programming necessary to solve the crystal structure, and Dr. R. A. Jacobson for the use of his diffractometer.

**Registry No.** $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$, 53966-20-4; $Ni(P(OCH_2)_3CCH_3)_4$, 14730-03-1; $NOBF_4$, 14635-75-7.

**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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC405469.

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# Crystal and Molecular Structure of Diiodotris(trimethyl phosphite)nickel(II), $NiI_2[P(OCH_3)_3]_3$[1]

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The crystal and molecular structure of the five-coordinate title complex has been determined from three-dimensional single-crystal X-ray data. The compound crystallizes in the monoclinic space group $P2_1/n$, with $a$ = 9.711 (2) Å, $b$ = 19.054 (5) Å, $c$ = 12.267 (3) Å, and $\beta$ = 94.75 (1)°. The structure was determined by Patterson and conventional least-squares methods with 2812 nonzero reflections to give a final $R$ factor of 0.034. The geometry around the Ni atom is nearly trigonal bipyramidal. The two axial Ni–P bond distances are 2.180 (2) and 2.183 (2) Å while the slightly shorter equatorial Ni–P length is 2.169 (2) Å. The two equatorial Ni–I bond distances are 2.664 (1) and 2.657 (1) Å and the I–Ni–I bond angle is compressed from the ideal equatorial angle of 120° to 112.11 (3)°.

## Introduction

Considerable interest has been shown in the monodentate five-coordinate geometry of nickel(II) compounds which include halogens or pseudohalogens in the primary coordination sphere. Electronic spectral assignments have been made for the model trigonal-bipyramidal system, *trans*-$Ni(CN)_2[C_6H_5P(OR)_2]_3$, based on self-consistent charge and configuration molecular orbital calculations.[3] From infrared evidence, we have also concluded that the cyano groups are trans in the $Ni(CN)_2L_3$ complexes where L can be any of the phosphite ligands, $P(OMe)_3$, $P(OC_6H_5)_3$, and $P(OCH_2)_3CCH_3$.[4] Later X-ray structural work on $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_3$[5] and $Ni(CN)_2[C_6H_5P(CH_3)_2]_3$[6] which are intermediate between the trigonal-bipyramidal and

tetragonal-pyramidal geometries have confirmed the cyano groups to be mutually trans. On the basis of an electronic study, it was concluded that the ground-state configuration for $NiBr_2[P(CH_3)_3]_3$ was consistent with a trigonal-bipyramidal structure involving trans bromines.[7] Another electronic study supported a cis structure although it was not possible to differentiate between equatorial-equatorial and equatorial-axial isomers in a trigonal bipyramid.[8] Recently, however, an X-ray diffraction study showed that the bromines are in equatorial positions.[9] This result is compatible with both the distorted trigonal-bipyramidal structure of $NiI_2[HP(C_6H_5)_2]_3$[10] and the nearly trigonal-bipyramidal structure[11] of $NiI_2(CO)$(Fdma) (Fdma = ferrocene-1,1'-bis(dimethylarsine)) which contain equatorial iodines. The present structural determination was therefore of interest. Moreover, only one other structure of a five-coordinate nickel(II) complex containing an adamantane-type phosphite ligand, $Ni[P(OCH)_3(CH_2)_3]_5[ClO_4]_2$, has been carried out[12] and differs from the present complex in that all five ligands are phosphites. Chemical aspects of the complex discussed here will be the subject of a forthcoming paper.[13]

## Collection and Reduction of the X-Ray Data

The compound $NiI_2[P(OCH_3)_3]_3$ which was prepared as described elsewhere[13] was crystallized slowly at −78° from a hexane solution to yield very dark purple prismatic crystals. Because the compound is sensitive to prolonged exposure to atmospheric conditions, the two crystals used to collect the necessary reflection data were mounted in 0.3-mm sealed Lindemann capillaries. Even with this precaution both crystals slowly decomposed in the X-ray beam. The crystals measured approximately 0.20 mm × 0.10 mm × 0.08 mm and 0.25 mm × 0.15 mm × 0.10 mm.

Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and is equipped with encoders (Baldwin Optical) and drive motors. The design of the base allows the encoders to be directly connected to the main $\theta$ and $2\theta$ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer. The $\chi$, $\omega$, and $2\theta$ angles of 13 reflections were tuned and these values were used to calculate[14a] the reduced cell. The cell was monoclinic with $a$ = 9.711 (2) Å, $b$ = 19.054 (5) Å, $c$ = 12.267 (3) Å, and $\beta$ = 94.75 (1)°. These parameters and their standard deviations were obtained by a least-squares fit[14b] to the $2\theta$ values of 18 independent reflections whose centers were determined by left–right, top–bottom beam splitting on a previously aligned four-circle diffractometer (Mo K$\alpha$ radiation, $\lambda$ 0.71069 Å). The unit cell scalars, in conventional orientation were $R(1, 1)$ = 94.83, $R(2, 2)$ = 363.42, $R(3, 3)$ = 150.50, $R(2, 3)$ = −0.53, $R(3, 1)$ = −9.98 and $R(1, 2)$ = −0.44. The same monoclinic cell was found for the second crystal after tuning on the $\chi$, $\omega$, and $2\theta$ angles for eight reflections.

The density of 2.009 g/cm$^3$ was computed from the unit cell volume of 2263.7 Å$^3$ on the basis of four $NiI_2[P(OMe)_3]_3$ molecules per unit cell. This agrees well with a density of 2.03g/cm$^3$ measured by the flotation method using aqueous $ZnI_2$.

Data were taken using a peak height data collection mode which maximizes in $\omega$. The data were collected within a $2\theta$ sphere of 45° ($(\sin\theta)/\lambda$ = 0.537 Å$^{-1}$) using unfiltered pyrolytic graphite-monochromatized Mo K$\alpha$ radiation (0.7107 Å) at a takeoff angle of 5°. The peak heights were measured for 10 sec and background readings were taken for 5 sec after which they were scaled up by a factor of 2 and subtracted from the total intensity. During data collection the intensities of three different standards, (600), (0,10,0), and (00$\bar{8}$), were monitored after every 50 reflections. These intensities decreased in a linear fashion with time to the extent of 18% after 1097 reflections had been measured on the first crystal. The remainder of the 3278 reflections in the two octants were collected from a second crystal which underwent 48% decomposition.

By investigation of the reflection data the systematic extinctions of $h + l = 2n$ for $h0l$ and $k = 2n$ for $0k0$ uniquely established the space group as $P2_1/n$. This choice as the space group was confirmed by the subsequent solution and refinement of the structure. Before data reduction the effect of the decomposition of the crystals on the intensity data was corrected by the algorithm: corrected intensity = (initial intensity)/(1 − fraction of decay). The intensities of the first crystal were then adjusted by a factor of 0.36 to render them comparable to those of the second crystal. The observed intensities were corrected for Lorentz and polarization effects and 2884 reflections which had intensities greater than $3\sigma$ above background were used in subsequent calculations. The linear absorption coefficient was 38.63 cm$^{-1}$ and no correction for absorption was applied. The maximum and minimum transmission factors for the first and second crystals were 0.734 and 0.461 and were 0.680 and 0.425 respectively.

## Solution and Refinement of the Structure

The positions of the two iodine atoms were determined from a three-dimensional Patterson function. After three cycles of least-square refinement of the positional parameters with the isotropic thermal parameters held at 3.0 and a single scale factor, the conventional unweighted and weighted discrepancy factors were 0.440 and 0.463, respectively. The iodine-phased electron density synthesis[15] revealed the position of the nickel atom. Three cycles of refinement[16] on the positional parameters with the isotropic thermal parameters of nickel also at 3.0 easily permitted the location of the phosphorus and oxygen atoms.

After one cycle of refinement on the positional and isotropic thermal parameters of these 15 atoms, an additional three cycles of refinement with anisotropic thermal models assumed for the iodine, nickel and phosphorus atoms led to $R$ and $R_w$ values of 0.088 and 0.147, respectively. All of the carbon atoms were now located from the difference Fourier map and refinement of positional and isotropic thermal parameters for them included in the model produced $R$ and $R_w$ values of 0.069 and 0.132, respectively.

Refinement was continued with anisotropic thermal parameters for all atoms and three cycles lowered $R$ to 0.060 and $R_w$ to 0.129. Since systematic errors were suspected, 72 of the 2884 reflections for which $|F_o - F_c|/F_c > 0.30$ were omitted, and a final refinement of four cycles in which the weights, $w$, were assigned $1/\sigma(F^2)$ gave discrepancy factors of $R$ = 0.034 and $R_w$ = 0.046. The ratio of the largest shift in the last refinement cycle to standard deviation in coordinate was 0.06. A final difference Fourier map showed no peaks larger than 0.6 e/Å$^3$. The hydrogen atoms were not located.

