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# Four-Coordinate Metal Nitrosyls. I. The Structure of Azidonitrosylbis(triphenylphosphine)nickel, $Ni(N_3)(NO)(P(C_6H_5)_3)_2$

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The structure of azidonitrosylbis(triphenylphosphine)nickel, $Ni(N_3)(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the space group $C_{2h}^5$-$P2_1/c$ with four molecules in a cell of dimensions $a$ = 13.691 (6), $b$ = 19.211 (10), $c$ = 12.582 (5) Å, and $\beta$ = 98.13 (3)°. The calculated and observed densities are 1.331 and 1.344 (5) g $cm^{-3}$, respectively. Full-matrix least-squares refinement of the structure has resulted in $R = 0.052$ for the 2126 data having $F_o^2 > 3\sigma(F_o^2)$. The structure consists of discrete $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ molecules, with the coordination geometry about the Ni atom being pseudotetrahedral. The P–Ni–P angle is 120.52 (8)°, the $N_3$–Ni–NO angle is 128.8 (3)°, and the dihedral angle between the P–Ni–P and $N_3$–Ni–NO planes is 85.1 (2)°. The coordination of the NO group is distinctly nonlinear with an Ni–N–O angle of 152.7 (7)°. Important interatomic distances are Ni–P = 2.257 (2) and 2.306 (2) Å, Ni–$N_3$ = 2.018 (8) Å, Ni–NO = 1.686 (7) Å, and N–O = 1.164 (8) Å.

## Introduction

The two-dimensional X-ray study[1] of $Co(NO)(S_2CN(CH_3)_2)_2$ provided the first structural evidence for distinctly nonlinear coordination to transition metals by the nitrosyl group (NO). Definitive proof of strongly bent NO coordination was provided by Hodgson and Ibers.[2] They found an Ir–N–O angle of 124° from an analysis of the three-dimensional X-ray diffraction data from $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$. This result led to a renewed interest in the structures of metal nitrosyl complexes. Both linear[3-8] and distinctly nonlinear[1,2,9-11] NO coordinations are now well documented for five- and six-coordinate complexes and in one instance[12] both modes of coordination occur in the same complex.

Less is known about the structural chemistry of four-coordinate transition metal nitrosyl complexes. $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ were *assumed*[13] to have linear nitrosyl groups when the structures were solved by electron diffraction. Recently[14] the ion $Ni(NO)(tep)^+$ (where tep is $CH_3C[CH_2P(C_2H_5)_2]_3$) has been shown to have an Ni–N–O angle of 180° by X-ray diffraction. A rigorously linear Ni–N–O grouping has also been found[15] for the isoelectronic complex $\pi$-$(C_5H_5)Ni(NO)$. On the other hand a distorted coordination geometry and Ir–N–O angles of 164° occur[16] in $Ir(NO)_2(P(C_6H_5)_3)_2^+$. Similar M–N–O angles appear[17a] in $[Fe(NO)_2I]_2$ (161°), $[Co(NO)_2I]_n$ (171°), and[17b] $[Co(NO)_2NO_2]_n$ (166°).

As part of a general study of the structures, bonding, and chemical reactivity of metal nitrosyl complexes being conducted in these laboratories we have undertaken a systematic investigation of four-coordinate metal nitrosyls. Of particular interest are the low-symmetry nickel complexes of the general formula $NiX(NO)L_2$, where X is a monoanion and L is a tertiary phosphine. Feltham[18] assigned these complexes tetrahedral structures on the basis of their large dipole moments and the similarity of their X-ray powder patterns to those of tetrahedral dihalobis(triphenylphosphine)nickel complexes, but no other structural information is available.

Most metal nitrosyls can satisfy the inert gas formalism if the NO ligand is regarded as a three-electron donor. The metal–ligand bonding is frequently represented[19] as $M{=}N^+{=}O$. In this electronic structure the ligand donates electron density to the metal *via* a $\sigma$ bond utilizing an sp orbital on nitrogen, and the metal back-donates density from its d orbitals into the two $\pi^*$ orbitals of the ligand. Molecular orbital calculations[20] have suggested that the metal d orbitals of $\pi$ symmetry and the $\pi^*$ orbitals of the NO group are similar in energy. If such is the case, then the nature of the $\pi$-bonding interaction could be quite sensitive to perturbations of the energies of the metal d orbitals. As long as the two d–$\pi^*$ interactions are nearly degenerate, then the M–N–O angle should be ~180°, with some $\pi$ bonding resulting from each of the interactions. However, if the ligand field is very asymmetric, then the two $\pi$-bonding interactions need not be the same. In the extreme case the bonding of the complex might be described by a $\sigma$ bond from the ligand to the metal and a $\pi$ bond between *one* d orbital and *one* $\pi^*$ orbital of the ligand. Such an electronic structure would still have a formal M=N double bond, but there

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would be no restriction on the M–N–O angle. Of course, a strong splitting of the degeneracy of the d–$\pi^*$ interactions could also change the M–N bond order (and hence the M–N bond length).

