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Nickel–Nitrosyl Complexes: Structure of Nitrosyltris(trimethylphosphine)nickel Hexafluorophosphate, $\{Ni(NO)(PMe_3)_3\}PF_6$

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The crystal and molecular structure of nitrosyltris(trimethylphosphine)nickel(0) hexafluorophosphate, $\{Ni(NO)(PMe_3)_3\}PF_6$*, has been determined from three dimensional single crystal X-ray analysis. The compound crystallizes in the orthorhombic space group Pnma with* $Z = 4$ *and a unit cell of dimensions:* $a = 16.253(3)$, $b = 10.536(1)$ *and* $c = 12.228(2)$ Å. *The structure was solved by conventional heavy atom techniques and refined by least-squares methods to* $R_1 = 0.036$ *and* $R_2 = 0.048$ *respectively for 1085 independent reflections. The coordination geometry around the nickel is a slightly distorted tetrahedron with an average P–Ni–P angle of 105.63° and P–Ni–N angle 113.03°. The nickel nitrosyl group is slightly bent with an Ni–N–O angle of 175.4(5)°. The bending occurs in the C1–P1–Ni–N–O plane toward P1. The structure is compared with other tetrahedral* $\{M\text{–}NO\}^{10}$ *phosphine complexes and the M–NO bonding is discussed.*

Introduction

It is now well established that the geometry of the triatomic $\{M\text{–}NO\}^x$ fragment in metal nitrosyl complexes is dependent on the nature of the metals, on the other coordinated ligands and also on the geometry of the coordination sphere [1]. In tetracoordinate $\{Ni\text{–}NO\}^{10}$ complexes, two limiting stereochemistries consistent with the amphoteric nature of NO have been proposed: square planar with a strongly bent Ni–NO group (120°, NO^-), and tetrahedral with a linear Ni–NO group (180°, NO^+). However, only tetrahedral and distorted tetrahedral geometries have been observed experimentally, with Ni–NO angles in the range 150–180°: 152.7(7) in $Ni(NO)(N_3)(PPh_3)_2$ [2] and 161.5(5) in $Ni(NO)(NCS)(PPh_3)_2$ [3], and 165.5(8)° in $Ni(NO)(NO_2)(PMe_3)_2$ [4] where the PMe_3 ligand is less sterically hindered. Ligand–ligand interaction, coordination geometry, vibronic distortion, packing interaction and electronic properties have all been suggested as the origin of this distortion. Although the other variables are difficult to control, it was thought that increasing the symmetry of the molecule by using three identical ligands would increase the linearity of the M–N–O moiety. For example, values close to 180° have been reported for $\{M(NO)P_3\}^{n+}$ complexes: 176.8(18)° for $\{Ni(NO)(P(OCH_2)_3CCH_3)_3\}^+$ [5], 180° for $\{Ni(NO)(TEP)\}^+$ (TEP = $CH_3C(CH_2PEt_2)_3$) and for $Ir(NO)(PPh_3)_3$ [7]. However there are still exceptions, which have been tentatively related to the electronic structure of the complex [1]: $\{Ni(NO)(NP_3)\}^+$ with Ni–N–O = 167.7(21)° (NP_3 = tris(2-diphenylarsinoethyl)amine) and $Rh(NO)(PPh_3)_3$ [9] where the Rh–N–O angle is 156.7(26)°.

It was thus of interest to investigate further the influence of ligand and symmetry on the M–N–O moiety, by carrying out structural studies of related complexes. We report here the crystal structure of $\{Ni(NO)(PMe_3)_3\}PF_6$ and its comparison with $Ni(NO)(NO_2)(PMe_3)_2$. This complex is easily obtained by oxygen atom transfer, on reacting CO with an acetone solution of $\{Ni(NO_2)(PMe_3)_3\}PF_6$ prepared *in situ* from $NiCl_2(PMe_3)_2$, $NaNO_2$, $NaPF_6$ and PMe_3. The solution electronic spectrum of this complex and of related $\{Ni(NO)(PEt_3)_3\}PF_6$ and $\{Ni(NO)(PMe_2Ph)_3\}PF_6$ have been measured and compared to $Ni(NO)(NO_2)(PR_3)_2$ (PR_3 = PMe_3, PEt_3, PMe_2Ph).

