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$CoX_2(NO)(PMe_3)_2$ Complexes: an Example of the Influence of X (X = Cl, Br, I, NO_2) on the Stereochemistry and Electronic Structure of the Five-coordinate $\{Co-NO\}^8$ Complexes

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Abstract

$CoX_2(NO)(PMe_3)_2$ complexes (X = Cl, Br, I, NO_2) exhibit markedly different ν(NO) stretching frequencies and different geometries. The structure of $CoI_2(NO)(PMe_3)_2$ (1) and $CoCl_2(NO)(PMe_3)_2$ (2) have been determined by X-ray diffraction. Both crystallize in the orthorhombic system, *Pnma* space group with four molecules in a cell of the following dimensions: for 1, $a = 10.497(2)$, $b = 10.694(2)$, $c = 13.975(2)$ Å, $V = 1568.8$ Å^3; for 2, $a = 9.607(2)$, $b = 10.689(2)$, $c = 13.512(3)$ Å, $V = 1387.5$ Å^3. The structures were refined to conventional R values of $R = 0.040$ from 1630 reflections for 1 and $R = 0.033$ from 976 reflections for 2. In both cases, the coordination geometry about the five-coordinate cobalt atom is approximately trigonal bipyramidal, with the NO group sharing the equatorial positions with the halide ligands. Structure 2 is disordered, which prevents any precise structural characterization. In (1), the Co–N–O angle is 179.2(19)° and the Co–NO distance is 1.728(23) Å; ν(NO) is 1753 cm^{-1}. $CoCl_2(NO)(PMe_3)_3$ shows a ν(NO) vibration at 1637 cm^{-1}. $Co(NO_2)_2(NO)(PMe_3)_2$ with $\nu(NO) = 1658$ cm^{-1} has been proposed as a square pyramidal structure with a bent apical Co–NO. These differences in NO stretching frequencies and geometries are discussed.

Introduction

The five-coordinate $CoCl_2(NO)(PR_3)_2$ complexes play a particular role in metal nitrosyl chemistry since they were the first examples suggesting the possible existence of two interconverting metal–NO coordination modes (linear and bent M–NO linkages) in the same $(Co-NO)^8$ complex. While the IR spectrum effectively indicated two ν(NO) stretching frequencies at 1725 and 1637 cm^{-1}, the X-ray determination of $CoCl_2(NO)(PMe_2Ph)_2$ showed only the trigonal bipyramidal isomer with a slightly bent Co–NO linkage [1]. Confirmation of this result has been discussed theoretically [2–3], but more experimental data are necessary to substantiate it unequivocally.

It is well known that in metal–NO complexes the ancillary ligands are essential in determining the stereochemistry of the resulting species and the nature of the M–NO linkage. The phosphine influence has been followed in the complexes $CoCl_2(NO)(PR_3)_2$ but has given no additional information. The halide role, however, has not been studied. Most of the time, the stereochemistry of the complexes is not sensitive to the replacement of Cl by I [4, 5], but replacing the halide by NO_2 or NCS may considerably modify the nature of the resulting species [6, 7].

Thus, in order to determine the nature of the Co–NO linkage in these $\{Co-NO\}^8$ complexes in relation to the oxygen transfer process between NO/NO_2 ligands, we have used a variety of X groups and prepared the $CoX_2(NO)(PMe_3)_2$ complexes with X = Cl, Br, I, NO_2, NCS. We report here their chemical characterization together with the X-ray determination of $CoI_2(NO)(PMe_3)_2$ and $CoCl_2(NO)(PMe_3)_2$. These two complexes have been selected because they present two different ν(NO): 1753 cm^{-1} when X = I, and 1637 cm^{-1} with a shoulder at 1725 cm^{-1} for X = Cl; ν(NO) is the criterior most often used to differentiate linear and bent M–NO linkages. Characterization of $Co(NO_2)_2(NO)(PMe_3)_2$ has been made by comparison with the related $Co(NO_2)_2(NO)(PMe_2Ph)_2$, the structure of which has been reported [8]. When X = NCS, a different behavior is observed, which will be reported in a later paper.

