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Structure of Trans-chloronitrosyltetrakis(pyridine)ruthenium(II) Bis(hexafluorophosphate) Hemihydrate

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The structure of trans-chloronitrosyltetrakis(pyridine)ruthenium(II) bis(hexafluorophosphate) hemihydrate, $[RuClpy_4NO](PF_6)_2\cdot 1/2H_2O$, was determined by X-ray structure analysis. The compound crystallizes in monoclinic form, space group $P2_1/c$, with $a = 16.0201(12)$, $b = 13.5306(15)$, $c = 27.0912(20)$ Å, $\beta = 91.78(1)°$, $Z = 8$. Least-squares refinement of the structure yielded a final R factor of 0.051 for 4229 independent reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ collected by a counter method. There are two crystallographically independent formula units in the asymmetric unit. Both have essentially the same structure.

The complex cation has a trans octahedral geometry with a nitrosyl and a chloride in the axial position and four pyridines in the equatorial position. The four pyridines form a propeller-like arrangement with an average pitch of about 46°.

The Ru–NO group is approximately linear: the Ru–N–O angle is 174.8(1.9)°, the Ru–N bond length is 1.760(9) and that of N–O is 1.132(13) Å. The Ru–Cl bond length is 2.314(1) Å; this is shortened by the trans-shortening effect of the nitrosyl. The average separation distance of Ru–N-(pyridine) is 2.111(6) Å.

NMR spectra, along with their temperature dependence, suggests that rapid cogwheel rotation of pyridine rings about Ru–N(py) axis is occurring in solution.

Introduction

In a recent paper, one of us reported the electrophilic behaviour of six-coordinated ruthenium tetrakis(pyridine)nitrosyl complexes, $[RuX(py)_4NO]Y_2$ (X = Cl, Br, OH. Y = ClO_4, PF_6) [1]. We now present the crystal structure of trans-chloronitrosyl tetrakisruthenium(II) bis(hexafluorophosphate) hemihydrate, $[RuCl(py)_4NO](PF_6)_2\cdot 1/2H_2O$ as a part of our continuing work on these complexes. The structure of the complex is closely comparable to those of other complexes of the type $[MXL_4NO]^{n+}$ which is abbreviated as the $\{MNO\}^6$ system [2, 3].

Experimental

Data Collection and Structure Determination

Preliminary oscillation and Weissenberg photographs were taken to determine the space group and to estimate the unit-cell parameters. The crystal, with the dimensions *ca.* 0.15 × 0.2 × 0.2 mm, was mounted for data collection on a RIGAKU four-circle automatic diffractometer which used graphite-monochromatized MoKα radiation. Accurate cell parameters were determined by least-squares treatment for 20 strong reflections in the 2θ range of 15 ~ 20°. Crystal data are: trans-$[RuCl(C_5H_5N)_4NO][PF_6]_2\cdot 1/2H_2O$, monoclinic, space group $P2_1/c$, $a = 16.0201(12)$, $b = 13.5306(15)$, $c = 27.0912(20)$ Å, $\beta = 91.78(1)°$, $U = 5869.5(9)$ Å^3, $Z = 8$, $d_x = 1.772$ g/cm^3, $d_m = 1.75$ (by flotation in CCl_4/CH_2I_2 mixtures), $\mu(MoK\alpha) = 8.248$ cm^{-1}. The intensity data were measured to $2\theta = 50°$ using the ω, $2\theta-\omega$ scan method. Three standard reflections were measured every 100 reflections; no significant change in intensities with time was noted. The usual Lorentz and polarization corrections were applied and 4229 independent reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ were obtained.

The positions of the ruthenium atom were determined from the Patterson map and those of the remaining non-hydrogen atoms from subsequent Fourier syntheses. The structure was refined by the

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block-diagonal least-squares with anisotropic temperature factors; the final R value was 0.051. Unit weight was given to all reflections. Of the 40 hydrogen atoms of the pyridine rings, more than one half were found at reasonable positions on the final difference Fourier map but were not included in the calculations. Calculations were performed on the FACOM 230-75 computer of the Institute of Physical and Chemical Research using the UNICS III program system [4].

