Syntheses and Structural Studies of Dinitrosylmolybdenum Complexes †

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The reaction of polymeric [$\{Mo(NO)_2Cl_2\}_n$] with ligands L or L_2 [L = MeCN, CH_2=CHCN, PhCN, PPh_3, or pyridine; L_2 = 2,2′-bipyridine (bipy) or 1,2-bis(diphenylphosphino)ethane] affords neutral monomeric [$Mo(NO)_2L_2Cl_2$] in high yield. The structure of [$Mo(NO)_2(bipy)Cl_2$] has been determined by *X*-ray diffraction. The compound crystallises in the monoclinic space group $P2_1/c$ with a = 8.142(3), b = 16.383(6), c = 11.948(3) Å, β = 121.43(4)°, and Z = 4. The structure was solved by conventional Patterson and Fourier methods to a conventional R = 0.045, R' = 0.050 for 1 687 independent reflections having $|F_o|^2 > 3\sigma|F_o|^2$. The crystal structure consists of well separated, discrete molecules. The co-ordination geometry around the molybdenum is described as distorted octahedral with *cis*-dinitrosyl-*trans*-dichloro-stereochemistry. The two NO groups are ordered and nearly linear [Mo–N–O = 175.9(10) and 177.4(13)°]. The characterization of all of the dinitrosylmolybdenum complexes by vibrational, ^1H and ^{31}P n.m.r., and u.v.–visible spectroscopy is described. From a comparison of the spectroscopic studies with the *X*-ray structures of [$Mo(NO)_2(bipy)Cl_2$] and the other known compound [$Mo(NO)_2(PPh_3)_2Cl_2$], two kinds of stereochemistry are formed: *cis*-dinitrosyl-*trans*-dichloro and *cis*-dinitrosyl-*cis*-dichloro.

Organometallic compounds have received considerable attention due to their utility in homogeneous catalysis. Specific auxiliary ligands as well as vacant sites are required. The nitrosyl ligands were suggested for the former because of their electronic properties,[1,2] and for the latter, halide abstraction has been proposed.[3] Halogenonitrosyl complexes of molybdenum form a large class of complexes.[4] A large proportion of them are also η-cyclopentadienyl complexes [4,5] and there are relatively few which contain only 'classical' ligands [6] such as tertiary phosphines or pyridine, for example, in addition to nitrosyl. Among these compounds, only one *X*-ray structure has been reported previously and often the geometries of the complexes are not unequivocally ascribed. We therefore set out to investigate the stereochemistry of several dichlorodinitrosylmolybdenum complexes in the solid state and in solution by means of *X*-ray and spectroscopic data. Reported here are our results on the syntheses and structural studies of neutral complexes [$Mo(NO)_2L_2Cl_2$] for a variety of ligands [L = acetonitrile, acrylonitrile, benzonitrile, pyridine (py), or triphenylphosphine; L_2 = 1,2-bis(diphenylphosphino)ethane (dppe) or 2,2′-bipyridine (bipy)].

Experimental

All reactions were carried out in the dark under an atmosphere of dry argon. Solvents were distilled under argon from appropriate drying agents. The compound [$\{Mo(NO)_2Cl_2\}_n$] (1) was prepared by the literature method.[7,8] The compounds [$Mo(NO)_2(PPh_3)_2Cl_2$] (2) and [$Mo(NO)_2(py)_2Cl_2$] (3) were prepared by the previous methods.[6] The compounds gave satisfactory elemental analyses.

Synthesis of [$Mo(NO)_2(RCN)_2Cl_2$] [R = Me (4), CH_2=CH (5), *and* Ph (6)].—These three complexes were obtained following essentially the same procedure. The green solution which was formed upon dissolving (1) (0.5 g, 2.2 mmol) in CH_2Cl_2 (20 cm^3) and the appropriate nitrile (5 cm^3) was stirred for 12 h. The yellow solid which precipitated was filtered off, washed with diethyl ether, and dried *in vacuo*. Yields and analytical data are given in Table 1.