The atomic scattering factors used in the refinement were those of Hanson, *et al.*,[17] and the real and imaginary corrections[18] for anomalous dispersion for I, Ni, and P were also included in the calculations. The final positional and anisotropic thermal parameters of the atoms are given in Table I. The final observed and calculated structure factor amplitudes (in electrons × 10) for the 2884 reflections, which were used until final refinement, have been tabulated.[19]

## Description of the Structure

The four molecules per unit cell exist as discrete monomeric units. All of the intermolecular contacts appear to be normal with the closest contact being 3.272 (10) Å. In this molecule the inner coordination sphere around the nickel atom is nearly trigonal bipyramidal with the two iodines occupying equatorial positions. A perspective drawing of the inner coordination sphere is displayed in Figure 1.[20] In Table II the immediate distances and angles around the Ni atom are tabulated. All distances, angles, and their deviations are computed from the final parameters and the correlation matrix.[21]

The Ni–I distances are very similar with an average separation of 2.661 Å. This is 0.045 Å longer than the average equatorial Ni–I distance found in $NiI_2(CO)$(Fdma)[11] and much longer than the basal Ni–I distances of 2.514 (5) and 2.567 (5) Å found in the low-spin square-pyramidal complex $Ni(DSP)I_2$ (DSP = bis(*o*-methylthiophenyl)phenylphosphine.[22] Previously it was noted that the radius of Ni(II) in the equatorial plane of a trigonal bipyramid was about 0.08 Å larger than in the basal plane of a square pyramid[22,23] whereas in the present structure this difference is about 0.12 Å. Comparison with the structure of $NiI_2[HP(C_5H_6)_2]_3$ which is distorted toward square pyramidal[10] shows the average Ni–I distance in the present species to be intermediate between the values of 2.80 (2) and 2.49 (2) Å found in the phosphine complex. The Ni–I distance in $NiI_2[P(OCH_3)_3]_3$ is actually very close to the sum[24] of the octahedral radius of Ni(II) (1.39 Å) and the I radius of 1.28 Å which is 2.67 Å.