Experimental

Procedure, Reagents and Solvents

All operations were carried out under a purified argon atmosphere in a conventional vacuum system or in a Jaram Glove Box.

Acetone, dichloromethane and dimethylether (Fluka *puriss.*) were distilled just before use over the following agents (acetone: molecular sieves 4 Å; CH_2Cl_2: Na_2CO_3; Na:dimethylether), transferred under argon and degassed on a vacuum line. Carbon monoxide was used without purification. Trimethylphosphine was prepared following [10] and stored under argon.

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TABLE I. Crystal Data and Experimental Details of the X-ray Diffraction Study of $[Ni(NO)(PMe_3)_3]PF_6$.

(A) Crystal Parameters at 22 °C [a]			
a, Å	16.253(3)	V, Å^3	2093.8
b, Å	10.536(1)	mol wt	461.59
c, Å	12.228(2)	F(000)	952
absences	$0kl$, $k + l = 2n + 1$ $hk0$, $h = 2n + 1$	cryst. syst.	orthorhombic
space group	Pnma or Pn2_1a	Z	4
ρ(obs)	not measured	ρ(calc), g/cm^3	1.464
cryst. dimens., mm	0.40 × 0.30 × 0.30	μ, cm^{-1}	12.77
(B) Measurement of Intensity Data			
radiation	MoK$\bar{\alpha}$ ($\bar{\lambda}$, 0.71069 Å) graphite monochromatized	instrument cryst. det. dist., mm	Nonius CAD4 210
det. window: height, mm	4	scan mode	$\theta - 2\theta$
det. window: width, mm	4	scan range, deg	0.75 + 0.35 tan θ
take-off angle, deg	4.45	scan speed, deg/mn	10
no. of reflections collected	2799	max 2θ, deg	57.0
standards: intensity [b]	3 reflections every 7200 s		
standards: orientation	3 reflections every 200 data reflections		
(C) Treatment of Intensity Data [c]			
reduction to F_o^2 and $\sigma(F_o^2)$	corrected for backgrounds, attenuators and Lorentz-polarization in the usual manner		
unique data, $F_o > 4\sigma(F_o)$	NO = 1085	no. of variables	NV = 115
R [d]	0.036	R_w [1]	0.048
$w = 1/[\sigma_{F_o}{}^2 + (pF_o{}^2)]$, p	0.037	S [f]	0.97

[a] From a least-squares fitting of the setting angles of 25 reflections. [b] Showed only random, statistical fluctuations. [c] All calculations were performed on an Iris 80 CII computer with use of local versions of SHELX 76, ORFLS and ORFFE programs. [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [1] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [f] $S = [\Sigma w(|F_o| - |F_c|)^2/(NO-NV)]^{1/2}$, error in an observation of unit weight.

Synthesis of the Complexes

$\{Ni(NO)(PR_3)_3\}PF_6$ complexes (PR_3 = PMe_3 (*1*), PEt_3 (*2*), PMe_2Ph (*3*)) were prepared according to the published method [11].

$\{Ni(NO)(PMe_3)_3\}PF_6$

To a refluxing solution of $NiCl_2(PMe_3)_2$ (4.5 mmol; 1.27 g) in 40 ml of acetone was added 0.3 g (4.5 mmol) of $NaNO_2$, 1 g (6 mmol) of $NaPF_6$ and 6 mmol (0.5 ml) of PMe_3. CO was allowed to bubble through this solution for 3 hours. Filtration and concentration of the solution gave a dark violet product, which was recrystallized from dichloromethane/diethylether (1/1) as violet parallelepipeds (Yield: 65%). *Anal.* (*1*) Calc. for $NiNOP_4C_9H_{27}F_6$: C% 23.40; H% 5.85; N% 3.03. Found: C% 23.45; H% 5.95; N% 3.01. (*2*) Calc. for $NiNOP_4C_{18}H_{45}F_6$: C% 36.76; H% 7.66; N% 2.38. Found C% 36.12; H% 7.41; N% 2.60. (*3*) Calc. for $NiNOP_4C_{24}H_{33}F_6$: C% 44.47; H% 5.10; N% 2.16. Found C% 44.56; H% 5.11; N% 2.50.