The low symmetry of the $NiX(NO)L_2$ complexes offers a good opportunity for studying the Ni–N distance and the Ni–N–O angle as a function of the asymmetry of the ligand field produced by different X and L groups. Herein is reported the structure of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$. Azide ion was chosen as the anion in order to minimize the possibility of disorder between NO and X.

## Experimental Section

Excellent deep blue-black crystals of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ were kindly supplied by Professor R. D. Feltham and Dr. E. Leicht. The compound was prepared by refluxing a suspension of $NiCl(NO)(P(C_6H_5)_3)_2$[18] with an excess of $NaN_3$ in methanol. Recrystallization was from benzene–heptane. The NO infrared stretching frequency occurred at 1710 $cm^{-1}$ (KBr pellet). *Anal.* Calcd for $NiC_{36}H_{30}P_2ON_4$: Ni, 9.0; C, 66.1; H, 4.6; P, 9.4; O, 2.4; N, 8.5. Found: Ni, 9.5; C, 65.1; H, 4.7; P, 9.4; O, 2.1; N, 8.4; total, 99.2.

Preliminary precession photographs taken with Mo K$\alpha$ radiation indicated that the crystals are monoclinic. The systematic absences of $h0l$ when $l \neq 2n$ and $0k0$ when $k \neq 2n$ are consistent with the space group $C_{2h}^5$-$P2_1/c$. At 23 ± 2° the unit cell parameters are $a$ = 13.691 (6), $b$ = 19.211 (10), $c$ = 12.582 (5) Å, and $\beta$ = 98.13 (3)°. These parameters were determined from a least-squares refinement of the setting angles of nine reflections that had been carefully centered on a Picker FACS-I computer-controlled four-circle X-ray diffractometer. The value of $2\theta$ for these reflections was 13–25°. In the refinement the wavelength of Mo K$\bar{\alpha}$ radiation was taken as 0.71069 Å. The crystal density of 1.344 (5) g $cm^{-3}$ determined by flotation in bromobenzene–heptane is in good agreement with the value of 1.331 g $cm^{-3}$ calculated for four molecules per unit cell.

For data collection a crystal of approximate dimensions 0.15 × 0.20 × 0.25 mm was mounted with its long axis (the reciprocal vector (102)) approximately collinear with the $\phi$ axis of the diffractometer. The mosaicity of the crystal was checked from $\omega$ scans at a takeoff angle of 0.7°. All reflections had peak widths at half-height of 0.15° or less. An incident-beam monochromator equipped with a graphite crystal was used to obtain Mo K$\alpha$ radiation. The $\theta$–$2\theta$ axis of the monochromator was perpendicular to the $\theta$–$2\theta$ axis of the diffractometer. Data were collected at a takeoff angle of 1.8° using the $\theta$–$2\theta$ scan technique and an asymmetric scan range from $2\theta_{MoK\alpha_1} - 0.85°$ to $2\theta_{MoK\alpha_2} + 0.85°$. The pulse height analyzer was set to admit ~90% of Mo K$\alpha$ peak, and the scintillation counter was 24 cm from the crystal. Cu foils having attenuator factors of ~1.7 were inserted into the diffracted beam whenever the counting rate exceeded ~$10^3$ counts/sec. During data collection the intensities of three reflections in diverse regions of reciprocal space were monitored every 50 reflections. None of the standard reflections showed any systematic changes during the time required to collect the data. The maximum variation of any standard from its mean value was 2%. A total of 3060 unique reflections having $2\theta \leqslant 40°$ were obtained. There were few data of useful intensity beyond $2\theta = 40°$.

The data were reduced to $F^2$ and $\sigma(F^2)$ by procedures similar to those previously described.[8,21,22] The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$, where $\theta_m$ is the Bragg angle of the monochromator crystal and $\theta$ is the Bragg angle of the reflection being observed. Standard deviations were assigned to the corrected intensities by the formula

$$\sigma(F^2) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pF^2)^2]^{1/2}$$

where $CT$ is the total integrated peak count obtained in time $t_c$, and $B_1$ and $B_2$ are the background counts each obtained in time $t_b$. $F^2$ is the corrected intensity and $p$ was taken as 0.04.

The absorption coefficient for the compound for Mo K$\alpha$ radiation is only 5.5 $cm^{-1}$. In order to investigate the importance of absorption in this crystal, the faces $\{010\}$, $\{110\}$, $\{1\bar{1}0\}$, $\{11\bar{1}\}$, and $\{1\bar{1}\bar{1}\}$ were identified by optical goniometry and the crystal was carefully measured. Sample calculations on several representative reflections showed that the magnitude of the absorption correction ranged from 1.07 to 1.09. Therefore, no correction was made for absorption. Secondary extinction is not a problem in this crystal and no extinction correction was made.