**Table I.** Final Positional and Anisotropic Parameters for $NiI_2[P(OCH_3)_3]_3$

| Atom | $x^a$ | $y$ | $z$ | $\beta_{11}{}^b$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | 0.21040 (7) | 0.12821 (3) | 0.26561 (5) | 0.00765 (8) | 0.00183 (2) | 0.00499 (5) | 0.00013 (3) | −0.00006 (5) | 0.00003 (2) |
| I(1) | 0.23778 (5) | 0.26160 (2) | 0.20776 (4) | 0.01591 (7) | 0.00202 (1) | 0.00957 (4) | −0.00070 (2) | −0.00046 (4) | 0.00100 (2) |
| I(2) | −0.04942 (4) | 0.08341 (2) | 0.23118 (3) | 0.00798 (5) | 0.00269 (1) | 0.00741 (4) | −0.00032 (2) | −0.00037 (3) | −0.00034 (1) |
| P(1) | 0.25029 (18) | 0.09901 (9) | 0.09854 (12) | 0.01181 (20) | 0.00270 (5) | 0.00569 (11) | 0.00024 (8) | 0.00163 (12) | −0.00001 (6) |
| P(2) | 0.16988 (15) | 0.16823 (7) | 0.42681 (11) | 0.00875 (17) | 0.00239 (4) | 0.00569 (10) | 0.00042 (7) | −0.00037 (11) | −0.00062 (5) |
| P(3) | 0.37438 (16) | 0.06347 (8) | 0.34213 (12) | 0.00801 (17) | 0.00233 (4) | 0.00688 (11) | 0.00083 (7) | −0.00087 (12) | −0.00010 (6) |
| O(1) | 0.3894 (6) | 0.1266 (3) | 0.0586 (5) | 0.0178 (8) | 0.0043 (2) | 0.0160 (6) | −0.0006 (3) | 0.0098 (6) | 0.0009 (3) |
| O(2) | 0.2575 (5) | 0.0207 (2) | 0.0588 (3) | 0.0192 (7) | 0.0031 (1) | 0.0078 (3) | −0.0000 (3) | 0.0030 (4) | −0.0008 (2) |
| O(3) | 0.1404 (6) | 0.1347 (3) | 0.0133 (3) | 0.0202 (8) | 0.0046 (2) | 0.0054 (3) | 0.0021 (3) | −0.0005 (4) | −0.0001 (2) |
| O(4) | 0.0722 (5) | 0.2334 (2) | 0.4399 (3) | 0.0115 (5) | 0.0031 (2) | 0.0093 (3) | 0.0016 (2) | −0.0000 (4) | −0.0016 (2) |
| O(5) | 0.1103 (5) | 0.1082 (2) | 0.5006 (3) | 0.0143 (6) | 0.0038 (1) | 0.0062 (3) | −0.0002 (3) | 0.0013 (3) | 0.0003 (2) |
| O(6) | 0.3038 (5) | 0.1936 (2) | 0.4958 (4) | 0.0110 (5) | 0.0036 (1) | 0.0095 (3) | 0.0000 (2) | −0.0023 (3) | −0.0019 (2) |
| O(7) | 0.3427 (5) | 0.0179 (2) | 0.4461 (3) | 0.0126 (5) | 0.0032 (1) | 0.0081 (3) | −0.0010 (2) | −0.0019 (3) | 0.0014 (2) |
| O(8) | 0.5071 (5) | 0.0997 (3) | 0.3994 (4) | 0.0100 (5) | 0.0037 (2) | 0.0136 (5) | 0.0002 (3) | −0.0038 (4) | −0.0003 (2) |
| O(9) | 0.4306 (5) | 0.0084 (2) | 0.2601 (3) | 0.0136 (6) | 0.0042 (2) | 0.0086 (3) | 0.0033 (3) | −0.0017 (4) | −0.0011 (2) |
| C(1) | 0.5181 (10) | 0.0976 (7) | 0.0504 (12) | 0.0149 (14) | 0.0088 (6) | 0.0314 (20) | 0.0019 (7) | 0.0082 (14) | 0.0079 (9) |
| C(2) | 0.1862 (9) | −0.0390 (4) | 0.0939 (6) | 0.0190 (11) | 0.0029 (2) | 0.0109 (6) | −0.0010 (4) | 0.0043 (7) | −0.0011 (3) |
| C(3) | 0.1414 (8) | 0.1268 (4) | −0.1035 (5) | 0.0189 (11) | 0.0051 (3) | 0.0059 (5) | −0.0018 (5) | −0.0002 (6) | −0.0003 (3) |
| C(4) | −0.0665 (9) | 0.2408 (5) | 0.3950 (9) | 0.0141 (12) | 0.0065 (4) | 0.0212 (11) | 0.0051 (6) | −0.0080 (10) | −0.0064 (6) |
| C(5) | 0.0965 (9) | 0.1200 (4) | 0.6173 (5) | 0.0193 (12) | 0.0059 (3) | 0.0067 (5) | −0.0003 (5) | 0.0039 (6) | −0.0001 (3) |
| C(6) | 0.3362 (10) | 0.2612 (4) | 0.5424 (8) | 0.0209 (14) | 0.0037 (3) | 0.0176 (10) | −0.0013 (5) | −0.0062 (10) | −0.0029 (4) |
| C(7) | 0.2326 (9) | −0.0334 (4) | 0.4365 (6) | 0.0194 (12) | 0.0030 (2) | 0.0125 (7) | −0.0012 (4) | −0.0002 (8) | 0.0020 (3) |
| C(8) | 0.5704 (8) | 0.1621 (4) | 0.3611 (7) | 0.0120 (9) | 0.0041 (3) | 0.0170 (9) | −0.0017 (4) | −0.0008 (8) | 0.0008 (4) |
| C(9) | 0.5401 (10) | −0.0415 (5) | 0.2952 (7) | 0.0232 (15) | 0.0051 (3) | 0.0132 (7) | 0.0076 (6) | −0.0030 (9) | −0.0019 (4) |

