_{41}	0.1891(20)	0.3912(12)	0.4098(19)	4.6(5)
O_{42}	—0.0135(21)	0.4042(13)	0.4113(20)	5.2(6)
O_{43}	0.0208(23)	0.3318(15)	0.2448(22)	6.2(6)
O_{51}	0.2131(23)	0.1468(14)	0.5647(22)	6.1(6)
O_{52}	0.0457(20)	0.0826(12)	0.4165(18)	4.4(5)
O_{53}	0.2051(22)	0.1658(14)	0.3681(21)	5.8(6)
C_{111}	0.2741(34)	0.3018(21)	0.8091(32)	5.4(9)
C_{102}	0.3895(36)	0.2949(21)	0.7738(34)	5.8(9)
C_{123}	0.3967(35)	0.3390(21)	0.6711(33)	5.4(9)
C_{104}	0.3799(35)	0.4168(21)	0.7045(33)	5.8(10)
C_{135}	0.2593(27)	0.4223(16)	0.7362(26)	3.2(7)
C_{106}	0.2464(48)	0.3860(30)	0.8302(46)	9.4(14)
C_{211}	0.6838(41)	0.2311(25)	0.1843(38)	7.3(11)
C_{204}	0.7650(43)	0.2011(26)	0.1007(41)	7.8(12)
C_{235}	0.8345(33)	0.1404(20)	0.1169(31)	5.0(9)
C_{202}	0.7601(35)	0.0808(21)	0.1641(33)	5.5(9)
C_{223}	0.7083(31)	0.1038(19)	0.2546(31)	4.6(8)
C_{206}	0.6191(58)	0.1725(36)	0.2157(53)	11.7(17)
C_{306}	0.6837(39)	0.1743(24)	0.6235(37)	6.7(10)
C_{335}	0.6801(33)	0.2561(21)	0.5801(32)	5.2(9)
C_{304}	0.7215(43)	0.3186(26)	0.6685(41)	7.8(12)
C_{323}	0.8453(32)	0.3125(32)	0.7439(30)	4.6(8)
C_{302}	0.8383(37)	0.2371(23)	0.7883(36)	6.3(10)
C_{311}	0.8090(32)	0.1796(19)	0.6972(30)	4.6(8)
C_{435}	0.0449(42)	0.3933(26)	0.1859(39)	7.2(11)
C_{404}	—0.0363(52)	0.4377(32)	0.2203(50)	10.4(15)
C_{423}	—0.0061(37)	0.4736(22)	0.3589(35)	6.0(9)
C_{402}	0.1308(49)	0.5039(29)	0.4027(45)	9.3(14)
C_{411}	0.2128(41)	0.4567(27)	0.3583(39)	7.4(11)
C_{406}	0.1669(42)	0.4232(25)	0.2203(39)	7.4(11)
C_{511}	0.2891(36)	0.0928(22)	0.5522(35)	5.9(10)
C_{502}	0.1858(37)	0.0206(22)	0.5158(36)	6.4(10)
C_{523}	0.1162(35)	0.0217(21)	0.4112(33)	5.4(9)
C_{504}	0.1722(44)	0.0289(27)	0.3076(42)	8.4(13)
C_{535}	0.2737(34)	0.1047(20)	0.3597(31)	5.1(9)
C_{506}	0.3570(35)	0.1023(21)	0.4660(33)	5.6(9)
Cl_1	0.4259(9)	0.9409(5)	0.1890(8)	4.9(2)
O_1	0.3008(29)	0.9290(17)	0.1544(27)	8.4(8)
O_2	0.4767(26)	0.8738(16)	0.1922(25)	7.6(7)
O_3	0.4640(29)	0.9828(18)	0.2997(28)	8.9(9)
O_4	0.4655(28)	0.9851(17)	0.1136(26)	8.4(8)
Cl_2	0.2901(11)	0.5757(6)	0.0394(11)	6.5(3)
O_5	0.3274(49)	0.5658(30)	—0.0565(48)	16.7(17)
O_6	0.3477(31)	0.5650(19)	0.1490(30)	9.6(9)
O_7	0.1836(43)	0.5455(25)	0.0314(38)	13.5(13)

[a] Numbers in parentheses here and in the succeding table are estimated standard deviations in the least significant digits.

