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Preparation, Properties, and Crystal Structure of a Cationic Nickel Nitrosyl Bicyclic Phosphite Complex

J. H. MEINERS, C. J. RIX, J. C. CLARDY,[1] and J. G. VERKADE*

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Nitrosonium tris(1,3,7-trioxa-2-phospha-5-methylbicyclo[2.2.2]octane)nickel(0) tetrafluoroborate, $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$, was synthesized by direct reaction of $NOBF_4$ with the zerovalent $Ni[P(OCH_2)_3CCH_3]_4$. The complex exhibited a strong absorbance at 1867 cm^{-1} in its infrared spectrum, and a conductivity measurement indicated it to be a uni-univalent electrolyte. The crystal structure of this salt has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 27.29$ (3) Å, $b = 12.63$ (1) Å, $c = 24.84$ (3) Å, and $\beta = 135.55$ (2)°. The structure was solved by conventional heavy-atom techniques and refined by least-squares methods to weighted and unweighted R factors of 0.085 and 0.090, respectively, for 2000 independent reflections which had intensities greater than 2σ above background. The density of 1.60 g/cm^3 computed from the unit cell volume of 6048 Å^3 on the basis of eight $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4{\cdot}CHCl_3$ molecules per unit cell agrees well with the 1.61 g/cm^3 determined by flotation methods. The coordination geometry around the nickel is a slightly distorted tetrahedron with an average P–Ni–P angle of 104.2° and an average P–Ni–N angle of 114.3 (2)°. The nitrosyl is nearly linear with the Ni–N–O angle equal to 176.8 (18)°. One chloroform molecule per molecule of complex was found in the lattice.

Introduction

Nitrosyl derivatives of nickel[2,3] have generally been obtained by direct reaction of NO,[4-6] nitrosyl chloride,[7,8] or nitrite ion[9] with a suitable nickel substrate. Nitrosyl complexes of several other transition metals, notably from the chromium,[10,11] iron,[12] and cobalt[13] groups, have been prepared utilizing the nitrosonium cation as both an oxidizing and a nitrosylating agent. Here we report the use of NO^+ to synthesize a cationic nitrosyl of nickel which has been fully characterized by an X-ray structure determination. Although four similar cationic derivatives containing *tert*-butyl isocyanide,[4] triphenylphosphine,[3] and tripodlike phosphine ligands[9] have been isolated previously, the present compound represents the first phosphite derivative of this class. Nickel nitrosyl phosphite complexes are relatively rare, the only other compounds of which we are aware being the $P(OPh)_3$ derivatives $Ni(NO)_2(P(OPh)_3)_2$,[6] $[Ni(NO)(PPh_3)_2(P(OPh)_3)]PF_6$,[3] $[Ni(NO)(P(OPh)_3)X]_2$,[14-16] and $Ni(NO)(P(OPh)_3)_2X$[8,14,15] (X = Cl, Br, I).

Recent reviews[17,18] on nitrosyl complexes divide the known molecular structures into three classes. The first group contains "linear" M–N–O angles in the range 167–180°, the second group has distinctly "bent" M–N–O angles in the range 119–128°, and the third group has intermediate M–N–O angles. Of the more than 50 known structures about 60% fall into the "linear" classification, while the "bent" and intermediate groups contain approximately 15 and 25%, respectively. The M–N–O angle of 176.8 (18)° found in the present investigation places this nitrosyl in the "linear" classification.

To our knowledge this is the first reported crystal structure of a transition metal complex containing both the nitrosyl ligand and a phosphite.

Experimental Section

All solvents used were reagent grade and were thoroughly purged with prepurified nitrogen prior to use. Ether was refluxed with and distilled from $LiAlH_4$. Acetonitrile and benzene were refluxed with and distilled from CaH_2.

$Ni(P(OCH_2)_3CCH_3)_4$ was prepared as previously described.[19a] $NOBF_4$ was purchased from Alfa Inorganics Inc. and used without further purification. Conductivity measurements were made on an Industrial Instruments Inc. Model RC 16B2 conductivity bridge using approximately 10^{-3} *M* acetonitrile solutions. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Visible–uv spectra were obtained on a Cary 14 spectrophotometer and deconvoluted using a "log fit" computer program.

Phosphorus-31 nmr spectra were run on a Bruker HX-90 spectrometer operating in the Fourier transform mode. The magnetic susceptibility was determined by the Gouy method. Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz.

The title compound was prepared by adding 0.420 g (0.036 mol) of $NOBF_4$ to a suspension of 2.33 g (0.036 mol) of $Ni(P(OCH_2)_3CCH_3)_4$ in 100 ml of acetonitrile and 40 ml of methylene chloride. The mixture was stirred under pre-purified nitrogen for 4 hr whereupon almost all the suspended white solid had dissolved to give a blood red solution. After filtering and concentrating to approximately 10 ml, 100 ml of anhydrous ether was added and a tan powder precipitated. This was filtered and washed first with a 1:1 mixture of benzene and ether and then with ether alone. The solid was purified by redissolving it in a small volume of CH_2Cl_2 and adding hexane to precipitate the compound as a tan powder. The powder was filtered off and dried *in vacuo* to give 2.0 g (91%) of product. *Anal.* Calcd for $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$: C, 29.0; H, 4.36; N, 2.26; P, 15.0. Found: C, 28.8; H, 4.03; N, 2.18; P, 14.2.