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

**Table II.** Intramolecular Bond Distances and Angles in $I_2Ni[P(OMe)_3]_3$

| | | | |
|---|---|---|---|
| | Distances, Å | | |
| Ni-I(1) | 2.657 (1) | Ni-P(2) | 2.180 (2) |
| Ni-I(2) | 2.664 (1) | Ni-P(3) | 2.169 (2) |
| Ni-P(1) | 2.183 (2) | | |
| | Angles, Deg | | |
| I(1)-Ni-I(2) | 112.11 (3) | I(2)-Ni-P(2) | 91.30 (5) |
| I(1)-Ni-P(1) | 88.02 (5) | I(2)-Ni-P(3) | 122.72 (5) |
| I(1)-Ni-P(2) | 86.31 (5) | P(1)-Ni-P(2) | 174.27 (9) |
| I(1)-Ni-P(3) | 125.05 (5) | P(1)-Ni-P(3) | 94.84 (7) |
| I(2)-Ni-P(1) | 90.12 (4) | P(2)-Ni-P(3) | 89.05 (6) |

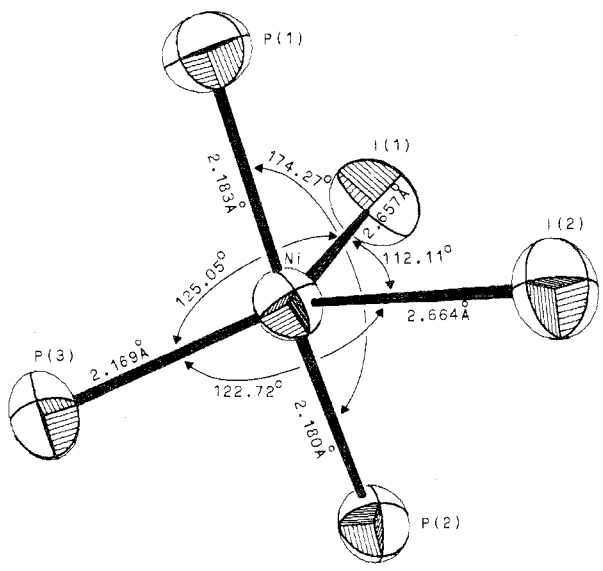


**Figure 1.** Computer drawing of the $NiP_3I_2$ portion of $NiI_2[P(OCH_3)_3]_3$ showing the angles and distances within the inner coordination sphere.

The difference in the average axial Ni–P bond lengths of 2.182 Å and the equatorial bond length of 2.169 Å is 0.013 Å. On the basis of repulsions between bonding electron pairs and an oblate ellipsoid found in low-spin $d^8$ or $d^9$ complexes when the $d_{z^2}$ orbital is empty or half-filled, Gillespie has predicted that the axial bond length will be shorter than the equatorial bond length.[25] This is reasonably evident when one examines the axial and equatorial bond lengths of 2.14 (1) and 2.19 (1) Å found[12] in $Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$ and is even more convincing in the corresponding lengths of 2.2964 (12) and 2.3912 (13) Å found[26] in $CuCl_5{}^{3-}$. Although the difference in lengths is small, a rationale for the longer axial bond distances in the present structure may lie in the $\pi$ acid competition of the d orbitals of the axial phosphorus atoms for the electron density of the nickel center. The d orbitals of the equatorial phosphorus atom need not compete with another strong $\pi$ acid and thus would tend to participate in $\pi$ back-bonding to a greater extent resulting in a slightly shorter Ni–P distance. A second possibility in the present structure is that the sterically larger trimethyl phosphite ligands are exerting substantial ligand–ligand repulsions with a concomitant lengthening of the axial bonds. Some support for the latter rationale is that the axial phosphite ligands are tilted toward the iodine atoms so that the $P_{ax}$–Ni–$P_{ax}$ angle is 174.27 (9)°. At the same time the I–Ni–I angle of 112.11 (3)° is smaller than the ideal equatorial angle of 120° found in a trigonal bipyramid while the other two equatorial angles are widened to 122.72 (5) and 125.05 (5)°. Other Ni–P distances reported are 2.186 Å in $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$,[27] 2.18 Å in $NiI_2[HP(C_6H_5)]_3$,[10] 2.21 Å in $[Ni(TAP)CN]ClO_4$ (TAP = $P(CH_2CH_2CH_2As(CH_3)_2)_3$),[28] 2.20 Å in $Ni[P(CH_3)_3]_3Br_2$,[9] and 2.23 Å in $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_3$,[5] and all compare favorably with those in $NiI_2[P(OCH_3)_3]_3$.