## Solution and Refinement

The heavy atoms were located by direct methods using Sayre's equation[23] in the form of a modified version of Long's computer program.[24] Normalized structure factors were computed and the 340 reflections having $E \geqslant 1.60$ were utilized. Three linearly independent reflections were chosen to fix the origin and the signs of four additional reflections were assumed to initiate phasing. An $E$ map calculated from the 340 reflections for the solution with the highest consistency index[24] ($C$ = 0.97) readily revealed the Ni and the two P atoms. Successive structure factor calculations and difference electron density maps revealed the remaining nonhydrogen atoms.

Refinement of the structure based upon $F$ was begun, the quantity minimized being $\Sigma w(|F_o| - |F_c|)^2$, with the weights $w$ taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for C, N, O, and P were from the usual tabulation.[25] Those for Ni were from Cromer and Waber.[26] Hydrogen scattering factors were from the calculation of Stewart, *et al.*[27] The effects of anomalous dispersion were included in $F_c$;[28] the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer[29] were used for Ni and P. The initial structure factor calculation including all nonhydrogen atoms gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.247$ and $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.308$ for the 2126 reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$. These reflections were the only ones used in subsequent cycles of least-squares refinement. Phenyl rings were treated as rigid groups[30] (C–C = 1.392 Å, $D_{6h}$-$6/mmm$ symmetry) with a single isotropic thermal parameter assigned to each ring; all nongroup atoms were allowed to assume individual isotropic thermal parameters. Three cycles of full-matrix refinement resulted in convergence of this model to $R_1$ = 0.081 and $R_2$ = 0.010. The positions of the H atoms of the phenyl rings were calculated (C–H = 1.084 Å) and included as fixed contributions to $F_c$. Each H atom was assigned the same isotropic temperature factor as the ring to which it was bonded. Three additional cycles of least-squares refinement were carried out assuming anisotropic thermal motion for all nongroup atoms and individual isotropic thermal parameters for all group C atoms (145 variable parameters). These cycles lowered $R_1$ and $R_2$ to 0.053 and 0.063, respectively.

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TABLE I

FINAL ATOMIC AND GROUP PARAMETERS

| Atom[a] | $x$ | $y$ | $z$ | $10^4\beta_{11}$ | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | 0.74371 (7) | 0.42630 (5) | 0.21902 (8) | 47.7 (7) | 19.3 (3) | 47.6 (8) | 1.5 (4) | 7.8 (5) | −0.1 (4) |
| $P_1$ | 0.7325 (1) | 0.3711 (1) | 0.3751 (2) | 38 (1) | 19 (1) | 41 (2) | 1 (1) | 7 (1) | 0 (1) |
| $P_2$ | 0.7148 (2) | 0.5443 (1) | 0.2022 (2) | 43 (2) | 20 (1) | 54 (2) | 2 (1) | 11 (1) | 2 (1) |
| $N_1$ | 0.8912 (6) | 0.4334 (4) | 0.2222 (7) | 50 (6) | 20 (3) | 81 (7) | 8 (3) | 0 (5) | 11 (4) |
| $N_2$ | 0.9414 (7) | 0.3979 (5) | 0.2442 (6) | 63 (9) | 38 (4) | 61 (8) | −26 (4) | 22 (7) | −17 (5) |
| $N_3$ | 1.0127 (7) | 0.3551 (5) | 0.2708 (8) | 89 (8) | 50 (4) | 142 (10) | −19 (4) | 26 (7) | −21 (5) |
| $N_4$ | 0.6600 (5) | 0.3819 (4) | 0.1328 (5) | 65 (6) | 25 (2) | 56 (6) | −4 (3) | −13 (5) | −4 (3) |
| O | 0.5844 (6) | 0.3539 (4) | 0.1093 (6) | 95 (6) | 51 (3) | 131 (8) | −24 (4) | −33 (5) | −8 (4) |

| Group[b] | $x_c$ | $y_c$ | $z_c$ | $\delta$ | $\epsilon$ | $\eta$ | $B_1$ | $B_2$ | $B_3$ | $B_4$ | $B_5$ | $B_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | 0.8380 (2) | 0.4467 (2) | 0.5911 (2) | 1.436 (3) | −2.654 (3) | −2.125 (3) | 2.6 (2) | 3.2 (2) | 3.7 (2) | 3.4 (2) | 3.7 (2) | 3.1 (2) |
| $R_2$ | 0.8440 (2) | 0.2227 (2) | 0.3858 (3) | 0.510 (4) | −2.575 (3) | −1.564 (4) | 2.5 (2) | 3.0 (2) | 3.6 (2) | 4.2 (2) | 4.5 (2) | 4.0 (2) |
| $R_3$ | 0.5069 (3) | 0.3467 (2) | 0.4095 (3) | −2.929 (4) | 3.426 (4) | −2.844 (4) | 3.1 (5) | 5.6 (2) | 6.8 (3) | 6.5 (2) | 7.2 (3) | 5.7 (2) |
| $R_4$ | 0.4894 (3) | 0.5939 (2) | 0.2013 (3) | −0.376 (4) | −2.561 (3) | −0.130 (4) | 3.0 (2) | 4.0 (2) | 4.8 (2) | 5.2 (2) | 5.5 (2) | 4.4 (2) |
| $R_5$ | 0.7630 (3) | 0.5967 (2) | −0.0284 (3) | −2.055 (3) | −3.085 (3) | 1.178 (3) | 3.3 (2) | 4.7 (2) | 5.8 (2) | 5.6 (2) | 5.2 (2) | 4.6 (2) |
| $R_6$ | 0.8409 (2) | 0.6466 (2) | 0.3741 (3) | 2.721 (5) | −2.248 (3) | 1.788 (5) | 3.0 (2) | 4.2 (2) | 5.3 (2) | 4.6 (2) | 4.5 (2) | 3.5 (2) |