Experimental

Procedure, Reagents, Solvents

All preparations were carried out in degassed solvents under a purified argon atmosphere in a conventional vacuum system or in a Jaram Vacuum Glove box. All solvents were routinely purified and

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TABLE I. Summary of Crystal and Intensity Collection Data

Compound	$CoI_2(NO)(PMe_3)_2$	$CoCl_2(NO)(PMe_3)_2$
Formula	$CoI_2NOP_2C_6H_{18}$	$CoCl_2NOP_2C_6H_{18}$
Formula weight	494.67	371.77
a (Å)	10.497(2)	9.607(2)
b (Å)	10.694(2)	10.689(2)
c (Å)	13.975(2)	13.512(3)
V (Å^3)	1568.8	1387.5
Crystal system	orthorhombic	orthorhombic
Space group	D_{2h}^{16}-$Pnma$	D_{2h}^{16}-$Pnma$
Z	4	4
D_c (g/cm^3)	2.094	1.492
F(000)	928	640
Crystal size	spheroid $\phi \sim 0.45$ mm	spheroid $\phi \sim 0.32$ mm
$\mu_{\text{Mo K}\alpha}$ (cm^{-1})	51.6	18.2
Temperature	20 °C	20 °C
Radiation	Mo K$\bar{\alpha}$, $\lambda = 0.71069$ Å graphite monochromatized	Mo K$\bar{\alpha}$, $\lambda = 0.71069$ Å graphite monochromatized
Receiving aperture	4.0 × 4.0 mm 30 cm from crystal	4.0 × 4.0 mm 30 cm from crystal
Take-off angle	2.3°	4.75°
Scan mode	$\theta - 2\theta$	$\theta - 2\theta$
Scan range	0.80° + 0.35° tan θ	0.80° + 0.35° tan θ
Scan speed	10°/min	5°/min
2θ limits	60°	56°

dried by refluxing and distilling over the following agents under argon: acetonitrile (molecular sieves 4 Å), tetrahydrofuran (Na/benzophenone), methanol (molecular sieves 4 Å), dimethylether (Na), and pentane (Na). They were distilled just before use, transferred under argon and degassed on the vacuum line by three freeze-pump thaw cycles. Nitric oxide (Air liquide) was purified by passage through a trap cooled at −77 K. Trimethylphosphine was synthesized following a procedure derived from the method of Wolfsberger and Schmidbaur, and stored under argon [9]. The cobalt complexes $CoX_2(PMe_3)_2$ have been prepared as previously reported [10].

Physical Measurements

Infrared spectra of nujol mulls or of solutions were recorded with Perkin-Elmer 137 and a Perkin-Elmer 983 spectrometers equipped only for room temperature measurements. Magnetic susceptibilities of the compounds were determined by using a Cahn-Faraday electrobalance equipped with a low temperature probe. The $^{31}P\{^1H\}$ NMR spectra were measured at 36.43 MHz with a Bruker HX-90 spectrometer in the Fourier transform mode, with ^2D as internal lock and complete ^1H decoupling. Chemical shifts were measured in acetone/acetone d_6 at low temperature with $\delta(PMe_3) = -62$ ppm as external reference.

Syntheses of the Complexes

The complexes with X = I, Br, Cl, were prepared following the same procedure.

$CoI_2(NO)(PMe_3)_2$

$CoI_2(PMe_3)_2$ (2.0 g; 4.3 mmol) was dissolved in methanol (20 ml) at 20 °C. NO was bubbled through the solution for 20 min. The color changed immediately from blue to brown and the complex precipitated as brown crystals at −50 °C. They were filtrated and dried under NO. *Anal.* Calc. for $CoI_2NOP_2C_6H_{18}$: C, 14.55; H, 3.64; N, 2.83; P, 12.53; I, 51.30; Co, 11.91. Found: C, 14.70; H, 3.68; N, 2.71; P, 12.29; I, 50.04; Co, 11.22%. Calc. for $CoBr_2NOP_2C_6H_{18}$ (brown crystals): C, 17.96; H, 4.49; N, 3.49. Found: C, 17.83; H, 4.05; N, 3.41%. Calc. for $CoCl_2NOP_2C_6H_{18}$, (brown crystals): C, 23.09; H, 5.77; N, 4.49; P, 19.88; Cl, 22.74; Co, 18.90. Found: C, 22.78; H, 5.63; N, 4.39; P, 19.20; Cl, 21.60; Co, 18.70%.