Crystals were grown by allowing vapor diffusion of pentane into a saturated solution of the complex in 10% acetonitrile and 90% chloroform. Deep red (almost black) diamond-shaped crystals were formed. The crystal chosen was a diamond-shaped plate measuring approximately 0.10 × 0.10 × 0.04 mm. Inasmuch as the compound is sensitive to prolonged exposure to atmospheric conditions, the crystal was mounted in a 0.2-mm sealed Lindemann capillary tube.

Data were collected at room temperature using an automated four-circle diffractometer designed and built in 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 θ and 2θ

shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer in a real-time mode and is equipped with a scintillation counter. The χ, ω, and 2θ angles of 13 reflections were tuned and these values were used to calculate[19b] the reduced cell. The cell was triclinic with cell constants $a = 15.06$ Å, $b = 10.04$ Å, $c = 12.66$ Å, $\alpha = 109.6°$, $\beta = 114.6°$, and $\gamma = 70.34°$ and a cell volume of 3024.7 Å^3. Four octants of data (5937 reflections) were taken while monitoring three standards: (006), $(2\bar{4}2)$, and (600) after every 100 reflections. Crystal decomposition (43%) was linear throughout the data-taking process and was scaled up to offset this decomposition. By applying the matrix [(1, 1) = −1, (1, 2) = 0, (1, 3) = 0, (2, 1) = 0, (2, 2) = 1, (2, 3) = 1, (3, 1) = 0, (3, 3) = −1] the reduced cell in the conventional orientation was found. This cell has the dimensions $a = 15.06$ Å, $b = 19.04$ Å, $c = 12.66$ Å, $\alpha = 109.6°$, $\beta = 114.6°$, and $\gamma = 70.34°$ with a volume of 3024 Å^3. The cell scalars are $R(1, 1) = 226.80$, $R(2, 2) = 361.08$, $R(3, 3) = 160.28$, $R(2, 3) = -79.42$, $R(3, 1) = -79.37$, and $R(1, 2) = 96.27$. To this cell the transformation matrix [$T(1, 1) = -2$, $T(1, 2) = 0$, $T(1, 3) = -1$, $T(2, 1) = 0$, $T(2, 2) = 0$, $T(2, 3) = 1$, $T(3, 1) = 1$, $T(3, 2) = -1$, $T(3, 3) = 0$] was applied to give the monoclinic cell used in the structure solution [$a = 27.29$ (2) Å, $b = 12.63$ (1) Å, $c = 24.84$ (3) Å, and $\beta = 135.55$ (2)°]. The calculated cell volume was 6048 Å^3. These parameters and their standard deviations were obtained by a least-squares fit[20] to the 2θ values of 14 independent reflections whose centers were determined by left–right, top–bottom beam splitting on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.71069 Å). The 2θ values ranged from 25 to 31°.

The data were reindexed by using the transformation matrix given above with the condition that $k > 0$ and the signs of the values of h and l were determined by assigning them both nonnegative values if the product of h and l was greater than or equal to zero and by assigning h negative and l positive if the product was less than zero. Equivalent reflections were averaged. The agreement was 18.8% for net intensities greater than 100 and 8.2% for those greater than 1000. The observed intensities were corrected for Lorentz and polarization effects and the 2216 reflections which had intensities greater than $2\sigma_F$ above background were used in subsequent calculations. The systematic extinctions [(hkl), $h + k = 2n$; $(h0l)$, $l = 2n$ $(h = 2n)$; $(0k0)$, $k = 2n$] in the data limited the possible space groups to two, Cc and $C2/c$. Since there were eight molecules per unit cell, attempted refinement in both space groups was necessary to distinguish between the two alternatives. The centrosymmetric assignment was confirmed by subsequent solution and refinement of the structure. The density of 1.60 g/cm^3 computed from the unit cell volume of 6048 Å^3 on the basis of eight $[\mathrm{Ni(P(OCH_2)_3CCH_3)_3NO]BF_4{\cdot}CHCl_3}$ molecules per unit cell agrees well with the 1.61 g/cm^3 determined by the flotation method in a mixture of CCl_4 and 1,2-dibromoethane. Using a hexane–1,2-dibromoethane mixture, the experimental density was 1.58 g/cm^3.

Data were taken using a peak height data collection mode which maximizes in ω. The data were collected within a 2θ sphere of 40° ($(\sin\theta)/\lambda = 0.488$ Å^{-1}) using unfiltered pyrolytic graphite-monochromatized Mo Kα radiation (0.7107 Å) at a takeoff angle of 5°. The peak heights were measured for 5 sec and background readings were taken for 2.5 sec after which the background values were scaled up by a factor of 2. The linear absorption coefficient calculated using the (μ/ρ) values published in ref 21a was 11.2 cm^{-1} and the intensity data were not corrected for this absorption. The maximum and minimum transmission factors were 0.956 and 0.894, respectively.