[a] $x$, $y$, and $z$ are in fractional monoclinic coordinates. Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the least significant figure is given in parentheses. [b] $x_c$, $y_c$, and $z_c$ are the fractional coordinates of the center of the ring. The angles $\delta$, $\epsilon$, $\eta$ (in radians) which bring about alignment (except for translation) of an internal-coordinate system within the ring with a fixed external-coordinate system are those previously described.[30] $B_i$ is the isotropic thermal parameter in square ångströms of atom $i$ in a given ring. The rings are numbered so that atom $C_1$ is attached to P; $C_4$ is para to $C_1$.

Although refinement had essentially converged, the two Ni–P distances differed by 0.049 Å (20$\sigma$). In addition one of the N–N distances of the azide group was only 0.97 (1) Å. Several possible causes of these differences were next investigated.

An abnormal azide group might result from partial disorder between the nitrosyl group and the azide group. However, of these two groups, only the central atom of the azide group showed any unusual thermal motion in a plot of the thermal ellipsoids of the atoms. A difference electron density which was calculated from the refined model showed no peak greater than 0.5 $e^-$ Å$^{-3}$ (phenyl ring residual) and the maximum residuals around the nitrosyl and azide groups were ~0.25 $e^-$ Å$^{-3}$. On the same scale a C atom appeared as ~5.5 $e^-$ Å$^{-3}$. Moreover, both the azide and nitrosyl groups were clearly resolved in the initial difference electron density map phased by the Ni and P atoms. It was concluded that no significant disorder of the nitrosyl and azide groups occurs in this structure.

Unusual bond distances might also result from an improper weighting scheme. The standard deviation for an observation of unit weight for the model was 1.96. An analysis of $\sigma_1'$, the normalized weighting parameter,[8] as a function of $|F_o|$, $\lambda^{-1} \sin \theta$, and $h$, $k$, $l$ showed no unusual trends; $\sigma_1'$ ranged from 1.4 to 2.4 with weak reflections at small values of $\lambda^{-1} \sin \theta$ showing the largest values for $\sigma_1'$. These results suggested that the *relative* weights were nearly correct and no changes were made in the weighting scheme.

Since one of the Ni–P bonds is nearly parallel to $b$, the unequal Ni–P distance could result from a polar dispersion error due to improper handling of the anomalous dispersion terms if the true space group were $P2_1$ rather than $P2_1/c$. Therefore, the $h0l$ zone was reexamined to verify the presence of the $c$ glide. An overexposed $h0l$ precession photograph (Cu K$\alpha$) showed one reflection (201) forbidden in space group $P2_1/c$. This reflection was weak and very sharp, suggesting a Renninger reflection.[31] This was verified by the disappearance of the reflection upon changing to Mo K$\alpha$ radiation. Thus, $P2_1/c$ is the preferred space group.

Finally, the possibility was considered that the model had converged to a false minimum very close to true solution. New P atom positions were calculated so that the two Ni–P distances were interchanged. The central N atom of the azide group was moved midway between the terminal atoms and assigned an isotropic thermal parameter of 3.0 Å$^2$. Three cycles of complete full-matrix least-squares refinement as described above resulted in convergence to a model whose parameters were all within one standard deviation of the previous model.

The difference in the two Ni–P distances is probably real and is discussed in greater detail below. An N–N distance of 0.98 (1) Å and the shape of the thermal ellipsoid for the central atom of the azide group indicate that the present model does not adequately describe the azide group. However, refinement has been terminated with the present model. This is justified on the basis that (1) the azide ion is not the primary object of interest in the structure, (2) the correlation coefficients between the parameters of the azide ion and the other parameters are small, (3) the final difference electron density map is quite flat (see above), (4) the weighting analysis is not grossly skewed, and (5) the search for a better model would require unwarranted amounts of computer time.[32]

The final parameters appear in Table I. The derived fractional coordinates of the group C atoms appear in Table II. Important bond distances and angles are shown in Table III. Values of $10|F_o|$ and $10|F_c|$ for the reflections used in the refinement are available.[33]

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[31] For a brief discussion of the Renninger effect see G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 143.