**Table III.** Intramolecular Nonbonded Distances (Å)

| | | | |
|---|---|---|---|
| I(1)-I(2) | 4.414 (1) | I(2)-P(2) | 3.481 (2) |
| I(1)-P(1) | 3.380 (2) | I(2)-P(3) | 4.249 (2) |
| I(1)-P(2) | 3.326 (2) | P(1)-P(2) | 4.358 (2) |
| I(1)-P(3) | 4.288 (2) | P(1)-P(3) | 3.205 (2) |
| I(2)-P(1) | 3.448 (2) | P(2)-P(3) | 3.050 (2) |

It can be seen from Table III which lists all of the nonbonded intramolecular distances that the I–I distance of 4.414 (1) Å is slightly larger than two van der Waals radii[29] of 4.30 Å while the other nonbonded distances in the equatorial plane (I(1)–P(3) and I(2)–P(3)) are significantly larger than the van der Waals distance[29] of 4.05 Å. All of this is apparently due to the bulky trimethyl phosphite ligand in the equatorial plane.

**Table IV.** Least-Squares Plane for Equatorial Atoms

Equation[a] for plane
$-0.265X + 0.296Y + 0.918Z - 3.249 = 0$

| Atom Deviation from Plane (Å) | | | |
|---|---|---|---|
| Ni | I(1) | I(2) | P(3) |
| −0.017 | 0.002 | 0.002 | 0.075 |

[a] The equation is expressed in cartesian coordinates relative to *a*, *b*, and *c*. Equal weighting factors were assigned to each atom in the plane.

**Table V.** Intramolecular Distances and Angles in the Trimethyl Phosphite Ligands

| Distance, Å | | | |
|---|---|---|---|
| P(1)-O(1) | 1.561 (5) | O(1)-O(1) | 1.376 (12) |
| P(1)-O(2) | 1.573 (4) | O(2)-C(2) | 1.414 (8) |
| P(1)-O(3) | 1.588 (5) | O(3)-C(3) | 1.440 (7) |
| P(2)-O(4) | 1.577 (4) | O(4)-C(4) | 1.422 (9) |
| P(2)-O(5) | 1.592 (4) | O(5)-C(5) | 1.463 (8) |
| P(2)-O(6) | 1.572 (4) | O(6)-C(6) | 1.434 (8) |
| P(3)-O(7) | 1.590 (4) | O(7)-C(7) | 1.446 (9) |
| P(3)-O(8) | 1.578 (5) | O(8)-C(8) | 1.434 (9) |
| P(3)-O(9) | 1.578 (4) | O(9)-C(9) | 1.466 (8) |
| **Angles, Deg** | | | |
| O(1)-P(1)-Ni | 115.2 (2) | P(2)-O(6)-C(6) | 129.6 (5) |
| O(2)-P(1)-Ni | 123.2 (2) | P(3)-O(7)-C(7) | 119.3 (4) |
| O(3)-P(1)-Ni | 110.5 (2) | P(3)-O(8)-C(8) | 124.9 (5) |
| O(4)-P(2)-Ni | 121.2 (2) | P(3)-O(9)-C(9) | 121.4 (4) |
| O(5)-P(2)-Ni | 111.2 (2) | O(1)-P(1)-O(2) | 99.4 (3) |
| O(6)-P(2)-Ni | 113.4 (2) | O(1)-P(1)-O(3) | 101.7 (3) |
| O(7)-P(3)-Ni | 118.5 (2) | O(2)-P(1)-O(3) | 104.3 (3) |
| O(8)-P(3)-Ni | 119.4 (2) | O(4)-P(2)-O(5) | 105.1 (2) |
| O(9)-P(3)-Ni | 112.3 (2) | O(4)-P(2)-O(6) | 100.5 (2) |
| P(1)-O(1)-C(1) | 134.2 (6) | O(5)-P(2)-O(6) | 103.6 (2) |
| P(1)-O(2)-C(2) | 129.4 (4) | O(7)-P(3)-O(8) | 94.8 (3) |
| P(1)-O(3)-C(3) | 123.7 (5) | O(7)-P(3)-O(9) | 104.2 (3) |
| P(2)-O(4)-C(4) | 126.7 (4) | O(8)-P(3)-O(9) | 105.3 (3) |
| P(2)-O(5)-C(5) | 120.5 (4) | | |

It is interesting that a comparable situation[11] exists in $NiI_2(CO)(Fdma)$ while in the nickel complex,[10] $NiI_2[HP(C_6H_5)_2]_3$, distortion toward a square pyramid occurs.