Results and Discussion

The crystal structure is made up of discrete monomer units and all intermolecular contacts appear

---

(11) L. E. Alexander and G. S. Smith, *Acta Cryst.*, *15*, 983 (1962).

(12) T. Furnas, « Single Crystal Orienter Instruction Manual », General Electronic Company, Milwaukee, Wisconsin (1957).

(13) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.*, (A), 1203 (1966).

(14) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Cryst.*, *14*, 598 (1961).

(15) W. R. Busing, K. O. Martin, and H. A. Levy, « ORFLS, A FORTRAN Crystallographic Least-Squares Program », ORNL-TM-305 (1962).

(16) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, *17*, 1040 (1964).

(17) « International Tables for X-ray Crystallography », Vol. III, The Knoch Press, Birmingham, England, pp. 215-6 (1962).

Table III. Selected Distances (Å) and Angles (°)

Atoms	Distances
Ni—P$_1$	2.14(1)
Ni—P$_2$	2.15(1)
(Av. Ni—P$_{ax}$)	2.144(15)
Ni—P$_3$	2.16(1)
Ni—P$_4$	2.21(1)
Ni—P$_5$	2.20(1)
(Av. Ni—P$_{eq}$)	2.190(10)
P$_1$—O$_{11}$	1.54(2)
P$_1$—O$_{12}$	1.52(2)
P$_1$—O$_{13}$	1.63(3)
P$_2$—O$_{21}$	1.52(3)
P$_2$—O$_{22}$	1.61(3)
P$_2$—O$_{23}$	1.55(3)
P$_3$—O$_{31}$	1.55(2)
PP$_3$—O$_{32}$	1.66(3)
P$_3$—O$_{33}$	1.61(2)
P$_4$—O$_{41}$	1.59(3)
P$_4$—O$_{42}$	1.54(3)
P$_4$—O$_{43}$	1.61(3)
P$_5$—O$_{51}$	1.57(3)
P$_5$—O$_{52}$	1.59(3)
P$_5$—O$_{53}$	1.61(3)
(Av. P—O)	1.58(2)
O$_{11}$—C$_{111}$	1.50(4)
O$_{12}$—C$_{123}$	1.42(4)
O$_{13}$—C$_{135}$	1.45(4)
O$_{21}$—C$_{211}$	1.60(4)
O$_{22}$—C$_{223}$	1.44(4)
O$_{23}$—C$_{235}$	1.56(4)
O$_{31}$—C$_{311}$	1.49(4)
O$_{32}$—C$_{323}$	1.48(4)
O$_{33}$C—$_{335}$	1.46(4)
O$_{41}$—C$_{411}$	1.49(5)
O$_{42}$—C$_{423}$	1.54(4)
O$_{43}$—C$_{435}$	1.48(5)
O$_{51}$—C$_{511}$	1.44(5)
O$_{52}$—C$_{523}$	1.49(4)
O$_{53}$—C$_{535}$	1.48(4)
(Av. O—C)	1.49(3)
Cl$_1$—O$_1$	1.39(3)