Structure Determination and Refinement

The position of the nickel atom was determined from a three-dimensional Patterson function. After three cycles of least-squares refinement of the positional parameters with the isotropic thermal parameters held at 3.0 and a single scale factor, the discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ were 0.564 and 0.618, respectively. The nickel-phased electron density synthesis[22] was used to calculate a difference Fourier map which revealed the position of the phosphorus atoms. Three cycles of refinement[23] on the positional parameters of the three phosphorus atoms combined with positional and isotropic thermal parameters of the nickel lowered the R_1 and R_2 values to 0.435 and 0.517, respectively. In three steps the positions of the 30 atoms in the $\mathrm{Ni(P(OC)_3CC)_3NO}$ framework were located and three cycles of varying all positional parameters, the anisotropic thermal parameters of the nickel and phosphorus atoms, and the isotropic thermal parameters of the other 26 atoms yielded R_1 and R_2 values of 0.286 and 0.342. An electron density difference map was generated and the BF_4 and CCl_3 moieties were found. In several steps the anisotropic thermal parameters of all 39 atoms were refined yielding R_1 and R_2 values of 0.113 and 0.106. Since systematic errors were suspected, 216 of the 2216 reflections for which $|F_o - F_c|/F_c > 0.50$ were omitted and a final refinement of three cycles in which the weights, w, were assigned $1/\sigma(F_o^2)$ gave discrepancy factors R_1 and R_2 of 0.090 and 0.085, respectively. The ratio of the largest shift in the last refinement cycle to standard deviation was 0.23. The hydrogen atoms were not located. The atomic scattering factors used in the refinement were those of Hanson, *et al.*,[24] and the real and imaginary corrections[21b] for anomalous dispersion for nickel were also included in the calculations.

Results and Discussion

Synthesis and Properties. The reaction of NO^+ with Ni(phosphite)$_4$ compounds is part of a program we have initiated in the study of oxidative addition–elimination reactions on phosphorus-rich metal substrates. The recognition of such complexes as Lewis bases has been discussed by Shriver[25] and previous work by us[26] and Tolman[27] has shown that Ni(phosphite)$_4$ compounds are capable of ready protonation to give HNi(phosphite)$_4^+$ species as might be expected for a simple Lewis acid–base reaction. In addition, bromination of Ni(phosphite)$_4$ produces [Ni(phosphite)$_4$Br]Br salts.[28] Both protonation and bromination are thus examples of oxidative addition reactions, whereas reaction with NO^+ (eq 1) could

$$\text{Ni(phosphite)}_4 + \text{NO}^+\text{BF}_4^- \xrightarrow{\text{MeCN}} [\text{Ni(phosphite)}_3(\text{NO})]\text{BF}_4 + \text{phosphite} \qquad (1)$$

be regarded as either an oxidative elimination, whereby Ni(0) is oxidized to Ni(II) with the concomitant loss of ligand, or simply ligand replacement on Ni(0). We prefer the latter description since it is more consistent with the available physical data presented below. Thus, we consider $[\mathrm{Ni(NO)(P(OCH_2)_3CCH_3)_3]BF_4}$ to be a nitrosonium derivative of zerovalent nickel. A similar description has been used for the analogous $[\mathrm{Ni(NO)(TEP)]BF_4}$ (TEP = $\mathrm{CH_3C(CH_2P(C_2H_5)_2)_3}$) complex.[9,29]

Physical measurements on the tan powder obtained from the reaction of $\mathrm{Ni(P(OCH_2)_3CCH_3)_4}$ with $NOBF_4$ indicated the product to be a diamagnetic, uni-univalent ionic salt (conductivity in acetonitrile 167 ohm^{-1} cm^2 mol^{-1} at 298°K; for $(C_4H_9)_4NI$, 158 ohm^{-1} cm^2 mol^{-1} under similar conditions) containing a single nitrosyl ligand (see Table I). The downfield shift of the CH_3 and CH_2 proton absorptions in the nmr spectrum (by approximately 0.3 ppm each) relative to those in the parent NiL_4 complex was consistent with deshielding due to the cationic nature of the nickel–nitrosyl moiety. In addition, the single sharp resonance in the ^{31}P nmr spectrum (at −101 ppm in CH_3CN relative to an external capillary of 85% H_3PO_4) suggested all the phosphorus atoms in the complex were equivalent on the nmr time scale. Such data are consistent with a tetrahedral (C_{3v}) $\mathrm{Ni(NO)L_3}^+$, a square-pyramidal (C_{4v}) $\mathrm{Ni(NO)L_4}^+$ or a conformationally mobile structure for the cation. Unfortunately, visible–uv spectral data (see Table I) were not definitive, because although the spectrum was similar to that of the TEP derivative,[9] it was also comparable to those obtained for five-coordinate $\mathrm{NiP_4X^+}$ species.[30] The effective atomic number rule suggested a four-coordinate structure for the complex and this was supported by an elemental analysis which gave the stoichiometry as $\mathrm{Ni(NO)(P(OCH_2)_3CCH_3)_3BF_4}$ as well as the single-crystal diffraction study which confirmed the tetrahedral structure of the nickel cation.