Physical Measurements

Infrared spectra (KBr or nujol mull) were recorded with a Perkin Elmer 137 Spectrophotometer. UV spectra were measured with a Cary 14 spectrophotometer equipped with a low temperature Oxford cryostat (1.00 or 2.00 mm cells) on 10^{-2}–10^{-3} *M* solutions in acetone and dichloromethane. Solution ^{31}P $\{^1H\}$ NMR spectra were measured in acetone/acetone-d_6 at 36.43 MHz with a Bruker WHX-90 spectrometer in the Fourier Transform mode, with ^2H as internal lock and complete ^1H decoupling. Chemical shifts were referenced to $P(OMe)_3$ δ = 141 ppm downfield from H_3PO_4 (85%).

Collection and Reduction of X-ray Data

A suitable purple parallelepiped-shaped single crystal was obtained by recrystallization in dichloromethane and diethylether (1/1), stable enough to be handled in air, and then sealed in a Lindemann glass capillary filled with nitrogen.

Preliminary Weissenberg photographs indicated that the crystal was orthorhombic, space group Pnma or $Pn2_1a$. The space group was assumed to be Pnma, confirmed by subsequent successful solution and refinement of the structure. The crystal was mounted on a Nonius CAD4 diffractometer. The details of the data collection and reduction are given in Table I. Because of the small intensity changes of standards and the dimensions of the crystal, corrections for decomposition and absorption were not required.

Structure Solution and Refinement

The structure was determined by the heavy-atom method. A Patterson map revealed the position of the nickel atom. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms, which were refined anisotropically. The hydrogen atoms were located from a difference electron density map. Their geometry was idealized (C–H = 0.97 Å, H–C–H = 109.5°); they were introduced in the last cycles of refinement with an isotropic temperature factor equivalent to that of their bonding atom.

Neutral atom scattering factors for non-hydrogen atoms and corrections for anomalous dispersion effects for nickel, phosphorus and fluorine atoms were obtained from the tabulation of Cromer and Waber [12]. Scattering factors for the hydrogen atoms were those of Stewart *et al.* [13].

The final full-matrix least-squares refinement converged to $R_1 = 0.036$ and $R_2 = 0.048$. The weighting scheme used in the minimization of the function $\Sigma w(|F_o| - |F_c|)^2$ is defined as $w = 1/\{\sigma_{F_o}{}^2 + (pF_o)^2\}$ where p is the factor to prevent overweighting of strong reflections. An analysis of variance according to F_o and $\sin\theta/\lambda$ showed satisfactory consistency. A final difference Fourier map showed no excursions of electron density greater than 0.35 e/Å^3.

Non-hydrogen atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are reported in Table II.

TABLE II. Final Least-Squares Coordinates with Estimated Standard Deviations for $[Ni(NO)(PMe_3)_3]PF_6$.

Atom	*x/a*	*y/b*	*z/c*
Ni	0.18069(4)	1/4	0.24687(6)
N	0.2483(3)	1/4	0.1468(4)
O	0.2908(4)	1/4	0.0728(5)
P1	0.05350(10)	1/4	0.17872(14)
C1	−0.0348(5)	1/4	0.2690(6)
C2	0.0329(3)	0.1161(5)	0.0911(4)
P2	0.18601(8)	0.42091(12)	0.35550(10)
C3	0.1957(4)	0.5667(6)	0.2789(5)
C4	0.2732(4)	0.4288(7)	0.4480(6)
C5	0.1004(4)	0.4578(6)	0.4432(5)
P3	0.06387(13)	1/4	0.74875(18)
F1	0.0049(3)	1/4	0.6460(4)
F2	0.1232(3)	1/4	0.8496(4)
F3	0.1413(3)	1/4	0.6704(4)
F4	−0.0128(3)	1/4	0.8273(4)
F5	0.0650(3)	0.1016(4)	0.7469(3)

Anisotropic thermal parameters and hydrogen atomic coordinates are listed in Tables IIB and IIC, respectively, of the Supplementary Material.