[$Mo(NO)_2(dppe)Cl_2$] (7).—Compound (1) (0.5 g, 2.2 mmol) suspended in CH_2Cl_2 (20 cm^3) was treated with dppe (0.78 g, 2.1 mmol). The mixture was stirred at room temperature for 30 min. Addition of n-hexane gave a yellow solid which was filtered off, washed with n-hexane, and then dried *in vacuo*. Yield 80%.

[$Mo(NO)_2(bipy)Cl_2$] (8).—*Method A*. Compound (1) (0.5 g, 2.2 mmol) suspended in CH_2Cl_2 (20 cm^3) was treated with an excess of 2,2′-bipyridine (0.4 g, 2.56 mmol). The mixture was stirred at room temperature for 12 h. Addition of n-hexane gave a yellow-green powder. The solid was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 90%.

Method B. The green solution which was formed upon dissolving (1) (0.25 g, 1.1 mmol) and bipy (0.2 g, 1.28 mmol) in ethanol (50 cm^3) was allowed to stand at room temperature for several days. Green crystals, suitable for *X*-ray diffraction study, were obtained. The elemental analyses agree with the formulation.

Crystal Data for (8).—$C_{10}H_8Cl_2MoN_4O_2$, M = 383, Monoclinic, a = 8.142(3), b = 16.383(6), c = 11.948(3) Å, β = 121.43(4)°, U = 1 360 Å^3, D_m = 1.85 g cm^{-3} (flotation), Z = 4, D_c = 1.87 g cm^{-3}, $F(000)$ = 752, μ(Mo-K_α) = 13.41 cm^{-1}, λ(Mo-K_α) = 0.7107 Å.

X-*Ray Data Collection*.—A well formed green crystal was mounted in a glass capillary to prevent atmospheric contamination and examined, using Cu-K_α radiation by the Weissenberg method. Monoclinic diffraction symmetry with the systematic absences $h0l$ with l odd and $0k0$ with k odd was observed and the space group $P2_1/c$ thereby deduced.

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† *Supplementary data available* (No. SUP 23548, 29 pp.): observed and calculated structure factors, intermolecular non-bonded contacts, full bond length and bond angle data, selected least-squares planes, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Yields and analytical data

Complex	Yield (%)	Analysis [a] (%) C	H	Cl	Mo	N
(4) $[Mo(NO)_2(MeCN)Cl_2]$	80	15.5 (15.55)	1.9 (1.95)	22.4 (23.0)	31.15 (31.15)	17.85 (18.1)
(5) $[Mo(NO)_2(CH_2{=}CHCN)Cl_2]$	70	21.0 (21.6)	1.85 (1.8)	21.3 (21.3)	28.8 (28.85)	16.9 (16.8)
(6) $[Mo(NO)_2(PhCN)Cl_2]$	80	38.9 (38.8)	2.3 (2.3)	15.8 (16.4)	—	13.0 (12.9)
(8) $[Mo(NO)_2(bipy)Cl_2]$ [b]	90	32.1 (31.3)	2.2 (2.0)	17.9 (18.5)	—	14.2 (14.6)

[a] Calculated values are given in parentheses. [b] Prepared by method A.

Table 2. Fractional atomic co-ordinates for $[Mo(NO)_2(bipy)Cl_2]$ (8), with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.003 23(9)	0.159 38(5)	0.279 51(8)
Cl(2)	−0.040 4(3)	0.015 3(1)	0.304 3(2)
Cl(1)	0.127 1(4)	0.291 9(2)	0.274 5(3)
N(1)	−0.219 7(9)	0.166 3(6)	0.119 9(8)
O(1)	−0.360(1)	0.166 7(6)	0.023 8(7)
N(2)	−0.118(1)	0.196 4(4)	0.366 6(8)
O(2)	−0.183(1)	0.219 6(5)	0.417 1(8)
C(5′)	0.257(2)	0.066 9(7)	0.050(1)
C(4′)	0.441(1)	0.047 2(7)	0.145(1)
C(3′)	0.503(1)	0.063 3(5)	0.274(1)
C(2′)	0.377(1)	0.097 1(5)	0.307 3(8)
C(6′)	0.135(1)	0.098 6(7)	0.087(1)
N′	0.194(1)	0.114 7(4)	0.213 6(7)
C(2)	0.431(1)	0.115 3(5)	0.442 7(8)
C(3)	0.617(1)	0.107 7(6)	0.549(1)
N	0.286(1)	0.143 0(4)	0.458 2(7)
C(4)	0.653(1)	0.127 6(7)	0.679(1)
C(6)	0.323(1)	0.160 6(6)	0.578 3(9)
C(5)	0.505(1)	0.152 2(7)	0.687 9(9)
H(4)	0.80(1)	0.125(7)	0.75(1)
H(6′)	0.00(1)	0.114(7)	0.02(1)
H(5)	0.53(1)	0.172(7)	0.77(1)
H(6)	0.21(1)	0.176(7)	0.58(1)
H(4′)	0.53(1)	0.019(7)	0.13(1)
H(3′)	0.64(1)	0.050(6)	0.35(1)
H(3)	0.73(1)	0.079(7)	0.55(1)
H(5′)	0.19(1)	0.066(7)	0.05(1)