$Co(NO_2)_2(NO)(PMe_3)_2$

1 g (3.0 mmol) of $Co(NO_2)_2(PMe_3)_3$ dissolved in 20 ml of methanol was stirred in the presence of 3 mmol of NO for 20 min, until the green solution turned brown. The solution was then cooled at −20 °C. The brown crystals which precipitated were collected by filtration and dried under argon. *Anal. Calc. for* $CoN_3O_5P_2C_6H_{18}$: C, 21.62; H, 5.41; N, 12.61. Found: C, 21.10; H, 5.42; N, 13.40%.

Data Collection and Structural Work

$CoI_2(NO)(PMe_3)_2$

The red-brown spheroid crystal was selected and sealed in a Lindemann glass capillary under nitrogen atmosphere and mounted on an Enraf-Nonius CAD 4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. The summary of crystal and intensity collection data are given in Table I. 2144 independent reflections were recorded out to $2\theta = 60°$. The three standard reflections monitored every 4800 s showed only random statistical fluctuations. Data reduction was then performed. Spheric absorption corrections ($\mu R = 1.2$) were made [11]. 1630 reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$ were used in subsequent calculations. All calculations were performed on a CII Honeywell-Bull DPS 8 computer at the 'Centre Universitaire de Calcul de Toulouse' [12].

The structure was determined by the heavy-atom method. A Patterson map revealed the positions of iodine and cobalt atoms. A subsequent Fourier map revealed the positions of all non-hydrogen atoms, which were refined anisotropically. The hydrogen atoms were located from a difference electron density map. In the last cycles of refinement, they were included using a riding model for the positional parameters. The temperature factors were defined as the equivalent isotropic temperature factors of the related C atoms. Neutral atom scattering factors for non-hydrogen atoms [13] and corrections for anomalous dispersion for I, Co, and P atoms were taken from the usual tabulation [14]. The hydrogen scattering factors were those of Stewart *et al.* [15]. Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and the weights were taken as $w = \{\sigma^2(F_o) + (pF_o)^2\}^{-1}$ with $p = 0.035$. Refinement converged to $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o| = 0.040$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.056$. The standard deviation of an observation of unit weight was 1.3. During the last cycle of least-squares refinement, all the parameter shifts were less than 0.04 σ. The largest peak in the final difference electron density map was 2 e/Å^3 around iodine atom.

$CoCl_2(NO)(PMe_3)_2$

The brown approximately spheric crystal was selected and sealed in a Lindemann glass capillary under nitrogen atmosphere and mounted on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. Crystal and intensity collection data are summarized in Table I. The three standard reflections monitored every hour gave no evidence of any decomposition. 1751 independent reflections were recorded up to $2\theta = 56°$. Data reduction was then performed. No absorption corrections were made. 976 reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$ were used in structure resolution.

The systematic absences, $0kl : k + 1 = 2n + 1$ and $hk0 : h = 2n + 1$, are consistent with the space groups *Pnma* or *$Pn2_1a$*. The space group was assumed to be the centrosymmetric choice, *Pnma*, and the structure was solved by heavy-atom technics. The Patterson map revealed unambiguously the cobalt, phosphorus and one chlorine atom, Cl(1), all in special positions, with Co–Cl(1) distance being slightly shorter than expected. A series of structure factor calculations, least-square refinements and difference electron density maps revealed the other non-hydrogen atoms and a disorder between the NO group and the Cl(2) atom, with an unreasonable pattern of distances and angles involving these atoms. Hydrogen atoms were introduced with idealized geometry (C–H = 0.95 Å; H–C–H = 109.5°).

At this point, we checked to see if this disorder problem could also be observed in the non-centrosymmetric *$Pn2_1a$* space group. Both enantiomers were generated and refined with all non-hydrogen atoms anisotropic to convergence $R_1 = 0.038$ and $R_2 = 0.036$, respectively. In both cases, disorder was still present and there were severe correlation matrix elements in the refinement of the methyl groups and of the N and Cl(2) atoms.