Results and Discussion

The physical properties of the three complexes are reported in Table III. They are tetracoordinate, cationic and diamagnetic. They are fairly stable in the solid state, and in solution if kept under argon or (better) in a reducing CO atmosphere. In the solid state and in solution they exhibit only one infrared band ν(NO) at 1745 cm^{-1} (PEt_3), 1750 cm^{-1} (PMe_3) and 1775 cm^{-1} (PMe_2Ph). Table III indicates that ν(NO) increases from the triethylphosphine complex to the triphenylphosphine complex and follows the decrease of the basicity of the phosphine ligand. The $^{31}P\ \{^1H\}$ NMR spectra show that the phosphine ligands of $\{Ni(NO)P_3\}^+$ are equivalent on the NMR time scale. No evidence of phosphine dissociation was

TABLE III. Physical Data for the $\{Ni(NO)(PR_3)_3\}PF_6$ Complexes.

	Color	ν(NO)[a]	μ_{eff} (293 K)[b]	Conductivity[c]	δ (Δδ)[d]
$\{Ni(NO)(PMe_3)_3\}PF_6$	violet	1750	0.99	20.1	−6.7(55.3)
$\{Ni(NO)(PEt_3)_3\}PF_6$	violet	1745	0.48	23.2	22.7(42.8)
$\{Ni(NO)(PMe_2Ph)_3\}PF_6$	violet	1775	0.53	24.5	4.3(50.3)
$\{Ni(NO)(PMePh_2)_3\}PF_6$ [e]		1785			
$\{Ni(NO)(PPh_3)_3\}PF_6$ [e]		1790			

[a] $\bar{\nu}$(NO) in cm^{-1}. [b] Magnetic susceptibility value corrected from the diamagnetism of the ligands—the higher value of the trimethylphosphine complex is related to some decomposition of the complex due to its greater air sensitivity [14]. [c] Molar conductivity of 10^{-3} *M* CH_2Cl_2 solutions (Ω^{-1} mol^{-1} cm^2). For comparison $\Omega(10^{-3}$ *M* $(NBu)_4Cl$ in CH_2Cl_2 = 19 Ω^{-1} mol cm^{-1}. [d] δ in ppm (Δδ = δ (P compl) − δ (P free ligand)). [e] Ref. 11.

apparent, as was reported for $\{Ni(NO)(PPh_3)_3\}PF_6$. Lowering the temperature to 183 K did not affect the spectra. A good correlation was obtained between the variation of the phosphine chemical shift ($\Delta\delta = \delta P$(complex) $- \delta P$(free ligand)) and Tolman's cone angle of the phosphine, indicating similar solution structures for the three complexes.

TABLE IV. Selected interatomic distances (Å) and angles (°) for $[Ni(NO)(PMe_3)_3]PF_6$.[a]