The general rule[30] that the more electronegative substituents prefer axial positions in trigonal-bipyramidal structures is found not to be true here nor in the distorted[10] $NiI_2[HP(C_6H_5)_2]_3$ structure. On the other hand, the cyano groups in $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_3$[5] and $Ni(CN)_2[C_6H_5P(CH_3)_3]_3$[6] are found in the axial positions. The electronegativity difference[31] of CN (3.3) and P (2.19) of 1.1, however, is substantially larger than the difference between I (2.66) and P which is 0.47. In spite of the small difference of 0.47, steric considerations might have been expected to lead to equatorial phosphorus ligands in the halogen complexes.

As seen from Table IV, a least-squares plane can be fitted to the equatorial atoms including nickel. The deviations from that plane indicate no significant distortion toward a square pyramid.

Table V shows the important bond lengths and angles which exist in the trimethyl phosphite ligands and Figure 2 shows the orientation of the methoxy groups relative to the overall geometry. In Table VI is a compilation of averaged structural parameters for $P(OMe)_3$ as a ligand complexed to a transition metal. It is seen that the average POC and OPO angles as well as the average P–O and C–O distances in the present structure compare favorably with those tabulated. Moreover, the nickel–cyano–phosphonite complex $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_3$[5] possesses POC and OPO angles of 122 and 105.6°, respectively, and P–O and C–O distances of 1.58 and 1.48 Å, respectively, which are also comparable to those in $NiI_2[P(OCH_3)_3]_3$. It might be expected that the methoxy groups would follow each other in a "head-to-tail" fashion and this is true for those on P(1), but C(4), C(7), and C(8) point outward and appear to bend backward toward the nickel. This behavior may be due to crystal packing forces. While a few other structural studies have been completed on complexes containing the trimethyl phosphite ligand,[37,38] the geometric parameters for this ligand were not reported.

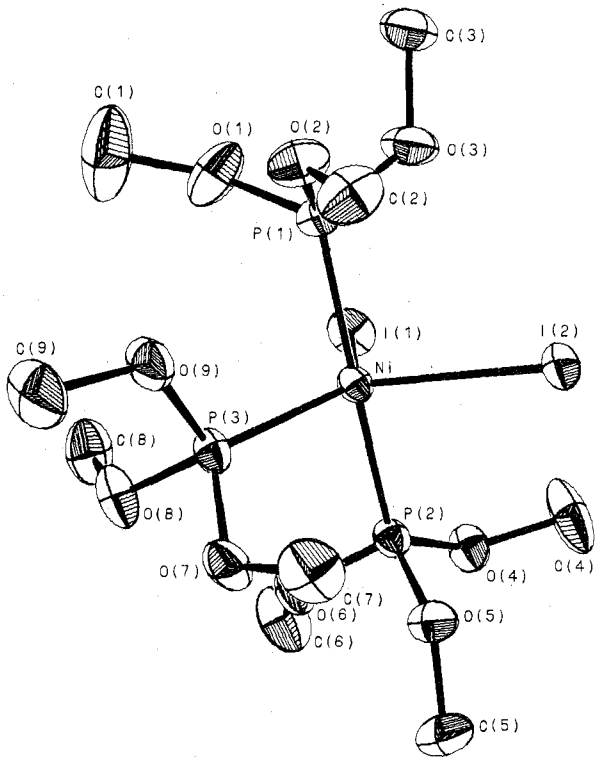


**Figure 2.** Computer drawing of $NiI_2[P(OCH_3)_3]_3$ showing the conformations of the methoxy groups in the $P(OCH_3)_3$ ligands.