In the centrosymmetric space group *Pnma*, the crystallographically disordered N, O and Cl(2) atoms were assigned occupancies of 0.5. Constrained Co–N and Co–Cl(2) distances [1, 8] were tested but thermal parameters were obsolete. The ambiguous results for this part of the molecule, previously observed in the structure of $NiCl(NO)(PPh_3)_2$ [16], were not totally unexpected because the NO group and the Cl atom have similar numbers of electrons (15 and 17 respectively) and because the midpoint of the NO vector and the Cl(2) atom can be nearly superposed (distance 0.26 Å) by the mirror symmetry operation.

The last cycles of refinement were made with all non-hydrogen atoms anisotropic and no geometrical constraints. Atomic scattering factors and corrections for anomalous dispersion for Co, Cl, and P atoms are those of refs. 14, 15 and 16. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weights were taken as $w = \{\sigma^2(F_o) + (pF_o)^2\}^{-1}$ with $p = 0.014$. Refinement converged to $R = 0.033$ and $R_w = 0.039$. The standard deviation of an observation of unit weight was 1.2. During the last cycle of least-squares refinement, the parameter shifts were less than 0.2σ and 1.2σ for ordered and disordered atoms parameters, respectively. The largest peak in the final difference electron density map was 0.45 e/Å^3.

Final atomic coordinates are given in Table II.

Results

1. Reaction of NO with $CoX_2(PMe_3)_z$ ($X = Cl, Br, I, NO_2$; $z = 2,3$)

These complexes were prepared by bubbling NO gas through a methanol solution of the tetracoordinate $CoX_2(PMe_3)_2$ or pentacoordinate $CoX_2(PMe_3)_3$ complexes until the solution turned brown. Dia-

TABLE II. Final Least-squares Atomic Coordinates with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c
[$CoI_2(NO)(PMe_3)_2$]			
Co	0.18931(9)	3/4	0.51970(6)
I	0.27918(4)	0.55033(3)	0.60169(3)
P(1)	0.36222(19)	3/4	0.42384(13)
P(2)	0.03242(18)	3/4	0.62906(14)
O	0.0278(9)	3/4	0.3666(5)
N	0.0880(8)	3/4	0.4242(5)
C(1)	0.5193(7)	3/4	0.4780(6)
C(2)	0.3619(7)	0.6162(7)	0.3440(5)
C(3)	0.0732(9)	3/4	0.7522(5)
C(4)	−0.0740(7)	0.6167(8)	0.6147(5)
[$CoCl_2(NO)(PMe_3)_2$]			
Co	0.28432(8)	3/4	0.51808(5)
Cl(1)	0.43110(21)	3/4	0.39252(14)
Cl(2)	0.2063(7)	0.5876(5)	0.5885(7)
P(1)	0.46819(14)	3/4	0.61902(11)
P(2)	0.10922(16)	3/4	0.40777(11)
O	0.2273(19)	0.9540(18)	0.6205(12)
N	0.2073(26)	0.9128(27)	0.5656(24)
C(1)	0.4255(7)	3/4	0.7479(5)
C(2)	0.5799(4)	0.6157(4)	0.6029(4)
C(3)	−0.0625(7)	3/4	0.4633(6)
C(4)	0.1109(5)	0.6152(4)	0.3274(3)

magnetic brown crystals were isolated. $Co(NO_2)_2(NO)(PMe_3)_2$ was obtained by using the square pyramidal Co(II) species $Co(NO_2)_2(PMe_3)_3$ as starting material. $Co(NO_2)_2(PMe_3)_3$ was characterized by its ERP spectrum: two g values of $g_\perp = 2.16 > g_\parallel = 2.03$ [16]. No nitronitrosyl complex was observed during this reaction [17].

Table III and Fig. 1 report the solid state (nujol) and solution (dichloromethane) NO stretching vibrations. Only one ν(NO) (1753 cm^{-1}) is apparent in the $CoI_2(NO)(PMe_3)_2$ spectrum, in agreement with the existence of only one TBP isomer with a linear Co–N–O group (*vide infra*).

$CoCl_2(NO)(PMe_3)_2$ exhibits a broad ν(NO) signal at 1637 cm^{-1} with a shoulder at 1725 cm^{-1} in the solid and at 1655 cm^{-1} with a second medium intensity band at 1750 cm^{-1} in solution, as was reported for the $CoCl_2(NO)(PR_3)_2$ complexes [1].