[32] A referee has suggested that the anomalous behavior of the central atom of the azide group might arise from the presence of some of the chloride complex starting material in the crystal. Replacement of azide by chloride in this complex will change the molecular weight by only 1% and, hence, small amounts of chloride contamination would have no observable effect on the density of the crystal. The satisfactory total analysis (see Experimental Section) shows that chloride contamination in the *bulk sample* is very small, probably less than 1%. However, *individual* crystals could contain larger amounts of chloride complex. Chloride contamination would introduce electron density in the region between $N_1$ and $N_2$. This could affect the $N_1$–$N_2$ distance and the $N_2$ thermal ellipsoid.

[33] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

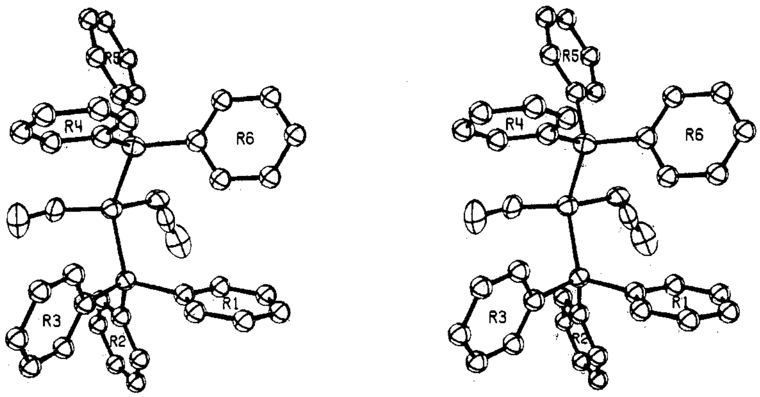

Figure 1.—Stereopair showing a perspective view of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$. $R_1$, $R_2$, and $R_3$ are attached to $P_1$; $R_4$, $R_5$, and $R_6$ are attached to $P_2$. The identities of the other atoms can be inferred from Figure 2. For clarity phenyl C atoms have been arbitrarily assigned isotropic thermal parameters of 3.0 Å². The ellipsoids are drawn to enclose 50% of the probability distribution.

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

| | *x* | *y* | *z* |
|---|---|---|---|
| | | $R_1$ | |
| $C_1$ | 0.7902 (3) | 0.4127 (2) | 0.5001 (3) |
| $C_2$ | 0.8922 (3) | 0.4223 (2) | 0.5137 (3) |
| $C_3$ | 0.9400 (2) | 0.4562 (3) | 0.6048 (4) |
| $C_4$ | 0.8858 (3) | 0.4806 (2) | 0.6822 (3) |
| $C_5$ | 0.7839 (3) | 0.4711 (2) | 0.6686 (3) |
| $C_6$ | 0.7361 (2) | 0.4371 (2) | 0.5775 (4) |
| | | $R_2$ | |
| $C_1$ | 0.7942 (3) | 0.2861 (2) | 0.3823 (4) |
| $C_2$ | 0.8177 (4) | 0.2569 (2) | 0.2881 (3) |
| $C_3$ | 0.8675 (4) | 0.1936 (2) | 0.2916 (3) |
| $C_4$ | 0.8938 (4) | 0.1594 (2) | 0.3893 (4) |
| $C_5$ | 0.8703 (4) | 0.1886 (2) | 0.4835 (3) |
| $C_6$ | 0.8205 (4) | 0.2519 (2) | 0.4800 (3) |
| | | $R_3$ | |
| $C_1$ | 0.6048 (3) | 0.3555 (3) | 0.3946 (4) |
| $C_2$ | 0.5378 (4) | 0.4100 (2) | 0.3722 (4) |
| $C_3$ | 0.4399 (4) | 0.4012 (3) | 0.3870 (5) |
| $C_4$ | 0.4090 (3) | 0.3379 (4) | 0.4243 (5) |
| $C_5$ | 0.4760 (5) | 0.2834 (3) | 0.4468 (5) |
| $C_6$ | 0.5739 (4) | 0.2922 (2) | 0.4319 (5) |
| | | $R_4$ | |
| $C_1$ | 0.5869 (3) | 0.5722 (3) | 0.2055 (4) |
| $C_2$ | 0.5108 (4) | 0.5343 (2) | 0.1463 (4) |
| $C_3$ | 0.4132 (3) | 0.5559 (3) | 0.1421 (4) |
| $C_4$ | 0.3918 (3) | 0.6155 (3) | 0.1971 (5) |
| $C_5$ | 0.4680 (4) | 0.6535 (2) | 0.2563 (4) |
| $C_6$ | 0.5656 (4) | 0.6318 (2) | 0.2605 (4) |
| | | $R_5$ | |
| $C_1$ | 0.7399 (4) | 0.5739 (3) | 0.0698 (3) |
| $C_2$ | 0.6728 (3) | 0.6144 (3) | 0.0022 (4) |
| $C_3$ | 0.6959 (4) | 0.6372 (3) | −0.0960 (4) |
| $C_4$ | 0.7862 (4) | 0.6195 (3) | −0.1266 (3) |
| $C_5$ | 0.8533 (3) | 0.5789 (3) | −0.0590 (4) |
| $C_6$ | 0.8302 (3) | 0.5561 (3) | 0.0392 (4) |
| | | $R_6$ | |
| $C_1$ | 0.7887 (4) | 0.6026 (2) | 0.2977 (4) |
| $C_2$ | 0.8376 (4) | 0.6605 (3) | 0.2650 (3) |
| $C_3$ | 0.8898 (4) | 0.7045 (2) | 0.3414 (4) |
| $C_4$ | 0.8931 (4) | 0.6906 (2) | 0.4504 (4) |
| $C_5$ | 0.8442 (4) | 0.6327 (3) | 0.4832 (3) |
| $C_6$ | 0.7920 (4) | 0.5887 (2) | 0.4068 (4) |