The cell dimensions were obtained from a least-squares refinement against the setting angles of 25 reflections measured on a Philips PW 1100 diffractometer using graphite-monochromated Mo-K_α radiation. The θ—2θ scan technique was used to record the intensities for half-reciprocal space limited by $2 < \theta < 28°$. The intensities of three standard reflections monitored at intervals of 2 h showed no significant fluctuations. The raw intensity data were corrected for Lorentz-polarization effects. Absorption corrections were neglected, the linear absorption coefficient being 13.41 cm^{-1}. Of the 5 298 recorded intensities, there were 3 033 with $|F_o|^2 > \sigma|F_o|^2$ and $\sigma|F_o|^2$ was estimated from counting statistics. After averaging equivalent reflections, 1 687 independent reflections remained which were used in the refinement of the structural parameters.

Structure Solution and Refinement.—The structure was solved by using a Patterson synthesis to locate the Mo atoms. Subsequent refinements and difference-Fourier syntheses led to the location of all remaining non-hydrogen atoms. The refinement was carried out by means of full-matrix analysis incorporating anisotropic thermal parameters; this gave $R = 0.049$ and $R' = 0.054$. The use of a Fourier-difference function permitted location of all hydrogen atoms which were included in the final refinement with fixed isotropic thermal parameters. The model converged with $R = 0.045$ and $R' = 0.050$. Ionic scattering factors for Cl^- and neutral ones for Mo, C, N, O, and H[9] were used, and the real and imaginary corrections due to anomalous dispersion[10] were applied.

Spectroscopic Measurements.—The i.r. spectra were recorded on a Bruker IFS 113 V Fourier-transform spectrometer, as Nujol mulls (4 000—400 cm^{-1}) and using polyethylene discs (420—50 cm^{-1}). The u.v.-visible spectra were run on a Jobin-Yvon DUOSPAC 203 instrument. The ^1H n.m.r. spectra were obtained with a Bruker WP 60 instrument with $SiMe_4$ as internal standard. The ^{31}P n.m.r. spectra were recorded on the same instrument with white-noise proton decoupling, shifts being positive downfield with respect to external 85% H_3PO_4. The elemental analyses were determined by the Microanalysis Laboratory of the C.N.R.S., Villeurbanne, France.

Results and Discussion

Syntheses.—Previous synthetic routes to neutral dinitrosyl complexes $[Mo(NO)_2L_2Cl_2]$ have included (*a*) the method[6b,7,8,11,12] used in the present work, (*b*) the action of NO on $[Mo(CO)_3L_2Cl_2]$,[6a,13] (*c*) the reaction of NOBr with $[Mo(CO)_4(PPh_3)_2]$,[13] and (*d*) the reaction of NO with Mo^{II} dimers containing Mo≡Mo bonds.[14] The compounds (2),[6] (3),[6] (4), (5), (6), (7), and (8) were prepared by the reaction of the corresponding free ligand (L or L_2) with the polymeric compound $[\{Mo(NO)_2Cl_2\}_n]$ (1).[7,8] The formation occurs by the ligand-assisted splitting of the di-μ-chloro-bridges with the ligands PPh_3, py, MeCN, $CH_2{=}CHCN$, PhCN, dppe, and bipy respectively. Other ligands such as alcohols,[11] ketones, and amines have been used previously.[6] However, no reaction is observed with olefins and chelating diolefins such as norborna-2,5-diene or *cis,cis*-cyclo-octa-1,5-diene.