Ni–P1	2.229(2)	P1–Ni–P2	104.92(5)
Ni–P2	2.239(1)	P1–Ni–N	109.98(16)
Ni–N	1.645(5)	P2–Ni–N	114.55(16)
N–O	1.139(9)	P2–Ni–P2*	107.06(5)
		Ni–N–O	175.4(5)
P1–C1	1.811(8)	P1–C2	1.803(6)
Ni–P1–C1	120.5(2)	C1–P1–C2	102.4(3)
Ni–P1–C2	113.2(2)	C2–P1–C2*	103.0(3)
P2–C3	1.806(6)	P2–C4	1.814(7)
		P2–C5	1.799(6)
Ni–P2–C3	112.3(2)	C3–P2–C4	102.5(3)
Ni–P2–C4	115.9(2)	C3–P2–C5	101.1(3)
Ni–P2–C5	119.8(2)	C4–P2–C5	102.9(3)
P3–F1	1.580(5)	P3–F3	1.582(5)
P3–F2	1.566(5)	P3–F4	1.574(6)
		P3–F5	1.564(4)
F1–P3–F2	179.3(2)	F2–P3–F4	90.4(2)
F1–P3–F3	90.1(2)	F2–P3–F5	90.2(2)
F1–P3–F4	90.3(2)	F3–P3–F4	179.7(2)
F1–P3–F5	89.8(2)	F3–P3–F5	89.0(2)
F2–P3–F3	89.2(2)	F4–P3–F5	91.0(2)
		F5–P3–F5*	177.9(2)
Non-bonded Intramolecular contacts (Å)			
P1–N	3.190(6)	P1–P2	3.543(2)
P2–N	3.283(5)	P2–P2*	3.601(2)

[a] Asterisks represent the equivalent position x, 1/2 − y, z.

Description of the X-Ray Structure of $\{Ni(NO)(PMe_3)_3\}PF_6$

Selected interatomic distances and angles are reported in Table IV. A perspective view of the $\{Ni(NO)(PMe_3)_3\}^+$ cation, along with the atom labelling scheme, is shown in Fig. 1. The crystal structure consists of discrete, well-separated $\{Ni(NO)(PMe_3)_3\}^+$ cations and PF_6^- anions. The coordination geometry around the nickel atom is pseudo-tetrahedral with the atoms C1, P1, Ni, N, O located in the symmetry plane of the molecule. There is no C_3 symmetry axis as was observed in $Rh(NO)(PPh_3)_3$ and $Ir(NO)(PPh_3)_3$, and no disorder is apparent for the NO group. The cation however is more symmetrical than $\{Ni(NO)(P(OCH_2)_3CCH_3)_3\}^+$ where no element of symmetry is present. It is the first complex where the dihedral angle between the two P1–Ni–N–O and P2–Ni–P2* planes is exactly 90°.

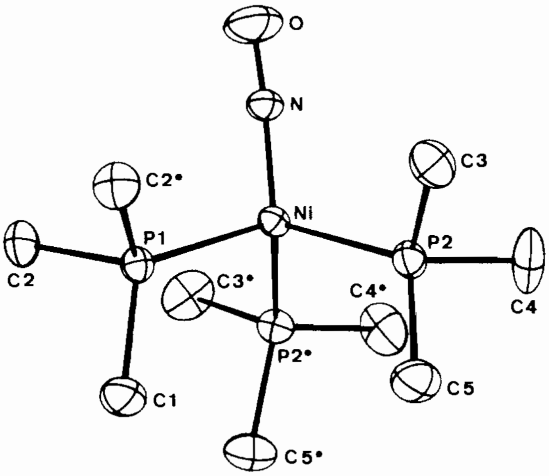

Fig. 1. ORTEP drawing of $\{Ni(NO)(PMe_3)_3\}^+$.

The deviations of the angles about the nickel atom from the ideal tetrahedral value are small. The average P–Ni–P angle is 105.63° and the average P–Ni–N is 113.03°. These values are not different from the average values reported for the other d^{10} complexes, especially those of $\{Ni(NO)(P(OCH_2)_3CCH_3)_3\}^+$, and confirm that the phosphorus ligands are slightly crowded away from NO and are as predicted by theoretical calculations [17].

Comparison of main bond distances and angles with those of known $\{M–NO\}^{10}$ complexes is reported in Table V. The two Ni–P bond lengths of 2.239(1) and 2.229(2) Å differ slightly but are in the range of the observed Ni–P distances. As expected they are longer than the Ni–phosphite distances, in agreement with the differences in steric and electronic properties of phosphite compared to phosphine ligands.