Several physical properties call for comment. The preparation of the nitrosyl complex described in this paper gives an excellent yield of diamagnetic product, in contrast to the analogous derivatives with tripodlike phosphines. The latter

Table I. Magnetic and Spectral Data for the Nickel Complexes

	μ_{eff}, BM	ν_{NO},[a] cm^{-1}	Color	Vis–uv[b] λ_{max}, kK (ϵ)
$Ni(P(OCH_2)_3CMe)_3NO^+BF_4^-$	Diamag[c]	1867 1872[b]	Red-black	20.49 (485) 24.69 (738) 29.41 sh (216)
$Ni(TTP)NO^+BPh_4^-$ [e]	0.58[d]	1765	Deep red	19.92 sh (840) 23.26 (1260) 28.49 (1000)
$Ni(TEP)NO^+BF_4^-$ [e]	0.46[d]	1750	Deep red	20.62 sh (703) 23.98 (1490) 28.74 (685)
Ni(*t*-BuNC)$_3$NO$^+$NO$_3^-$ [f]	Diamag[g]	1825	Dark purple	
$NiP_4Br^+BPh_4^-$ [h,i]	Diamag		Brick red	19.2 (356) 25.0 (1461)

[a] In Nujol mull. [b] In CH_2Cl_2 solution. [c] Measured on a bulk sample by the Gouy method. [d] Using a Faraday balance. [e] Reference 9. [f] Reference 4. [g] Deduced by inference from well-resolved proton nmr. [h] Reference 30. [i] P_4 is an alkyl or aryl tetradentate phosphine.

compounds were prepared *via* reaction of nickel halides, free phosphine, and nitrite ion and invariably showed some residual paramagnetism as a result of contaminating tetrahedral nickel(II) derivatives.[9] A more suitable preparative route for the "tripodlike" phosphine derivatives might be the reaction of nitrosonium salts with the zerovalent Ni(CO)(triphosphine) substrates. Such a synthesis would avoid the use of nickel halides and the possibility of exposing the free phosphine ligand to a potentially oxidizing medium, both of which tend to be conducive to the production of tetrahedral nickel(II).

The infrared spectrum of $[NiNO(P(OCH_2)_3CCH_3)_3]BF_4$ in a KBr disk shows that apart from ligand absorptions, the only additional infrared frequencies appear as a band at 1867 cm^{-1} (assigned to ν_{NO}) and a broad band between 1000 and 1100 cm^{-1} attributed to the BF_4^- anion as observed by Meek.[9] Attempts to correlate nitrosyl stretching frequencies with the "linear" (NO^+ like) and "bent" (NO^- like) coordination modes of the nitrosyl ligand have not been universally successful.[3,17] Early workers[31] suggested that nitrosyl stretching frequencies in the range 1500–1700 cm^{-1} be considered as coordinated NO^-, whereas a recent report[32] suggests $\nu_{\mathrm{NO^-}}$ be considered to span the range 1500–1940 cm^{-1}. Nevertheless, it is quite clear from the structural results obtained so far[17,18] that no simple correlation exists, and any future relationship will have to take account of the electronic configuration of the metal atom, the stereochemistry of the complex, and the nature of the ligands, since each of these factors exerts a rather significant effect on the final observable nitrosyl stretching frequency. It is interesting to compare the ν_{NO} of the phosphite complex with those of the TEP and TPP ($CH_3C(CH_2PPh_2)_3$) complexes. The 100-cm^{-1} difference (see Table I) is presumably a reflection of either or both the higher π acidity or lower σ basicity of phosphites relative to phosphines.

The bonding in metal nitrosyls has been discussed elsewhere in terms of valence-bond theory.[3,17,18] An extension of this concept, the so-called "increased-valence" approach, has also been used to describe the bonding in these systems.[33] Molecular orbital bonding schemes have been developed[18,34,35] which give a quantitative basis for the interpretation of electronic spectra and bonding in nitrosyl complexes. A recent paper[35] gives an MO scheme for a tetrahedral $M(NO)L_3$ moiety wherein it was concluded that electron-rich complexes, similar to the one discussed here, would show no real preference for either "linear" or "bent" M–N–O groups. In fact, examples of both linear and bent nitrosyls in tetrahedral complexes are known,[18] and $[Ni(NO)(P(OCH_2)_3CCH_3)_3]BF_4$ is simply another example belonging to the former group.

In the present case the Ni atom has a d^{10} configuration and so, as proposed by Meek,[9] the color of the complex must originate from either Ni-to-NO or NO-to-Ni charge transfer with a third possibility being intraligand electronic transitions in the NO group. Mingos[35] has suggested that as a result of the relatively low-energy π^* orbital on NO, the highest filled MO in a C_{3v} ML_3NO molecule would possess predominantly π^* NO character, whereas the lowest empty MO would have mainly metal character. This implies that the lowest energy electronic transitions arise from ligand-to-metal charge transfer. Unfortunately the MO scheme does not admit any significant π interactions from the three additional ligands; thus we do not feel justified in using the simplified scheme to assign the visible–uv spectral bands of $Ni(NO)(P(OCH_2)_3CCH_3)_3^+$ to definite electronic transitions.