Cl$_1$—O$_2$	1.46(3)
Cl$_1$—O$_3$	1.47(3)
Cl$_1$—O$_4$	1.45(3)
Cl$_2$—O$_5$	1.44(4)
Cl$_2$—O$_6$	1.38(6)
Cl$_2$—O$_7$	1.30(5)
(Av. Cl—O)	1.41(3)
P$_1$—P$_3$	3.08(2)
P$_1$—P$_4$	3.05(2)
P$_1$—P$_5$	3.05(2)
P$_2$—P$_3$	3.05(2)
P$_2$—P$_4$	3.05(2)
P$_2$—P$_5$	3.11(2)
P$_3$—P$_4$	3.77(2)
P$_3$—P$_5$	3.73(2)
P$_4$—P$_5$	3.87(2)
C$_{111}$—C$_{102}$	1.51(5)
C$_{102}$—C$_{123}$	1.63(5)
C$_{123}$—C$_{104}$	1.53(5)
C$_{104}$—C$_{135}$	1.54(5)
C$_{135}$—C$_{106}$	1.46(6)
C$_{106}$—C$_{111}$	1.67(7)
C$_{211}$—C$_{202}$	1.66(7)
C$_{202}$—C$_{223}$	1.48(6)
C$_{223}$—C$_{204}$	1.59(5)
C$_{204}$—C$_{235}$	1.45(5)
C$_{235}$—C$_{206}$	1.79(7)
C$_{206}$—C$_{211}$	1.41(7)
C$_{311}$—C$_{302}$	1.44(5)
C$_{302}$—C$_{323}$	1.59(5)
C$_{323}$—C$_{304}$	1.55(5)
C$_{340}$—C$_{335}$	1.48(6)
C$_{335}$—C$_{306}$	1.70(6)
C$_{306}$—C$_{311}$	1.51(5)
C$_{411}$—C$_{402}$	1.53(6)
C$_{402}$—C$_{423}$	1.56(6)
C$_{423}$—C$_{404}$	1.74(7)
C$_{404}$—C$_{435}$	1.44(7)
C$_{435}$—C$_{406}$	1.41(6)
C$_{406}$—C$_{411}$	1.72(6)
C$_{511}$—C$_{502}$	1.65(5)
C$_{502}$—C$_{523}$	1.38(5)
C$_{523}$—C$_{504}$	1.60(5)
C$_{504}$—C$_{535}$	1.70(6)
C$_{535}$—C$_{306}$	1.47(5)
C$_{506}$—C$_{511}$	1.49(5)
(Av. C—C)	1.56(4)
Atoms	**Angle**
P$_1$—Ni—P$_3$	91.5(6)
P$_1$—Ni—P$_4$	89.3(6)
P$_1$—Ni—P$_5$	89.2(6)
P$_2$—Ni—P$_3$	90.1(6)
P$_2$—Ni—P$_4$	88.7(7)
P$_2$—Ni—P$_5$	91.3(7)
P$_3$—Ni—P$_4$	119.3(6)
P$_3$—Ni—P$_5$	117.5(6)
P$_4$—Ni—P$_5$	123.2(5)
Ni—P—O (Av.)	115(1)
P—O—C (Av.)	116(2)
O—P—O (Av.)	104(1)
C—C—C (Av.)	112(4)
O—Cl—O (Av.)	111(3)

to be normal. A stereoscopic view[19] of the molecular structure is given in Figure 2.

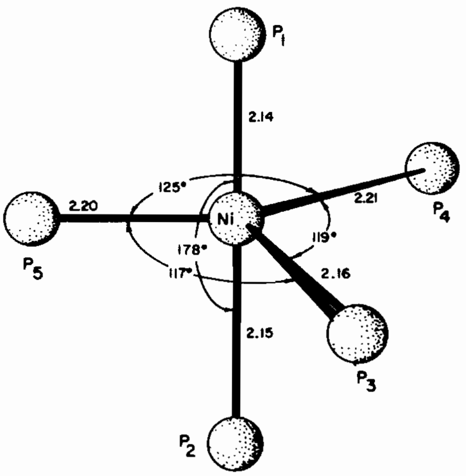


Figure 1. A drawing showing the inner coordination sphere of Ni[P(OCH)$_3$(CH$_2$)$_3$]$_5$$^{2+}$ with selected distances and angles. All P$_{ax}$—Ni—P$_{eq}$ angles are 90±2°.