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analysis on inter-ring distances. The intra-ring C–C distance is 1.392 Å.

A final structure factor calculation on all 3060 data gave $R_1$ = 0.083 and $R_2$ = 0.066. All reflections with $F_o^2 < \sigma(F_o^2)$ had $F_c^2 < 3\sigma(F_o^2)$.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES

| | | | |
|---|---|---|---|
| $Ni-P_1$ | 2.257 (2) | $P_1-Ni-P_2$ | 120.52 (8) |
| $Ni-P_2$ | 2.306 (2) | $P_1-Ni-N_1$ | 102.4 (2) |
| $Ni-N_1$ | 2.018 (8) | $P_1-Ni-N_4$ | 101.1 (2) |
| $Ni-N_4$ | 1.686 (7) | $P_2-Ni-N_1$ | 95.3 (2) |
| $N_1-N_2$ | 0.977 (9) | $P_2-Ni-N_4$ | 110.4 (2) |
| $N_2-N_3$ | 1.282 (11) | $N_1-Ni-N_4$ | 128.8 (3) |
| $N_4-O$ | 1.164 (8) | $Ni-N_1-N_2$ | 128.1 (9) |
| $P_1-R_1C_1$ | 1.832 (5) | $Ni-N_4-O$ | 152.7 (7) |
| $P_1-R_2C_1$ | 1.836 (5) | $N_1-N_2-N_3$ | 175.1 (11) |
| $P_1-R_3C_1$ | 1.827 (5) | $R_1C_1-P_1-R_2C_1$ | 102.2 (2) |
| $P_2-R_4C_1$ | 1.838 (5) | $R_1C_1-P_1-R_3C_1$ | 104.6 (2) |
| $P_2-R_5C_1$ | 1.842 (5) | $R_2C_1-P_1-R_3C_1$ | 106.8 (2) |
| $P_2-R_6C_1$ | 1.831 (5) | $R_4C_1-P_2-R_5C_1$ | 103.9 (2) |
| $N_1-N_4$ | 3.344 (11) | $R_4C_1-P_2-R_6C_1$ | 103.9 (2) |
| $P_1-N_1$ | 3.335 (9) | $R_5C_1-P_2-R_6C_1$ | 104.2 (2) |
| $P_1-N_4$ | 3.066 (7) | $(N_1-Ni-N_4)-(P_1-Ni-P_2)$ | 85.1 (2) |
| $P_2-N_1$ | 3.201 (8) | | |
| $P_2-N_4$ | 3.297 (7) | | |
| $P_1-P_2$ | 3.962 (3) | | |

## Description of the Structure

The crystal structure consists of well-separated $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ molecules. The molecular packing is dominated by the bulky triphenylphosphine ligands. All H···H interactions are greater than 2.1 Å, and only one is less than 2.3 Å.

The numbering scheme for the molecule and a perspective view of the molecule and its inner coordination geometry are shown in Figures 1 and 2. The size and shape of an atom are determined by its anisotropic thermal parameters and the perspective view. Interatomic distances and angles calculated from the final

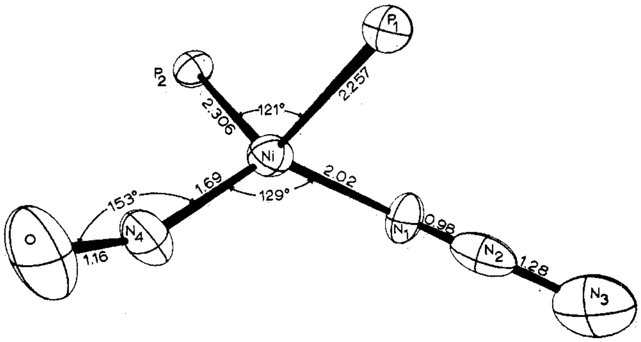

Figure 2.—Perspective view of the inner coordination sphere of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$. The ellipsoids are drawn to enclose 30% of the probability distribution.

atomic parameters of Table I are shown in Table III. Estimated standard deviations for the distances and angles were derived from the inverse least-squares matrix from the final refinement. Selected distances and angles are also given in Figure 2.