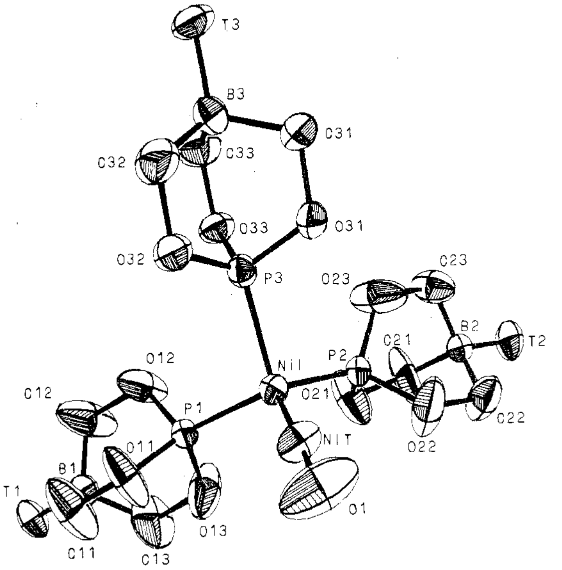

Figure 1. Computer drawing of the structure of the $[Ni[P(OCH_2)_3CCH_3)_3NO]^+$ cation.

Structure. The final positional and anisotropic thermal parameters of the atoms are given in Table II and the final F_o and F_c values (in electrons × 10) for the 2216 reflections used have been tabulated.[36] The structure of the $[Ni(P(OCH_3)_2CCH_3)_3NO]^+$ cation is shown in Figure 1.[37] One mole of chloroform and 1 mol of tetrafluoroborate were found per cation but these are omitted from the figure. Table III lists the important interatomic distances, angles, and their deviations which were calculated from the final parameters and the correlation matrix.[38]

Two other crystal structures containing the bicyclic phosphite moiety have been determined: $OP(OCH_2)_3CCH_3$[39] and $[Ag(P(OCH_2)_3CCH_3)_4]ClO_4$.[40] The average interatomic distances and angles in the $P(OCH_2)_3CCH_3$ moiety for the three structures are given in Table IV. In all cases the values found in the present structure agree well (within 2.5%) with those of the phosphate. Only the C–B bond distance (where B refers to the bridgehead carbon—see Figure 1) and the