Fig. 1. Infrared spectra of $CoCl_2(NO)(PMe_3)_2$ (1), $CoBr_2(NO)(PMe_3)_2$ (2), $CoI_2(NO)(PMe_3)_2$ (3), $Co(NO_2)_2(NO)(PMe_3)_2$ (4), recorded as nujol mulls.

$CoBr_2(NO)(PMe_3)_2$ presents one broad ν(NO) at 1750 cm^{-1} in the solid state, like the iodo complex, but in solution a second vibration appears at 1670 cm^{-1} as a medium intensity band, as in the chlorocomplex.

$Co(NO_2)_2(NO)(PMe_3)_2$ shows only one ν(NO) at 1658 cm^{-1} in the solid and 1660 cm^{-1} in solution; these values are in the same range as those observed for the chlorocomplex. An ν(NO) vibration at 1665 cm^{-1} has also been reported in $Co(NO_2)_2(NO)(PMe_2Ph)_2$, the structure of which is a square pyramid with a bent Co–N–O linkage at the apex [4]. Thus, a similar structure with a bent Co–N–O group may be expected for the trimethylphosphine complex.

Considering that the 1660 cm^{-1} energy range corresponds to the ν(NO) of the bent Co–N–O linkage (isomer **A**) and the 1750 cm^{-1} range to the ν(NO) of the linear Co–N–O moiety (isomer **B**) (Scheme 1), the infrared results would indicate the

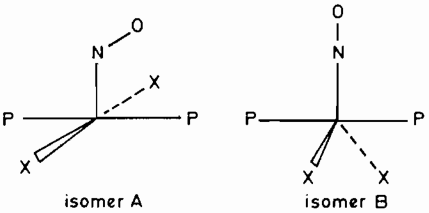

TABLE III. Infrared and $^{31}P\{^1H\}$ NMR Data for $CoX_2(NO)(PMe_3)_2$

Compounds	ν(NO) (cm^{-1})		$^{31}P\{^1H\}$ (ppm)
	Nujol mull	CH_2Cl_2 solution	
$CoI_2(NO)(PMe_3)_2$	1753s	1750s	2.5^a
$CoBr_2(NO)(PMe_3)_2$	1750br	1750s;1670m	9^a
$CoCl_2(NO)(PMe_3)_2$	1725sh ;1637s	1750sh; 1655s	10^a
$Co(NO_2)_2(NO)(PMe_3)_2$	1658s	1660s	7^b

[a] At 183 K in CD_2Cl_2/CH_2Cl_2 (1/1). [b] At 187 K in $(CD_3)_2CO/(CH_3)_2CO$ (1/1).

presence of isomer **A** for $Co(NO_2)_2(NO)(PMe_3)_2$ and isomer **B** for $CoI_2(NO)(PMe_3)_2$ and the presence of two isomeric forms for $CoCl_2(NO)(PMe_3)_2$ and $CoBr_2(NO)(PMe_3)_2$. The ^{31}P NMR spectra in CD_2Cl_2 at 183 K show broad singlets, indicating that the interconverting process is fast on the NMR time scale.

These considerations prompted us to investigate this system by X-ray diffraction when X = I, Cl, NO_2. However, the structure of $Co(NO_2)_2(NO)(PMe_2Ph)_2$ is being reported in a parallel work as the expected square pyramid with a bent Co–N–O group [8]. We have not determined the structure of the related PMe_3 complex.

2. *X-ray Structure of $CoI_2(NO)(PMe_3)_2$*

The perspective view of $CoI_2(NO)(PMe_3)_2$ is shown in Fig. 2. Selected interatomic distances and angles are given in Table IV.

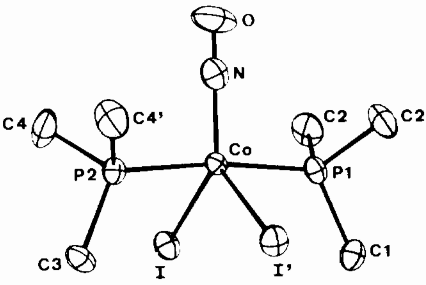

Fig. 2. ORTEP drawing of $CoI_2(NO)(PMe_3)_2$ (ellipsoids are drawn at 30% probability level).