The conformation of the NiP$_5$ cation is found to be trigonal bipiramidal with approximate D$_{3h}$ symmetry. All the angles are within a few degrees of the values expected for the trigonal bipiramidal configuration. This constitutes the first structural example of a d^8 complex containing five unidentate phosphorus ligands. It is of singular interest that there is a compression of the Ni–P bond distance along three-fold direction. The average nickel-phosphorus axial bond distances 2.14±0.01 Å while the average nickel-phosphorus equitorial bond distance is 2.19±0.01 Å. Because of the reasonably large standard deviations, this difference might be considered only marginally significant. However, similar axial contractions have been found in other studies, particularly in the trigonal bipyramid $Ni(CN)_5^{3-}$ ion[6] and $CuCl_5^{3-}$ ion.[20] The contraction of the axial bond length relative to the equitorial was especially evident in this last case and for a trigonal-bipyramidal low spin d^8 or d^9 complex was explained readily in terms of an electron pair repulsion model. A similar result can be obtained using a molecular orbital model.

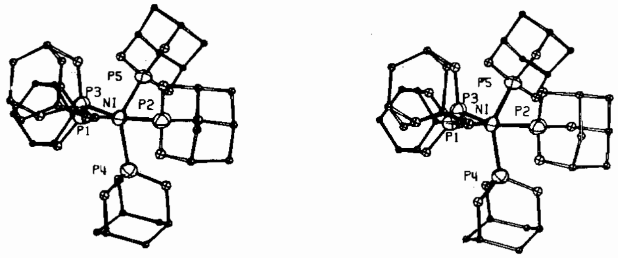


Figure 2. Stereoscopic view of $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$.

The equitorial Ni–P bond lengths are well within the range of values reported for similar bonds in other compounds, such as 2.18 Å in $Ni(HP(C_6H_5)_2)_3I_2$,[21] 2.22 Å in $Ni(P(C_2H_5)_2)_3(C{\equiv}CC_6H_5)_2$,[22] 2.21 Å in $Ni(TAP)CNClO_4$ (TAP = $P(CH_2CH_2CH_2As(CH_3)_2)_3$,[23] and 2.19 and 2.21 Å in $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$.[24] The average P–O and O–C distances in the ligands are 1.58 and 1.49 Å, respectively. These distances are close to those tabulated by Corbridge in a recent review,[25] in which the average P–O and O–C bond lengths for similar ligands are given at 1.59±0.05 1.44±0.04 Å. Other average distances and angles given in Table III also agree well with values previously reported. Because of the size of the cation, some disorder in the perchlorate groups would not be unexpected, particularly since perchlorates have a tendency to disorder.

In our attempts to obtain crystals, we found that the crystals obtained from other solvents, although of poor quality, apeared to crystallize in one of several other space groups. There are several possible explanations for this. These crystals may contain molecules of solvent in the unit cell, or the solvent molecule may act as a ligand to form an octahedral complex, or an exchange may have taken place between a molecule of solvent and the ligand. Because of the poor quality of these crystals, no detailed crystallographic work could be done on these species.

Acknowledgement. Helpful discussions with J. G. Verkade are gratefully acknowledgement.

---

(18) W. R. Busing, K. O. Martin, and A. A. Levy, « ORFFE, A Fortran Crystallographic Function and Error Program », ORNL-TM-306 (1964).

(19) C. K. Johnson, « ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations », ORNL-3794, Revised (1965).

(20) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 7, 1111 (1968).

(21) J. A. Bertrand and D. L. Plymate, *Inorg. Chem.*, *5*, 879 (1966).

(22) W. A. Spofford, III, P. P. Carfagna, and E. L. Amma, *Inorg. Chem.*, 6, 1553 (1967).

(23) D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, *89*, 3424 (1967).

(24) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, *8*, 1084 (1969).

(25) D. E. C. Corbridge, « Topics in Phosphorus Chemistry », Vol. 3, Interscience Publishers, New York, N. Y., (1966), Table III.5.