Table II. Final Atomic Coordinates and Thermal Parameters

	Fractional Coordinates			Atomic temperature factors × 10^4					
Atom	X^a	Y	Z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni1	0.08891 (9)	−0.0011 (1)	0.4136 (1)	36.6 (6)	42 (1)	49.6 (7)	6.8 (9)	30.3 (6)	1 (1)
P1	0.1339 (1)	−0.0923 (3)	0.3823 (3)	38 (1)	24 (4)	45 (1)	1 (1)	31 (1)	2 (2)
P2	0.0625 (1)	−0.1128 (4)	0.4565 (2)	37 (1)	44 (4)	51 (1)	1 (2)	33 (1)	−5 (2)
P3	0.1775 (1)	0.0796 (3)	0.5211 (2)	38 (1)	19 (4)	52 (1)	6 (1)	34 (1)	4 (2)
NIT	0.0255 (6)	0.071 (1)	0.3464 (8)	46 (5)	0 (1)	76 (7)	14 (6)	34 (5)	−2 (7)
O1	−0.0208 (9)	0.122 (1)	0.299 (1)	86 (8)	4 (2)	3 (1)	5 (1)	31 (7)	1 (1)
O11	0.1306 (9)	0.035 (1)	0.3266 (9)	7 (1)	0 (1)	7 (1)	2 (1)	6 (1)	1 (1)
O12	0.2073 (6)	−0.129 (1)	0.4422 (6)	71 (5)	0 (2)	50 (5)	9 (1)	31 (4)	−9 (9)
O13	0.0952 (9)	0.191 (1)	0.336 (1)	4 (1)	0 (2)	6 (1)	−2 (1)	7 (1)	−8 (1)
C11	0.154 (1)	−0.093 (2)	0.296 (1)	4 (2)	8 (3)	1 (1)	5 (2)	0 (1)	1 (2)
C12	0.234 (1)	−0.189 (2)	0.417 (1)	9 (1)	6 (4)	75 (9)	2 (1)	50 (8)	−1 (1)
C13	0.121 (1)	−0.253 (2)	0.309 (2)	1 (2)	8 (2)	8 (3)	−8 (2)	2 (2)	−3 (2)
B1	0.1814 (9)	−0.196 (1)	0.3318 (9)	73 (7)	1 (1)	76 (8)	2 (9)	58 (7)	35 (9)
T1	0.2091 (9)	−0.261 (1)	0.304 (1)	94 (9)	6 (1)	0 (1)	2 (1)	85 (9)	35 (9)
O21	0.062 (1)	−0.229 (1)	0.447 (1)	3 (1)	5 (1)	5 (1)	−1 (1)	2 (1)	−3 (1)
O22	−0.0121 (6)	−0.104 (1)	0.4153 (8)	61 (5)	8 (3)	37 (9)	6 (1)	73 (6)	4 (1)
O23	0.1027 (8)	−0.109 (1)	0.5393 (7)	25 (8)	9 (2)	60 (6)	−4 (1)	56 (6)	−4 (1)
C21	0.045 (1)	−0.297 (1)	0.483 (2)	8 (2)	3 (2)	5 (3)	−1 (2)	0 (2)	1 (2)
C22	−0.037 (1)	−0.174 (2)	0.438 (1)	71 (9)	0 (4)	4 (1)	1 (1)	8 (1)	0 (2)
C23	0.082 (1)	−0.169 (1)	0.571 (1)	9 (1)	4 (2)	74 (9)	−8 (1)	58 (8)	−2 (1)
B2	0.0223 (8)	−0.234 (1)	0.508 (1)	55 (6)	4 (1)	76 (8)	−1 (9)	54 (7)	0 (1)
T2	0.0001 (9)	−0.307 (1)	0.537 (1)	73 (7)	9 (2)	9 (1)	−2 (1)	69 (8)	−0 (1)
O31	0.1575 (4)	0.1309 (8)	0.5606 (5)	43 (3)	6 (1)	80 (5)	−16 (5)	45 (4)	−32 (6)
O32	0.2118 (5)	0.1715 (9)	0.5155 (5)	59 (4)	7 (1)	56 (4)	−29 (6)	38 (4)	−2 (6)
O33	0.2435 (4)	0.123 (7)	0.5876 (5)	44 (3)	2 (8)	59 (4)	3 (4)	30 (3)	−5 (5)
C31	0.2141 (7)	0.183 (1)	0.6365 (9)	54 (5)	3 (2)	13 (9)	−33 (9)	58 (6)	−7 (1)
C32	0.2658 (8)	0.234 (1)	0.5869 (9)	83 (7)	6 (2)	86 (8)	−5 (1)	60 (7)	−2 (1)
C33	0.3009 (7)	0.067 (1)	0.6614 (8)	59 (6)	1 (2)	72 (7)	9 (9)	36 (6)	0 (1)
B3	0.2809 (7)	0.185 (1)	0.6544 (8)	53 (6)	1 (1)	60 (7)	10 (8)	40 (6)	3 (9)
T3	0.3404 (8)	0.240 (1)	0.7313 (8)	54 (6)	7 (1)	49 (6)	−35 (9)	27 (5)	−23 (9)
C1	0.077 (1)	0.458 (1)	0.414 (1)	2 (1)	3 (2)	0 (2)	−3 (1)	3 (1)	−1 (1)
Cl1	−0.0080 (6)	0.508 (1)	0.3369 (6)	68 (7)	3 (2)	61 (7)	3 (1)	59 (5)	12 (9)
Cl2	0.0679 (8)	0.343 (1)	0.375 (1)	8 (1)	8 (1)	7 (1)	1 (1)	3 (1)	2 (1)
Cl3	0.1298 (8)	0.525 (1)	0.4251 (8)	9 (1)	0 (3)	0 (1)	−8 (1)	6 (1)	−6 (1)
BOR^c	0.171 (1)	0.478 (2)	0.656 (2)	1 (1)	4 (3)	1 (1)	0 (1)	9 (1)	3 (2)
FW^d	0.239 (1)	0.442 (1)	0.721 (1)	3 (1)	8 (3)	6 (1)	9 (1)	1 (1)	7 (1)
FX^d	0.1794 (9)	0.577 (1)	0.6751 (9)	7 (1)	4 (1)	6 (1)	0 (1)	2 (1)	−2 (1)
FY^d	0.1359 (7)	0.425 (1)	0.6582 (9)	6 (8)	5 (2)	40 (9)	−5 (1)	84 (8)	2 (1)
FZ^d	0.1614 (9)	0.469 (1)	0.5978 (9)	1 (1)	9 (2)	5 (1)	−3 (1)	5 (1)	−3 (1)

[a] Standard deviations of the least significant figure are given in parentheses here and in subsequent tables. [b] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Boron atom in BF_4^-. [d] Fluorine atom in BF_4^-.

P–O–C angle in the silver salt are not in good agreement with the other two structures and this may be due to the limited stage of refinement at present ($R = 0.14$) of the silver complex.

The average Ni–P distance (2.186 Å) in the nickel complex agrees very well with other reported Ni–P distances[41–47] which average 2.190 Å. The Ni–P distances have ranged from 2.14 Å for the apical adamantane-like phosphites in $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$[44] to 2.23 Å in $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_3$.[46] The Ni–N distance of 1.581 (12)° agrees well with the 1.579-Å length reported for the similar complex [Ni(TEP)NO]BF_4.[9,29] This bond length is quite short for a first transition series metal nitrosyl. For the 28 compounds listed in a recent review[18] the average Ni–N value is 1.69 Å. The shortness of this bond indicates a significant amount of multiple-bond character and this is more consistent with the presence of NO^+ than NO^-. Both $[Ni(TEP)NO]^+$ and $[Ni(NO)(P(OCH_2)_3CMe)_3]^+$ have "linear" M–N–O fragments being 180 and 176.8 (18)°, respectively. The only other reported crystal structure of a nickel nitrosyl complex is $Ni(N_3)NO(PPh_3)_2$[48] in which the Ni–N distance is significantly longer at 1.686 (7) Å and the Ni–N–O angle is only 152.7 (7)°. Both the longer bond distance and the more "bent" angle classify this nitrosyl as more NO^--like than the other two linear nickel nitrosyl cases.