From Figure 2 it is readily apparent that the coordination geometry about the Ni atom is indeed distorted tetrahedral as suggested by Feltham.[18] The $P_1$–Ni–$P_2$ angle is 120.52 (8)°; the angle $N_1$–Ni–$N_4$ is 128.8 (3)°; and the dihedral angle between the plane defined by $N_1$, Ni, $N_4$ and the plane defined by $P_1$, Ni, $P_2$ is 85.1 (2)°. For comparison the pseudotetrahedral paramagnetic Ni(II) compound $NiBr_2(P(C_6H_5)_3)_2$[34] has a P–Ni–P angle of 110.4 (2)° and a Br–Ni–Br angle of 126.3 (1)°. In $NiBr_2[P(CH_2C_6H_5)(C_6H_5)_2]_2$[35] the P–Ni–P angle is 104.6 (3)° and the Br–Ni–Br angle is 119.6 (3)°. Unfortunately the bond angles for a related pseudotetrahedral Ni(0) complex such as $Ni(CO)_2(P(C_6H_5)_3)_2$ are not known.

The Ni–P distances are 2.257 (2) and 2.306 (2) Å. Inspection of Figures 1 and 2 and an examination of the nonbonded intramolecular interactions suggest a possible reason for the significant difference in the Ni–P bond lengths. The azide group is not symmetrically related to the two phosphine ligands. Consequently the lone pair of electrons in an $sp^2$ orbital on $N_1$ will point more toward $P_2$ than toward $P_1$. Moreover, the $N_1 \cdots P_2$ nonbonded distance is only 3.20 Å compared with 3.33 Å for the $N_1 \cdots P_1$ distance. Atom $N_1$ also has a close contact of 2.4 Å with one of the ortho H atoms on ring 5. This distance is 0.3 Å less than the sum of the van der Waals radii.[36] All other $N_1 \cdots H$ distances are 2.7 Å or greater. The Ni–P distances observed here can be compared with values of 2.251 (3)[37] and 2.26 Å[35,38] for diamagnetic trans planar $NiBr_2(PR_3)_2$ complexes and values of 2.315 (8)[35] and 2.33 (1) Å[34] found in paramagnetic tetrahedral $NiBr_2(PR_3)_2$ complexes.

The geometry of the coordinated NO group is of particular interest, and the Ni–N–O angle is 152.7 (7)°. This is the smallest M–N–O angle that has been reported for a four-coordinate nitrosyl complex but not significantly different from the 157 (3)° reported[17a] for one of the Fe–N–O angles in the dimeric complex $[Fe(NO)_2I]_2$. M–N–O angles as small as 120° have been found in five-[2,9,11b] and six-coordinate[10,11] nitrosyl complexes. The Ni–NO distance of 1.686 (7) Å is similar to the Ni–N distances of 1.68 (2) Å[15] in π-$(C_5H_5)$-Ni(NO) and 1.63 Å[14] in $Ni(tep)(NO)^+$. The N–O distance of 1.164 (8) Å is similar to the N–O distances tabulated[2] for a wide range of metal nitrosyl complexes. The small Ni–N–O bond angle is not due to packing forces because all O atom contacts are greater than van der Waals distances.

The coordination of the azide group is not unusual. The Ni–$N_1$–$N_2$ angle is 128.1 (9)°, and the Ni–N distance of 2.018 (8) Å is similar to M–N distances tabulated[39] for other azide complexes of first-row transition metals. The $N_1$–$N_2$ distance of 0.98 (1) Å is unrealistically short. The abnormal thermal ellipsoid for $N_2$ (Figure 2) also suggests that the azide group is not adequately described by the final model.[32]

## Discussion

The similarity of the Ni–N distances in π-$(C_5H_5)$-Ni(NO),[15] $Ni(tep)(NO)^+$,[14] and $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ suggests that the Ni–N bond order in all three complexes is nearly the same. These distances are also significantly shorter than the Ni–N($sp^2$) distance for a four-coördinate diamagnetic complex (1.84 Å in bis(salicylaldiminato)nickel(II)),[40] indicating a higher bond order for the Ni–NO bond. Moreover, the bonding in these $(Ni–NO)^+$ complexes is distinctly different from that found in the strongly bent five-[2,9,11b] and six-coordinate[10,11] complexes, which can be formulated either as $(NO)^-$ complexes[41,42] or complexes in which $(NO)^+$ acts as a Lewis acid.[43] In $Co(en)_2Cl(NO)^+$,[11] for example, the Co–N–O angle is 124° and the Co–N distance is 1.82 (1) Å.

Several years ago Kettle[44] pointed out that in most substituted metal carbonyl and nitrosyl complexes the two π* orbitals on each ligand belong to different irreducible representations and hence need not interact equally with the metal d orbitals. He suggested that this effect rather than crystal packing forces might be the reason that M–C–O and M–N–O angles are often significantly distorted from 180°. Although Kettle's discussion is concerned primarily with $M(CO)_3$ species, his symmetry arguments are particularly useful when applied to monocarbonyl and mononitrosyl metal complexes. If the complex possesses $C_3$ or higher symmetry, then the two π* orbitals of the NO (or CO) ligand will remain degenerate and belong to an E representation.[45] However, if the symmetry of the complex is lower than $C_3$, then the two π* orbitals will no longer belong to the same representation and need not interact equally with the metal d orbitals. Lowering the symmetry of the complex will also lower the symmetry of the total electron density distribution about the metal atom. This could, in turn, affect the repulsions between the metal d electrons and the ligands. In particular, the net repulsive force between the metal d electrons and the NO ligand could be quite different in high- and low-symmetry complexes. The equilibrium geometry of the NO group in the molecule will depend upon the interplay of d–π* bonding and d electron–ligand repulsions.