Structure of $[Mo(NO)_2(bipy)Cl_2]$ (8).—The atomic co-ordinates for (8) are given in Table 2; Figure 1 shows an ORTEP[15] plot of the molecule with the atom numbering. The unit-cell contents are shown in Figure 2.

The crystal structure consists of discrete molecules occupying general positions in the space group $P2_1/c$. The nearest intermolecular contact of 2.68 Å is found between O(1) and H(5). This distance agrees with a van der Waals interaction which therefore contributes to the stabilization of the crystal packing (sum of the van der Waals radii = 2.6 Å).[16] The molecular structure in the solid state revealed a distorted octahedral geometry for the central MoN_4Cl_2 skeleton with a *cis*-dinitrosyl-*trans*-dichloro-arrangement. A selection of distances and angles associated with the central MoN_4O_2 skeleton is given in Table 3.

The complex possesses approximately two-fold symmetry, and if the small distortions are neglected, the molecular symmetry is C_{2v}. In the equatorial plane the N(1)–Mo–N(2) angle is 91.9(8)°, whereas the chelate bite of bipy causes a N–Mo–N′ angle of only 74.3(4)° which induces the distortion. The Cl(1)–Mo–Cl(2) angle is found to be less than 180°

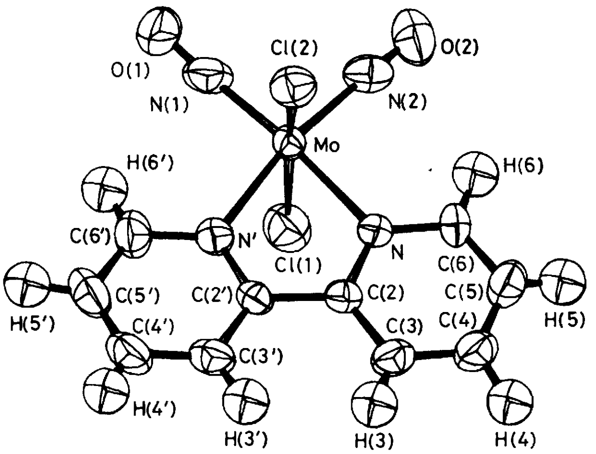


Figure 1. ORTEP projection of $[Mo(NO)_2(bipy)Cl_2]$ (8) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level

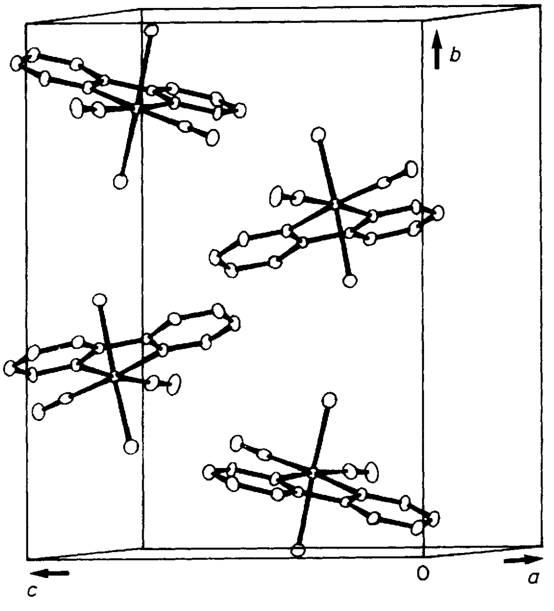


Figure 2. View of the unit cell of $[Mo(NO)_2(bipy)Cl_2]$ (8)

Table 3. Bond distances (Å) and angles (°) for $[Mo(NO)_2(bipy)Cl_2]$ (8), with estimated standard deviations in parentheses