Kettle[49] has pointed out that in substituted metal carbonyl or nitrosyl complexes which are of lower than C_3 symmetry, the two π^* orbitals on each ligand belong to different irreducible representations and hence do not interact equally with the metal d orbitals. He further 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 linearity. If the complex possesses C_3 or higher symmetry, then the two π^* orbitals are degenerate and belong to an E representation. Whereas Kettle's discussion is concerned only with the $M(CO)_3$ species, Enemark[48] has recently suggested that the argument is useful when applied to monocarbonyl and mononitrosyl metal complexes. Of the three cases [Ni(TEP)NO]BF_4,[9,29] $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$, and $Ni(N_3)(NO)(P(C_6H_5)_3)_2$,[48] only the last has less than C_3 symmetry, which may be responsible for the less "linear" M–N–O angle and the longer Ni–N bond distance. A microwave study on η^5-$(C_5H_5)Ni(NO)$[50] has revealed a rigorously linear M–N–O angle. The C_5 symmetry of the η^5-$(C_5H_5)Ni$ moiety would not split the degeneracy of the d–π^* interaction and thus would not cause a "bent" nitrosyl. The reported N–O distances range from 1.02 to 1.29 Å with the average being about 1.16 Å which is close to the value of 1.122 (15) Å for the present complex. As has been shown earlier,[18] a correlation between N–O distances and M–N–O angles cannot be made.

The geometry around the nickel in the present structure is a distorted tetrahedron with an average P–Ni–P angle of 104.2° and an average P–Ni–N angle of 114.3° as shown in Figure 2.[37] The phosphite ligands are crowded together away from the nitrosyl with substantially less than tetrahedral angles. The reason for this distortion is not clear but a similar situation

Table III. Bond Distances and Angles in $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4 \cdot CHCl_3$

	(a) Bonded Distances, Å		
Ni1-P1	2.191 (4)	O33-C33	1.48 (1)
Ni1-P2	2.176 (5)	C11-B1	1.45 (2)
Ni1-P3	2.191 (4)	C12-B1	1.48 (2)
Ni1-NIT	1.581 (12)	C13-B1	1.48 (2)
P1-O1	1.122 (15)	C21-B2	1.42 (2)
P1-O11	1.503 (11)	C22-B2	1.48 (2)
P1-O12	1.503 (11)	C23-B2	1.47 (2)
P2-O13	1.507 (14)	C31-B3	1.54 (2)
P2-O22	1.494 (14)	C32-B3	1.54 (2)
P2-O23	1.486 (12)	C33-B3	1.56 (2)
P3-O31	1.563 (9)	B1-T1	1.55 (2)
P3-O32	1.557 (10)	B2-T2	1.54 (2)
P3-O33	1.564 (9)	B3-T3	1.53 (2)
O11-C11	1.49 (2)	C1-Cl1	1.77 (3)
O12-C12	1.49 (2)	C1-Cl2	1.66 (2)
O13-C13	1.50 (2)	C1-Cl3	1.50 (2)
O21-C21	1.51 (2)	BOR-F*W*[a]	1.41 (3)
O23-C23	1.47 (2)	BOR-F*X*[a]	1.31 (3)
O31-C31	1.49 (1)	BOR-F*Y*[a]	1.21 (3)
O32-C32	1.49 (2)	BOR-F*Z*[a]	1.28 (3)
	(b) Bond Angles, Deg		
NIT-Ni1-P1	113.5 (5)	P1-O12-C12	118.0 (10)
NIT-Ni1-P2	113.5 (5)	P1-O13-C13	118.3 (13)
NIT-Ni1-P3	116.0 (5)	P2-O21-C21	116.4 (12)
P1-Ni1-P2	107.3 (2)	P2-O22-C22	118.9 (13)
P1-Ni1-P3	105.4 (1)	P2-O23-C23	122.7 (11)
P2-Ni1-P3	99.8 (2)	P3-O31-C31	117.9 (8)
Ni1-NIT-O1	176.8 (18)	P3-O32-C32	115.9 (9)
Ni1-P1-O11	113.5 (5)	P3-O33-C32	117.0 (9)
Ni1-P1-O12	120.6 (5)	O11-C11-B1	110.2 (14)
Ni1-P1-O13	116.1 (5)	O12-C11-B1	110.8 (14)
Ni1-P2-O21	122.1 (5)	O13-C13-B1	109.0 (16)
Ni1-P2-O22	112.7 (6)	O21-C21-B1	110.6 (17)
Ni1-P2-O23	118.6 (5)	O22-C22-B2	108.5 (14)
Ni1-P3-O31	112.4 (4)	O23-C23-B2	106.3 (13)
Ni1-P3-O32	116.7 (4)	O31-C31-B3	108.4 (11)
Ni1-P3-O33	118.1 (4)	O32-C32-B3	110.8 (12)
O11-P1-O12	102.9 (8)	O33-C33-B3	109.7 (11)
O11-P1-O13	98.6 (10)	C11-B1-C12	111.3 (19)
O12-P1-O13	102.1 (10)	C11-B1-C13	105.4 (19)
O21-P2-O22	96.4 (10)	C12-B1-C13	105.5 (18)
O21-P2-O23	99.3 (11)	C21-B2-C22	104.6 (19)
O22-P2-O23	104.1 (9)	C21-B2-C23	105.7 (17)
O31-P3-O32	104.4 (6)	C22-B2-C23	115.1 (18)
O31-P3-O33	102.6 (5)	C31-B3-C32	110.5 (13)
O32-P3-O33	100.8 (5)	C31-B3-C33	105.4 (13)
P1-O11-C11	118.3 (11)	C32-B3-C33	107.6 (13)