The Ni–N distance of 1.646(6) Å is in the range of the observed values for the nickel complexes (av. Ni–N: 1.69 Å). Three shorter distances are apparent in Table V: 1.58(1) Å in $\{Ni(NO)(P(OCH_2)_3CCH_3)_3\}^+$, 1.58(1) Å in $\{Ni(NO)(TEP)\}^+$, and 1.59(2) Å in $\{Ni(NO)(NP_3)\}^+$. Correspondingly, a lengthening of the N–O distance would be expected, which is not apparent in the Ni–phosphine complexes. Moreover, a short N–O distance is also present in the Ni–phosphite compound. The same trend is observed in the infrared NO stretching frequencies, which lie in a small range between 1700–1750 cm^{-1} for phosphine species but are higher (1820–1900 cm^{-1}) for the phosphite complexes [16]. This trend reflects the greater ability of phosphites, with reduced σ basicity and increased π acidity, of allowing greater electron drift from π^* NO on to the metal.

The nitrosyl group is coordinated in a nearly 'linear' fashion with an Ni–N–O angle of 175.4(5)°, very similar to the 176.8(18)° value reported for the phosphite complex. The most interesting point of this

TABLE V. Main Bond Distances and Bond Angles in Four Coordinate $\{M{-}NO\}^{10}$ Complexes.[a]

	M–P	M–N	N–O	M–N–O	N–M–X	P–M–P	N–M–P	Ref.
$\{Ni(NO)(PMe_3)_3\}^+$	2.235	1.645(5)	1.139(8)	175.4(5)		105.6	112.26	This work
$\{Ni(NO)(TEP)\}^+$	2.208	1.579	1.199	180		93.5	122.8	6
$\{Ni(NO)(P(OCH_2)_3CCH_3)_3\}^+$	2.186	1.58(1)	1.12(1)	176.8(18)		104.1	114.3	5
$\{Ni(NO)(NP_3)\}^+$	2.293	1.59(2)	1.14(3)	167.7(2)		105.1	113.5	8
$Ni(NO)(N_3)(PPh_3)_2$	2.281	1.686(7)	1.164(8)	152.7(7)	128.8(3)	120.52(8)	105.7	2
$Ni(NO)(NCS)(PPh_3)_2$	2.299	1.648(5)	1.159(6)	161.5(5)	116.82(22)	111.98(6)	112.5	3
$Ni(NO)(NO_2)(PMe_3)_2$								
293 K	2.243(2)	1.652(7)	1.158(8)	165.5(8)	126.2(3)	106.06(7)	113.1	4
135 K	2.236(3) 2.244(2)	1.648(6)	1.177(7)	166.9(6)	127.8(3)	105.1(1)	113.5	
$Rh(NO)(PPh_3)_3$	2.350(3)	1.759(13)	1.27(2)	156.7(26)		102.20(50)	116.02(49)	9
$Ir(NO)(PPh_3)_3$	2.31(1)	1.67(2)	1.24(3)	180		101.3(6)	116.8(5)	7

[a] Distances in angstroms and angles in degrees. Estimated standard deviations are given in parentheses when the values are not averaged.

structure is the fact that the bending occurs in the C1–P1–Ni–N–O plane toward P1. This trend was already apparent in $Ni(NO)(NO_2)(PMe_3)_2$ since the angle between the two planes O–N2–Ni and N2–Ni–N1 was 11.5° at 293 K but only 4.8° at 135 K. Consequently, the intramolecular O–P1 distance 4.069(7) Å is smaller than the two O–P2 distances, 4.254(6) Å (Fig. 2). The other calculated non-bonding intramolecular contacts between the donor atoms coordinated to Ni are reported in Table IV, and show the same trend. As has been observed for other monodentate phosphine complexes, the shortest N–P contact is to the P1 atom, which is the nearest to the metal center.