**Table VI.** Selected Structural Parameters for $P(OMe)_3$ (L) as a Ligand

| Compd | POC, deg | OPO, deg | P-O, Å | C-O, Å | Ref |
|---|---|---|---|---|---|
| $NiI_2L_3$ | 125.5 | 102.1 | 1.58 | 1.43 | This work |
| $[Ag(NO_3)L_2]_2$ | 125.3 | 100.8 | 1.56 | 1.42 | 32 |
| $RhL_2B(C_6H_5)_4$ | 123.6 | 101.7 | 1.59 | 1.44 | 33 |
| $RuL_2(\pi\text{-}C_4H_7)_2$ | 123 | 99.0 | 1.61 | 1.52 | 34 |
| $IMo(CO)_2(\pi\text{-}C_5H_5)L$ | 119.8 | 100.1 | 1.58 | 1.54 | 35 |
| $IMo(CO)_2(\pi\text{-}C_5H_4Me)L$ | 123.1 | 101.1 | 1.60 | 1.44 | 35 |
| $(NC)_2C{=}CMo(Cl)(\pi\text{-}C_5H_5)L_2$[a] | 123.7 | 101.5 | 1.58 | 1.41 | 36 |

[a] Only the parameters for a nondisordered ligand are included.

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**Registry No.** $NiI_2[P(OCH_3)_3]_3$, 53966-17-9.

**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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC405471.

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# Crystal Structures of Acetylene Sorption Complexes of Partially Manganese(II)-Exchanged and Partially Cobalt(II)-Exchanged Forms of Zeolite A

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The crystal structures of the acetylene sorption complexes of partially Mn(II)-exchanged and partially Co(II)-exchanged forms of the synthetic molecular sieve sodium zeolite 4A have been determined from three-dimensional X-ray diffraction data gathered by counter methods. Both structures were solved and refined in the cubic space group *Pm3m*; at 20 (1)° the cell constants are 12.205 (7) Å for the Mn(II) form, stoichiometry $Mn_{4.5}Na_3Al_{12}Si_{12}O_{48}\cdot 4.5C_2H_2$, and 12.171 (6) Å for the Co(II) form, stoichiometry $Co_4Na_4Al_{12}Si_{12}O_{48}\cdot 4C_2H_2$, per unit cell. Prior to the sorption of acetylene, activation of each zeolite was achieved in 48 hr at $1 \times 10^{-6}$ Torr and elevated temperatures (350° for the Mn(II) form; 400° for the Co(II) form). In each structure, each transition metal ion lies on a threefold axis in the large central cavity of the unit cell, close to three equivalent trigonally arranged zeolite framework oxygen atoms (Mn(II)–O = 2.177 (10) Å, Co(II)–O = 2.193 (7) Å) and symmetrically to both carbon atoms of a $C_2H_2$ molecule (Mn(II)–C = 2.63 (17) Å, Co(II)–C = 2.54 (7) Å). At these latter distances, the interactions are weak, probably resulting from electrostatic attractions between the bivalent cations and the polarizable $\pi$-electron density of the acetylene molecules. The $Na^+$ ions of each structure occupy similar threefold axial positions (at sites not containing transition metal ions) which are somewhat recessed into the small sodalite cages (to distribute positive charge more uniformly), where nearly planar coordination to framework oxygen atoms is attained. No interaction between $Na^+$ ions and $C_2H_2$ molecules is observed in either structure. Full-matrix least-squares refinement has converged to a conventional $R$ index (on $F$) of 0.065 for the Mn(II) system using 205 reflections for which $I_0 > 3\sigma(I_0)$ and 0.062 for the Co(II) structure using 297 similarly selected reflections.

## Introduction

Utilization of the selective sorptive and catalytic properties of aluminosilicates is widespread.[1] The petroleum industry, for example, relies heavily upon aluminosilicates for the catalytic cracking of large hydrocarbon molecules. In fundamental research, a great variety of chemical reactions (isomerizations, polymerizations, dehydrogenations, and oxidations, for example) are conducted over aluminosilicate surfaces.[2] Consequently, considerable effort has been expended in determining the nature of the aluminosilicate sorptive and catalytic sites in order to learn about the physical forces operative in aluminosilicate catalysis, to postulate reaction mechanisms, perhaps to observe reaction intermediates, and, ultimately, to devise highly specific catalytic systems. Structural characterization, to which the crystalline zeolites are amenable, can be most useful in pursuing these objectives.

The work of Pickert, *et al.*,[3] with Y-type zeolites[4,5] indicates that bivalent cation exchange does indeed augment zeolite catalysis. Their studies show that isomerization of *n*-hexane is enhanced in the order Na–Y < Sr–Y < Ca–Y < Mg–Y. It appears that this catalytic activity varies monotonically with the polarizing power of the cation or with metal ion acidity,