(*i*) Inner co-ordination sphere of Mo

Mo–Cl(1)	2.428(2) 2.425 *	Mo–N'	2.203(9)
Mo–Cl(2)	2.408(3) 2.404 *	Mo–N(1)	1.826(6) 1.831 *
Mo–N	2.192(5)	Mo–N(2)	1.875(11) 1.878 *
Cl(1)–Mo–Cl(2)	166(1)	Cl(2)–Mo–N(1)	96.8(4)
N(1)–Mo–N(2)	91.9(8)	Cl(2)–Mo–N'	83.9(3)
N–Mo–N'	74.3(4)	Cl(2)–Mo–N	84.7(4)
Cl(1)–Mo–N(2)	95.4(5)	Cl(1)–Mo–N	84.7(2)
Cl(1)–Mo–N(1)	93.4(4)	Cl(1)–Mo–N'	84.1(4)
Cl(2)–Mo–N(2)	94.1(5)	O(1)–Mo–O(2)	92(1)

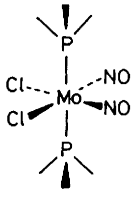
(*ii*) Nitrosyl ligands

N(1)–O(1)	1.123(9) 1.149 *	N(2)–O(2)	1.055(16) 1.067 *
Mo–N(1)–O(1)	175.9(10)	Mo–N(2)–O(2)	177.4(13)

* Corrected for thermal motion.

[166(1)°] and the chloro-ligands bend away from the NO groups. Nevertheless, the distortion of the octahedron is very small, since the angle between the mean equatorial plane N(1),N(2),N,N' and the axial plane Cl(1),Mo,Cl(2) is 91.1°. A slight twisting (5.4°) about the C(2)–C(2') axis is found for the two pyridine rings and the hydrogen atoms lie approximately in the mean plane of respective pyridine rings. This configuration agrees with those found in a variety of 2,2'-bipyridine complexes [17] and the average C–C and C–N bond lengths are similar to those of the free ligand,[17c] 1.40 and 1.36 Å, respectively. The five-membered ring Mo,N,C(2),C(2'),N' is strictly planar and the Mo atom lies in the bipy mean plane. Considering the five-atom $Mo(NO)_2$ moiety, the O(1) and O(2) atoms are displaced slightly from the equatorial plane Mo,N,N',N(1),N(2), by 0.10(1) and −0.056(8) Å respectively.

As deduced from Table 2 and Figure 1, no disorder exists in the structure. The relative size, shape, and orientation of the thermal motion is physically reasonable. The values of equivalent isotropic thermal parameters $\langle B \rangle_{eq}$ are 5.07 and 4.11 Å^2 for N(1) and N(2), respectively, and 7.68 and 6.58 Å^2 for O(1) and O(2), respectively. It seems likely that the crystal packing can generate minor changes in the interatomic angles and distances in the molecule. [Therefore, differences in comparable bond length and angle values of the $Mo(NO)_2$ moiety are significant.] The Mo–N(1)–O(1) and Mo–N(2)–O(2) angles are very similar, 175.9(10) and 177.4(13)°; moreover, no significant difference is detected between the O(1)–Mo–O(2) and N(1)–Mo–N(2) angles which shows that there are no interactions [18] between the two NO ligands. The Mo–N(1) and Mo–N(2) bond lengths of 1.826(6) and 1.875(11) Å, respectively, are similar to those reported for $[Mo(NO)_2(PPh_3)_2Cl_2]$ [19] [1.826(7) and 1.98(1) Å], but differ from the mean value reported for the 5,10,15,20-tetra-*p*-tolylporphyrinate derivative $[Mo(NO)_2(ttp)]$ [20] [1.70(1) Å]. The N(1)–O(1) and N(2)–O(2) bond lengths are 1.123(9) and 1.055(16) Å, respectively. This significant difference is also found after correction for thermal motion [1.149 and 1.067 Å respectively]. These distances are in the reported range for six-co-ordinate dinitrosyl complexes.[19-22] However, the parameters associated with the NO groups in the six-co-ordinate class are suspect because of disorder in these crystal structures.[19-22] The Mo–Cl(1) and Mo–Cl(2) bond lengths, 2.428(2) and 2.408(3) Å, respectively, are shorter than in the phosphine complex (2) (2.477 and 2.420 Å); [19] in the latter case, the chloro-ligands are *trans* to the NO groups (see below).