The cyclopentadienyl ring possesses a $C_5$ axis, and the tep ligand has a $C_3$ axis. Therefore, coordination of either of these ligands to a linear $(NiNO)^+$ fragment will not split the degeneracy of the d–π* interaction, and an Ni–N–O angle of 180° is observed. However, $N_3^-$ and $P(C_6H_5)_3$ are very dissimilar ligands. Consequently the effective coordination symmetry about the metal in $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ is far from $C_3$. The degeneracy of the d–π* interaction will be lifted, and the Ni–N–O group need not be linear.

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The results of the present structure determination support the idea that the M–N–O angle in complexes of the type $MX(NO)L_2$ may be sensitive to changes of M, X, L and the coordination geometry of the complex. Further studies of these compounds are in progress.

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# Thermodynamics of Ion Association. XXII. Nickel Complexes of Glycine, Diglycine, Triglycine, and Glycyl-$\gamma$-aminobutyric Acid[1]

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Calorimetric studies have been made at 25° of the formation of nickel complexes of diglycine, triglycine, and glycyl-$\gamma$-aminobutyric acid and of subsequent proton dissociation from the triglycinate species at higher pH. The data have been combined with potentiometric measurements to provide $\Delta G$, $\Delta H$, and $\Delta S$ data for each of the equilibria. Values of the thermodynamic data strongly support a common structure for all the mono complexes at lower pH in which the nickel ion is bound to the terminal $NH_2$ and the oxygen of the peptide group.

There is considerable interest in the elucidation of the structures of metal peptide complex species in aqueous solution in view of their importance as model systems in biological studies. The results of a recent calorimetric study[2] of copper di-, tri-, and tetraglycine complexes indicated a common structure for each $CuL^+$ species where $L^-$ represents the polyglycine anion. In these complexes, the copper ion is probably bound to the terminal amine nitrogen and the oxygen atom of the first peptide group in a five-membered chelate ring structure. Under progressively more alkaline conditions, stepwise ionization of the peptide hydrogen atoms takes place and metal coordination is transferred from the oxygen to the nitrogen atom of the peptide group in the formation of multichelated structures. Pasternack and his coworkers have recently studied the reactions of copper(II) with both glycylglycine and glycylsarcosine using temperature-jump techniques.[3] The kinetic results are consistent with the proposed bidentate nitrogen and oxygen binding at lower pH. The proton ionization from the glycylglycine complex at higher pH is much slower and takes place with a considerably larger activation energy than that for the formation of $CuL^+$ reflecting the proposed structural rearrangement.

The coordination changes which take place in the presence of copper ions appear to be quite well characterized, but in the case of the corresponding nickel complexes, the situation is much less clear. In the pH range 4.5–6, stability constants for complexes between the nickel ion and the polyglycine anions, $NiL^+$, were first reported by Evans and Monk[4] and by Li and Chen.[5] In one case,[4] it was suggested that the metal–ligand bonding involves neither the terminal amino nor the carboxylate groups. Li and Chen, however, proposed a metal–peptide chelate structure in which the nickel ion is attached to the terminal amino group and the immediately adjacent peptide group.[5] The kinetics of formation of the nickel–glycylsarcosine complex was studied, using a temperature-jump method by Kustin and Pasternack.[6] By comparing the kinetic data with those of the corresponding cobalt(II) complexes it was suggested that the coordination of the charged carboxylate group was not important in the formation of the nickel complexes. The rate constant for the glycylsarcosine complex was close to the values for the tri- and tetraglycine species[7] indicating the nonparticipation of the carboxylate group in the oligoglycine ligands as well. The results of a recent nmr investigation, on the other hand, have been interpreted in terms of the binding of the charged carboxylate group to the nickel ion under neutral and slightly acidic conditions.[8]

The magnitude of the enthalpy changes accompanying ion association reactions in solution can yield information concerning the nature of the ligand atom bound to the metal ion,[9] but hitherto, no direct calorimetric studies have been made of the nickel–polyglycine systems. In the present work, potentiometric and calorimetric investigations have been made of the formation of nickel complexes with glycine, diglycine, triglycine, and glycyl-$\gamma$-aminobutyric acid and also the proton dissociations from the nickel–polyglycine species.

## Experimental Section

Glycine was obtained from Baker and Adamson and the diglycine and glycyl-$\gamma$-aminobutyric acid were obtained from Nutritional Biochemical Corp. and used without further purification. The source of triglycine and the method of purification

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