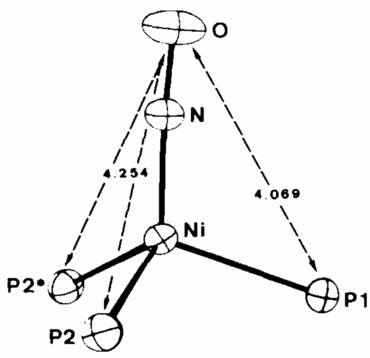

Fig. 2. A drawing of the inner coordination sphere of $\{Ni(NO)(PMe_3)_3\}^+$ showing the bending of Ni–N–O.

It is thus probable that this distortion of the Ni–N–O group is more electronic than steric in its origin. It has been pointed out that decreasing the symmetry of the $Ni(NO)L_3$ entity from C_{3v} lifts the degeneracy of the two π^* nitrosyl orbitals [1]. They may not interact equally with the metal d orbitals and be responsible for the bending of Ni–N–O. As shown in Fig. 3, the symmetry plane XOZ (N–Ni–P1) plays a special role since the empty $\pi_x^*(NO)$ (the filled d_{xz} orbital which is antibonding towards PMe_3) and an empty phosphorus d orbital are oriented in this plane. Thus in C_{2v} symmetry, the $\pi_x^*(NO)$ orbital is well located to share the d_{xz} electrons which removes the degeneracy of the two $\pi^*(NO)$ orbitals, π_x^*, π_y^*. Thus, this $\pi^*(NO)$ degeneracy splitting distorts the molecule and bends the Ni–N–O moiety in the direction where the π^*NO electron density is greater (toward P1). It is then tempting to conclude that there might be a relation between the electronic property of the ligand in the P1 position (P1 in $Ni(NO)(PMe_3)_3^+$, NO_2 in $Ni(NO)(NO_2)(PMe_3)_2$ . .) and the bending of the M–N–O group, the ligand giving the best energy fit between $\pi^*(NO)$ and the d_{xz} orbital giving the strongest distortion.

The trimethylphosphine ligands have the normal geometry. The values of the distances and angles are reported in Table IV. The PF_6^- ion shows an average

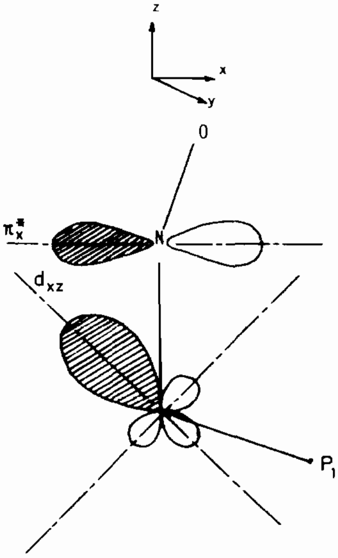

Fig. 3. π electrons interaction in the P1–Ni–N–O plane.

P–F bond length of 1.572 Å. The F–P–F angles are normal (Table IV). The CH_3–F shortest contact is 3.423(7) Å, which is in good agreement with the sum of the van der Waals radii of CH_3 and F (2.00 and 1.35 Å respectively) [18].

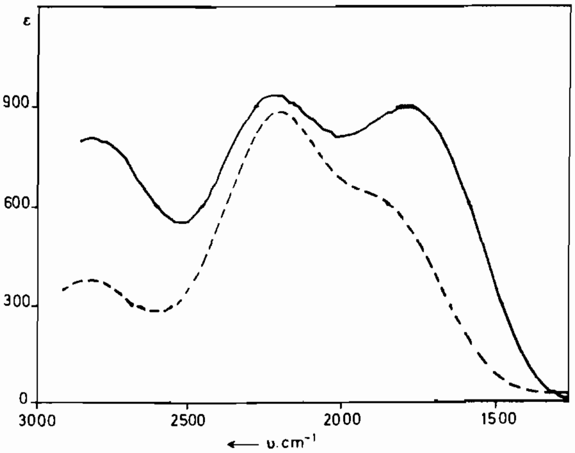

Fig. 4. 293 K electronic spectra of $\{Ni(NO)(PMe_3)_3\}PF_6$ (– – –) and $Ni(NO)(NO_2)(PMe_3)_2$ (——) in acetone saturated with CO.