In $[Mo(NO)_2(bipy)Cl_2]$ the NO groups are *trans* to the bipy ligand and the Mo–N(bipy) distances [Mo–N 2.192(5) Å and Mo–N' 2.203(9) Å] are longer than in other bipyridine complexes such as $[Mo(CO)_2(bipy)(SO_2)_2]$ [17b] or $[Mo(bipy)_2(CHOMe_2)_2]$.[17c]

Table 4. Characteristic i.r. (cm^{-1}), u.v.–visible, and ^1H n.m.r. data for the dichlorodinitrosylmolybdenum complexes

Complex	$\nu(C{=}N)$ [a]	$\nu_{sym}(NO)$ [a]	$\nu_{asym}(NO)$	$\nu_{asym}(MoCl)$	$\nu_{sym}(MoCl)$	λ_{max}/nm	^1H n.m.r. (δ/p.p.m.) [b]
(2) $[Mo(NO)_2(PPh_3)_2Cl_2]$		1 785s	1 670s	305s	288s	450	7.6—8.2 (m, 30 H)
(3) $[Mo(NO)_2(py)_2Cl_2]$		1 780s	1 680s	316s	290m	440	7.36—7.66 (m, 4 H), 7.87—8.20 (m, 2 H), 8.87—9.07 (m, 2 H)
(4) $[Mo(NO)_2(MeCN)_2Cl_2]$	2 320w 2 300w	1 805s	1 685s	310s	287s	460	2.46 (6 H)
(5) $[Mo(NO)_2(CH_2{=}CHCN)_2Cl_2]$	2 280m	1 800s	1 680s	312s	288s	457	5.77—6.93 (m, 6 H)
(6) $[Mo(NO)_2(PhCN)_2Cl_2]$	2 285m	1 800s	1 690s	315s	290s	455	7.57—8.06 (m, 10 H)
(7) $[Mo(NO)_2(dppe)Cl_2]$		1 775s	1 655s	305s	285w	460	
(8) $[Mo(NO)_2(bipy)Cl_2]$		1 780s	1 650s	320s	293m	450 (sh)	7.37—9.17 (m, 8 H)

[a] As Nujol mulls with AgCl plates. [b] In $CDCl_3$ at room temperature; $SiMe_4$ as standard; m = multiplet.

I.r. and Electronic Spectra.—The i.r. spectra of all of the complexes exhibit two strong bands in the $\nu(NO)$ region (1 850—1 650 cm^{-1}, Table 4). The bands at *ca.* 1 800 cm^{-1} are sharp and are assigned to the ν_{sym} mode, A_1, following C_{2v} symmetry. The others at *ca.* 1 650 cm^{-1} are broader and are assigned to the ν_{asym} mode, B_1. The shapes of the corresponding bands are very similar for all the compounds listed in Table 4; by analogy with the *X*-ray structures of (2) [19] and (8) we propose the *cis* geometry for all the compounds. As the two NO groups are structurally identical in $[Mo(NO)_2(bipy)Cl_2]$, the large difference between the two ν_{sym} and ν_{asym} frequencies indicates that the NO ligands are strongly coupled. It should be noted that several dinitrosylmolybdenum complexes exhibit only one N_{1s} binding energy [14] in agreement with two equivalent NO groups. The stereochemical arrangement of the ligands around the *cis*-$Mo(NO)_2$ fragment must be considered uncertain from the i.r. data (Table 4). However, different arrangements of the dichloro-derivatives may be distinguished by their far-i.r. spectra. Although ambiguities may arise owing to the occurrence of Mo–Cl and Mo–N, or Mo–P stretching vibrations in the same region,[23,24] ν(Mo–Cl) can be easily assigned taking into account (*i*) the spectral changes when the ligands L vary and (*ii*) the known different stereochemistries of (2) [19] and (8) (respectively *cis,trans,cis* and *cis,cis,trans*). Both compounds exhibit C_{2v} symmetry. Group theoretical considerations predict two i.r.-active Mo–Cl stretching vibrations A_1 and B_1 for (2), and A_1 and B_2 for (8). It has been found that the relative intensities of these bands are different for the *cis*-dichloro-isomer (2) (305s and 288s cm^{-1}) and the *trans*-dichloro-isomer (8) (320s and 293m cm^{-1}). The i.r. spectra also display characteristic bands in the $\nu(C{\equiv}N)$ region (L = MeCN, $CH_2{=}CHCN$, or PhCN) (Table 4) which indicates for (4), (5), and (6) 'classical' co-ordination through the nitrogen atom.[25]