[a] Boron-fluorine distances in the BF_4^- ion.

has been observed for $Ni(N_3)_3(NO)(P(C_6H_5)_3)_2$[48] where the average angle that the other ligands make with the nitrosyl nitrogen is 113.4° and the other three angles with the nickel at the vertex are 106.1° in spite of the very bulky triphenylphosphines. The structure of $[Ni(TEP)NO]BF_4$[9,29] shows this same phenomenon in a more pronounced manner with the average angles being 122.8 and 93.5°, respectively. The constrained nature of the "tripodlike" ligand in this instance may account for this, however.

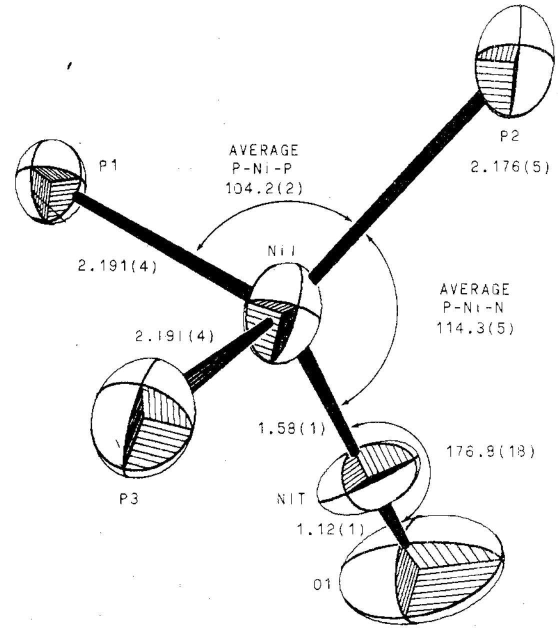

Figure 2. Computer drawing of inner coordination sphere around the nickel atom.

It is worthwhile to note that of the three pseudotetrahedral nickel nitrosyl structures $[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$, $[Ni(TEP)NO]BF_4$, and η^5-C_5H_5NiNO which have sufficient symmetry to preserve the degeneracy of the two π^* nitrosyl orbitals only the present structure has an M-N-O angle which is not rigorously linear. No atom in the chloroform or the tetrafluoroborate approaches the $[NiNO(P(OCH_2)_3CCH_3)_3]^+$ moiety within the sum of van der Waals radii with the possible exception of the Cl2-O1 distance (3.27 (2) Å). The van der Waals radii of Cl and O are 1.7-1.9 and 1.5 Å, respectively.[51] Thus our value falls within the range of 3.2-3.4 Å and this possible contact may account for the slight deviation from linearity in the M-N-O bond angle.

Finally, the manner in which the $CHCl_3$ and BF_4 moieties are juxtaposed is interesting. Both the probable position of the hydrogen (from the known carbon and three Cl positions) and the position of one of the fluorines, *FZ*, lie quite close to the line defined by the carbon and boron. Assuming a C-H distance of 1.14 Å,[51] the H-F distance would be 2.2 Å which is well within the sum of the van der Waals radii (2.70-3.05 Å[51]) thus suggesting a weak electrostatic ordering of the $CHCl_3$ and BF_4.

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Table IV. Comparison of Parameters in the Bicyclic Phosphite Moieties Found in the Three Crystal Structure Studies

(a) Comparison of Average Bond Distances (Å) in the $P(OCH_2)_3CCH_3$ Moiety

	P-O	O-C	C-B[a]	B[a]-T[b]
$OP(OCH_2)_3CCH_3$[c]	1.537 (15)	1.455 (20)	1.519 (24)	1.567 (23)
$[Ag(P(OCH_2)_3CCH_3)_4]ClO_4$[d]	1.563 (14)	1.44 (2)	1.60 (3)	1.54 (2)
$[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$	1.517 (11)	1.49 (2)	1.49 (2)	1.54 (2)

(b) Comparison of Average Angles (deg) in the $P(OCH_2)_3CCH_3$ Moiety

	O-P-O	P-O-C	O-C-B[a]	C-B[a]-T[b]	C-B[a]-C
$OP(OCH_2)_3CCH_3$[c]	103.7 (6)	115.2 (11)	108.7 (14)	109.2 (15)	109.6 (12)
$[Ag(P(OCH_2)_3CCH_3)_4]ClO_4$[d]	100.3 (9)	122.0 (13)	106.7 (17)	110.7 (17)	107.6 (16)
$[Ni(P(OCH_2)_3CCH_3)_3NO]BF_4$	101.2 (8)	118.2 (10)	109.4 (13)	110.9 (14)	107.9 (16)

[a] Bridgehead carbon. [b] Tail carbon. [c] Reference 39. [d] Reference 40.

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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Contribution from Gilman Hall and the Ames Laboratory—USAEC,
Iowa State University, Ames, Iowa 50010

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

L. J. VANDE GRIEND,[2a] J. C. CLARDY,[2b] and J. G. VERKADE*

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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