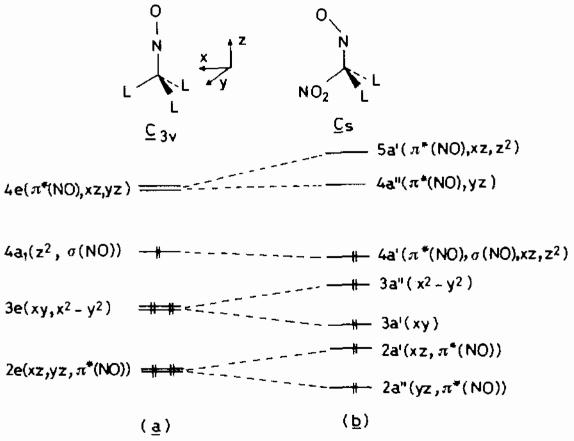

Fig. 5. Correlation diagram for a $\{MNO\}^{10}$ species: (a) C_{3v} symmetry, linear NO group; (b) C_s symmetry, bent NO group.

Electronic Spectra

The electronic spectra of $\{Ni(NO)(PMe_3)_3\}PF_6$ (*1*) and $Ni(NO)(NO_2)(PMe_3)_2$ (*4*) were obtained between 190 and 293 K in acetone and dichloromethane saturated with CO. They are shown in Fig. 4 and the corresponding data are reported in Table VI. No solvent dependence was observed and only the expected shift to higher energy was observed with decreasing temperature. A similar spectrum has been previously observed for $\{Ni(NO)P_3\}^+$ species and was tentatively attributed to configuration interaction [5, 8]. The spectra of the two complexes (*1*) and (*4*) are surprisingly very similar, despite the difference in symmetry (C_{3v} and C_s). Since the bands result from electronic transitions originating from the $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_1, {}^1A_2, {}^1E$ transitions (in C_{3v} symmetry) (Fig. 5), a possible explanation of the analogy of the two spectra is that substitution of PMe_3 by NO_2 has the consequence of decreasing the symmetry of the molecule and of splitting the first $^1A_1 \rightarrow {}^1E$ transition

TABLE VI. Solution Electronic Spectra of the $\{Ni(NO)(PR_3)_3\}PF_6$ and $Ni(NO)(NO_2)(PR_3)_2$ (PR_3 = PMe_3, PEt_3, PMe_2Ph) Complexes.

Compounds	$\bar{\nu} \times 10^{-3}$ cm^{-1} (ϵ) Acetone (293 K)		
$\{Ni(NO)(PMe_3)_3\}PF_6$	18400 (500)	22200 (840)	28000 (390)
$\{Ni(NO)(PEt_3)_3\}PF_6$	16900 (190)	20350 (350)	27800 (440)
$\{Ni(NO)(PMe_2Ph)_3\}PF_6$	17970 (300)	21250 (445)	–
$Ni(NO)(NO_2)(PMe_3)_2$	17500 (860)	22500 (830)	27900 (810)
$Ni(NO)(NO_2)(PEt_3)_2$	17100 (970)	21800 (1030)	27900 (860)
$Ni(NO)(NO_2)(PMe_2Ph)_2$	17400 (1020)	22200 (940)	28400 (900)

(17900 cm^{-1} in (*1*)) into two transitions in (*4*): one at 17500 cm^{-1} and the other at about 22500 cm^{-1}, nearly at the same energy as the second one (21500 cm^{-1} in (*1*)), which is not expected to be modified.

Conclusions

A series of d^{10} cationic complexes $\{Ni(NO)P_3\}$-PF_6 (P = PMe_3, PEt_3, PMe_2Ph) have been synthesized and characterized. The crystal structure indicated that the cation $\{Ni(NO)(PMe_3)_3\}^+$ is tetrahedral and not significantly distorted from C_{3v} symmetry, if thermal disorder is considered. The Ni–N–O angle of 175.4(5)° shows that the molecule belongs to the {M–NO} complexes with linear M–NO group.

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