Electron-deficient metal ions induce the co-ordination of $CH_2{=}CHCN$ through the N atom,[25] as occurs in the molybdenum complex (5) described here. The bipy heterocycle in (8) exhibits i.r. bands at 1 602, 1 640, 1 502, and 1 440 cm^{-1} (see ref. 26).

The electronic spectrum of $[Mo(NO)_2(bipy)Cl_2]$ in CH_2Cl_2 exhibits a broad absorption in the near-u.v. and visible region. This band is structured at room temperature $\lambda_{max} = 395$ nm (ε 600 $dm^3\ mol^{-1}\ cm^{-1}$) and exhibits a shoulder near 450 nm. The peak and the shoulder are tentatively assigned [27,28] to metal-to-ligand charge-transfer transitions ($b_1^* \longleftarrow b_2$ or a_2) and ($a_2^* \longleftarrow a_1$ or b_2) respectively with C_{2v} symmetry in solution. The absorption near 450 nm is present for all the complexes (Table 4). Very similar values have been obtained for another series of octahedral complexes $[Mo(NO)_2L_2X_2]$ [12] (L = $PEtPh_2$, PEt_3, or PBu^n_3; X = Cl, Br, or NCS). This band is not very sensitive to the nature of the ligands L or L_2.

Hydrogen-1 *and* ^{31}P *N.M.R. Data.*—Representative ^1H n.m.r. data were obtained for most of the complexes prepared in the present work (Table 4). Some structural information can be deduced which confirms the conclusions of the far-i.r. study. For the acrylonitrile derivative (5) an ABC system for the vinyl protons is observed at 5.77—7.50 p.p.m. For the benzonitrile derivative (6), multiplets around 7.7 p.p.m. are due to the AA′BB′C system of the aromatic protons.[29] The complex (3) exhibits three multiplets at 9.97, 8.03, and 7.53 p.p.m. due to the α, γ, and β protons respectively of the py ligand.[30] Complex (8) exhibits a complicated pattern due to the bipy ligand which comprises three multiplets at 7.75 (2 H), 8.30 (4 H), and 8.60 p.p.m. (2 H).[31] More informative with respect to the stereochemistry of the complexes is the spectrum of $[Mo(NO)_2(MeCN)_2Cl_2]$ (4) which exhibits one sharp signal at 2.46 p.p.m. (6 H) in $CDCl_3$, showing the equivalence of the two methyl groups. Indeed, no fast exchange occurs in the CD_3CN solvent. The complex $[Mo(NO)_2(PPh_3)_2Cl_2]$ (2) displays a ^{31}P n.m.r. spectrum in $CDCl_3$ or CD_3CN with one singlet at 48.1 p.p.m. which demonstrates the equivalence of the two phosphorus atoms in solution. This result is in accordance with previous ^1H n.m.r. results [7] on the parent complex $[Mo(NO)_2(PMePh_2)_2Cl_2]$.

On the basis of the *X*-ray and spectroscopic results, it appears that among the several possible isomers for $[Mo(NO)_2L_2Cl_2]$ only the two with C_{2v} symmetry are preferentially formed: the *cis*-dinitrosyl-*cis*-dichloro-*trans*-L_2 for L = PPh_3 or RCN and the *cis*-dinitrosyl-*trans*-dichloro-*cis*-L_2 for L = py and L_2 = bipy or dppe. The *trans*-phosphine isomer formation can be explained by steric requirements arising from PPh_3 and that for *cis*-bipyridyl by the *cis* chelating properties of the bipy ligand. However at this stage is it difficult to make generalisations on the basis of the few complexes characterised.

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