TABLE IV. Selected Bond Lengths (Å) and Angles (°) in $CoI_2(NO)(PMe_3)_2$

Co–I	2.6004(7)
Co–P(1)	2.256(2)
Co–P(2)	2.247(2)
Co–N	1.706(8)
N–O	1.024(11)
Co–N–O	179.6(9)
I–Co–P(1)	88.27(4)
I–Co–P(2)	88.06(4)
I–Co–I'	110.40(4)
I–Co–N	124.80(2)
P(1)–Co–P(2)	173.57(8)
P(1)–Co–N	92.1(3)
P(2)–Co–N	94.3(3)

The coordination geometry about the Co atom is best described as trigonal bipyramidal with the NO group occupying an equatorial position. The cobalt atom, the nitroxide N, O atoms, the phosphorus atoms and two of the methyl group carbon atoms lie in the mirror at $y = 3/4$. The iodine atoms and the other methyl groups are symmetrically related through this mirror. Such a structure has already been observed for $NiX_2(CO)(PMe_3)_2$ (X = Cl, I) [5]. Table V provides a comparison of the coordination geometry of this complex with several other structurally characterized five-coordinate $\{MNO\}^8$ nitrosyl $MX_2(NO)(PR_3)_2$ complexes and d^8 $NiX_2(CO)(PMe_3)_2$ compounds.

The nitrosyl group is coordinated in a linear fashion with a Co–N–O angle of 179.6(9)° and a Co–N distance of 1.706(8) Å. This distance is in good agreement with those observed in the trigonal bipyramidal cobalt complexes: 1.705(5) Å in $CoCl_2(NO)(PMe_2Ph)_2$ and 1.68(3) Å in $\{Co(NO)(das)\}^+$, where the NO is located in the equatorial plane of the trigonal bipyramid. However, the N–O distance of 1.024(11) Å is short compared to 1.16(2) Å obtained in $\{Co(NO)(das)\}^+$. Similarly, ν(NO) is 1750 cm^{-1} in the PMe_3 complex and 1852 cm^{-1} in the das compound. These values illustrate that ν(NO) is not a pure NO stretching frequency.

TABLE V. Structural Parameters (distances (Å), Angles (°)) Involving the M–N(C)–O Fragment in some $\{M-N(C)O\}^8$ Complexes

Compounds	M–N(C)	(C)N–O	M–N(C)–O	Structure	ν(NO)	Reference
$IrCl_2(NO)(PPh_3)_2$	1.94(2)	1.03(2)	123(2)	T.P.	1560	4a
$RhCl_2(NO)(PPh_3)_2$	1.912(10)	1.15	124.8(16)	T.P.	1630	4b
$RhBr_2(NO)(P(OPh)_3)_2$	2.04(4)	1.26(9)	109(5)	T.P.		4c
$CoCl_2(NO)(PPh_2Me)_2$	1.705(5)	1.076(6)	164.5(6)	T.B.P.	1630 1735	1
$\{Co(NO)(das)_2\}(ClO_4)_2$	1.68(3)	1.16(2)	178(2)	T.B.P.	1852	4d
$Co(NO_2)_2(NO)(PMe_2Ph)_2$	1.782(4)	1.146(5)	130.9(3)	T.P.	1650	8
$CoI_2(NO)(PMe_3)_2$	1.706(8)	1.024(11)	179.6(9)	T.B.P.	1753	this
$CoCl_2(NO)(PMe_3)_2$[a]	2.00(3)[a]	0.88(4)[a]	129(3)[a]	T.B.P.	1637	work
$NiI_2(CO)(PMe_3)_2$	1.728(23)	1.137(20)	179.2(19)	T.B.P.		5
$NiCl_2(CO)(PMe_3)_2$	1.730(2)	1.127(4)	179.8(2)	T.B.P.		5

[a] The structure is disordered.

The two Co–I distances (2.6004(7) Å) are normal but in the lower range of M–I distances for first row metal complexes (2.6048(13) Å in the isoelectronic $NiI_2(CO)(PMe_3)_2$ complex). The Co–P bond lengths of 2.256(2) and 2.247(2) Å are not significantly different and well in the range of other PR_3 complexes. The PMe_3 ligands present no distinctive features.

Comparison of the two isoelectronic complexes $CoI_2(NO)(PMe_3)_2$ and $NiI_2(CO)(PMe_3)_2$ indicates that the replacement of CO by NO does not influence the Co–I bond length, but results in a slight increase in the Co–P distances. Thus, the nitrosyl ligand acts as NO^+, isoelectronic with CO. The Co–N bond is multiple which is apparent in the short Co–NO distance.

Table V shows that the M–NO distances are significantly shorter in the trigonal pyramidal {Co–NO} complexes (NO^+) than in the square pyramidal {Rh–NO} or {Ir–NO} analogs (NO^-), as expected.

3. X-ray Structure of $CoCl_2(NO)(PMe_3)_2$

The crystal structure consists of discrete $CoCl_2(NO)(PMe_3)_2$ molecules. The perspective view of the structure is reported in Fig. 3, and the main bond distances and angles in Table VI.

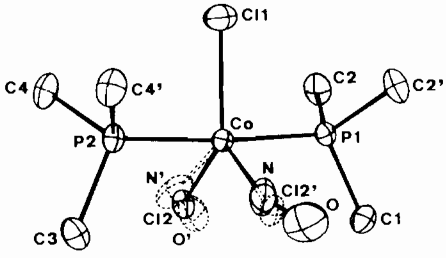

Fig. 3. ORTEP drawing of the disordered molecule $CoCl_2(NO)(PMe_3)_2$ (ellipsoids are drawn at 30% probability level).

TABLE VI. Selected Bond Lengths (Å) and Angles (°) in $CoCl_2(NO)(PMe_3)_2$

Co–Cl(1)	2.206(2)
Co–Cl(2)	2.116(7)
Co–P(1)	2.232(2)
Co–P(2)	2.248(2)
Co–N	2.00(3)
N–O	0.88(4)
Co–N–O	129.0(3)
Cl(1)–Co–P(1)	87.94(7)
Cl(1)–Co–P(2)	88.19(7)
Cl(1)–Co–Cl(2)	124.9(2)
Cl(1)–Co–N	118.9(9)
Cl(2)–Co–P(1)	90.3(2)
Cl(2)–Co–P(2)	91.9(2)
Cl(2)–Co–N	116.0(9)
P(1)–Co–P(2)	176.13(6)
P(1)–Co–N	95.5(8)
P(2)–Co–N	86.3(8)

$CoCl_2(NO)(PMe_3)_2$ also presents a distorted trigonal bipyramidal geometry with NO in the equatorial plane. However, in contrast to $CoI_2(NO)(PMe_3)_2$, the atoms lying in the crystallographic mirror plane are the cobalt atom, the two axial phosphine atoms, the two methyl carbon atoms C(1) and C(3) and the chlorine atom Cl(1). Consequently, the other two sites in the equatorial plane are occupied by the second Cl(2) atom and the nitroxide atoms N and O (*vide supra*). Thus, refinement of the molecule led to a P(1)–Co–P(2) angle of 176.13(6)° and Co–P distances of 2.232(2) and 2.248(2) Å. The Co–Cl(1) distance has a value of 2.206(2) Å, which is significantly shorter than those observed in $CoCl_2(NO)(PMe_2Ph)_2$ (2.289(2) Å) and in $NiCl_2(CO)(PMe_3)_2$ (2.3020(5) Å). The values obtained for the disordered part of the molecule are not satisfactory: Co–Cl(2) = 2.116(7) Å; Co–N = 2.00(3) Å; N–O = 0.88(4) Å and Co–N–O = 129(3)°. More precise determination is prevented by the disorder occurring between Cl (17e) and NO (15e) and by the mirror plane of the molecule which superposes the Cl(2) atom position and the midpoint of the NO vector. Such a difficulty has also been observed in $NiCl(NO)(PPh_3)_2$, where no accurate Ni–NO distances and angles could be obtained. Nevertheless, the Co–N–O group is not linear, as was observed in $CoCl_2(NO)(PMe_3)_2$, the structure of which is not disordered. The distances and angles of the PMe_3 ligands are normal: P–C: 1.803(7) Å (av.); C–P–C: 105.2(3)° (av.).

Discussion

Even though no satisfactory description of the coordinated NO group in $CoCl_2(NO)(PMe_3)_2$ could be obtained from X-ray data, it is apparent that this complex possesses a distorted trigonal bipyramidal structure with a bent Co–N–O group. Since no particular steric influence is expected on the replacement of Cl by I and PMe_3 by PMe_2Ph, the bending of the Co–N–O group may result from the electronic properties of the molecules.

Following Feltham and Enemark [2], $CoX_2(NO)(PR_3)_2$ are near the crossing point of the $4a_1$ and 3e orbitals. Figure 4 indicates the proposed molecular orbital scheme following ref. 2: (a) for the trigonal bipyramidal geometry of C_{2v} symmetry when all three orbitals are nearly degenerated, (b) for a trigonal bipyramid of *Cs* symmetry and (c) for a square pyramid of *Cs* symmetry.

In $CoI_2(NO)(PMe_3)_2$, the energy separation between the $4a_1$ and the $3b_1$, $3b_2$ orbitals is large enough to prevent orbital mixing. The $4a_1$ is filled and is the HOMO. This is consistent with a nearly regular trigonal bipyramid with linear Co–N–O located in the equatorial plane. In $CoCl_2(NO)$-

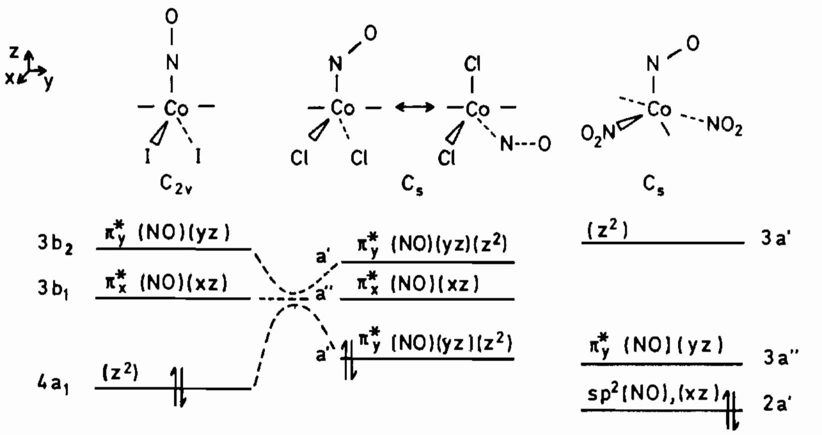

Fig. 4. A molecular correlation diagram of the HOMO and LUMO of the $\{Co-NO\}^8$ group in ligand fields of C_{2v} and C_s symmetries.

$(PMe_3)_2$, the symmetry of the molecule is lowered from C_{2v} to C_s, which consequently lifts the degeneracy of the orbitals and results in $a_1 \rightarrow a'_1$, $b_1 \rightarrow a''$ and $b_2 \rightarrow a'$ transformation. This allows the mixing of the a' orbitals (Fig. 4), thus populating the π_y^*(NO) and bending the Co–N–O group. On the other hand, it is well known that many idealized forms are theoretically possible in five-coordinate species. The energy difference between these forms is small and the potential energy surfaces involved are irregular [18] *. Thus, it is possible for molecules of different structures to exist under the influence of appropriate lattice or solvent interactions. Thus, the existence of two ν(NO) stretching frequencies is probably related to the presence of two complexes of different geometries and thus of different Co–N–O angle values.

In the square pyramidal $Co(NO_2)_2(NO)(PMe_3)_2$, the dz^2 (a') orbital energy increases so that the 2a' and 3a'' orbitals derived from the 3e orbital become lower in energy. 2a' is the HOMO, populated by 2 electrons. This leads to the bending of the NO group, which is experimentally observed.

Conclusion

A relation between ν(NO) and the structures of $CoX_2(NO)(PMe_3)_2$ seems to be apparent. ν(NO) at about 1750 cm^{-1} is related to the presence of a trigonal bipyramidal complex with a linear Co–N–O group, while ν(NO) at 1660 cm^{-1} corresponds to a square pyramidal complex with a bent Co–N–O. Thus, the presence of two ν(NO) in these trigonal bipyramidal $\{CoNO\}^8$ complexes seems to indicate the presence of two isomers, although they have not been observed crystallographically. The $CoX_2(NO)(PMe_3)_2$ (X = I, Br, Cl, NO_2) complexes, however, constitute an interesting series, the electronic structures of which are just before, at and after the crossing point of the dz^2; dxz, π_x^*; dyz, π_y^* molecular orbitals.

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