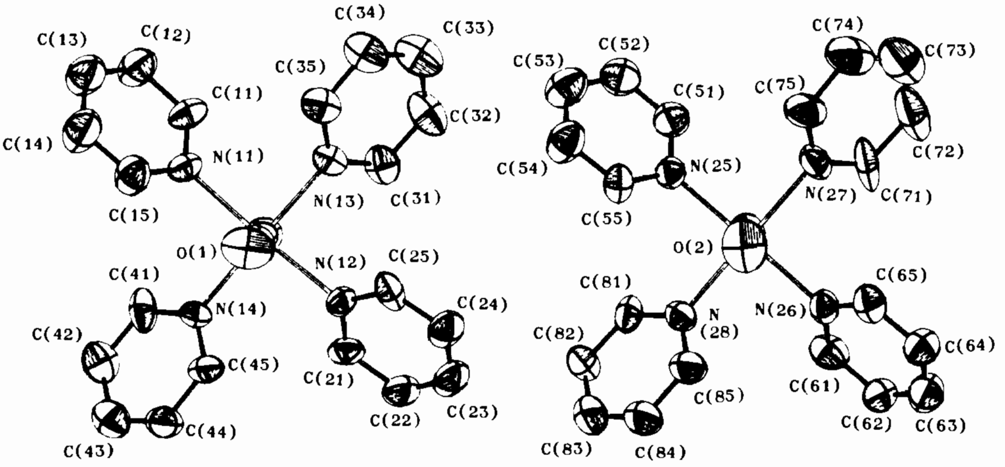
Results and Discussion

The crystal consists of the two crystallographically independent $[RuClpy_4NO](PF_6)_2$ complexes and a water molecule in an asymmetric unit. Both of the nitrosylruthenium complex cations have the expected trans octahedral coordination geometry, with four pyridine ligands in equatorial position and with a chloride ligand and a nitrosyl ligand in axial position, as shown in Fig. 1. The basic structures of these two cations, complex "1" and complex "2", are identical. Their important structural parameters are listed in Table II. The average value of Ru–N–O angle is 174.8(1.9)°. The near linearity of the Ru–N–O linkage is strong evidence that the nitrosyl moiety bonds as NO^+. The average separation distances for Ru–N(NO), 1.760(9) Å, and for N–O, 1.132(13) Å, fall within the range of the values found for such linear $\{RuNO\}^6$ systems [5], as listed in Table III. The Ru–N(NO) separation distance is also in fair agreement with the corresponding value of 1.738(16) Å found for Ru(II)–NO^+ moiety, but is quite different from the value of 1.859(16) Å for Ru–NO^- moiety in $[Ru(NO^+)(NO^-)Cl(P(C_6H_5)_3)_2]$ [6].

A remarkable feature of the structure is the shortening of the Ru–Cl bond trans to the nitrosyl. When a nitrosyl acts as a strong π acceptor to a metal ion, considerable shortening of the bond between the metal and a σ-only donor ligand such as Cl^- trans to a nitrosyl has been observed in Ru(II)–NO^+ complexes. The trans Ru–Cl bond distances of the complexes in Table III are all equal, within three times the standard deviations, independent of the kind of equatorial ligands. The observed Ru–Cl bond distance of 2.314(1) Å is the shortest in the known $\{RuNO\}^6$ complexes, and is *ca.* 0.04 Å shorter than the average value of the four in Table III.

The average equatorial Ru–N bond distance is 2.111(6) Å. This is comparable to the corresponding distance of 2.092(3) Å in $[Rupy_4(C_2O_4)Rupy_4(BF_4)_2$ [7]. The pyridine rings are all essentially planar within a maximum deviation of 1.5σ from the best planes [8]. These planes rotate in the same direction about their respective Ru–N bonds to give the pseudo-fourfold symmetric propeller-like structure around a pseudo-rotation axis, Cl–Ru–NO. The dihedral angles between the RuN_4 best plane and the best plane of the pyridine rings range from 40.4(3)–55.3(3)°, with an average value of 46(4)°. The angles between the two pyridine planes in trans position are about 90°, as shown in Fig. 3 and Table IV. A few studies have determined the accurate structure of a trans octahedral tetrakis(pyridine) complex: for example, $[Fe(SCN)_2py_4]$ [9], $[NiI_2py_4]$ [10], $[MCl_2py_4]$ (M = Fe, Ni, Co), $[FeCl_2py_4]H_2O$ [11] and $[Rupy_6](BF_4)_2$ [12]. All of these complexes have the same propeller-like structure.

Fig. 2 shows the complex "1" molecule with the interatomic distances between two non-bonded



Complex "1" Complex "2"

Fig. 1. Molecular structure of $[RuClpy_4NO]^{2+}$ complex cations viewed along the axial ON–Ru–Cl.

TABLE I. Positional Parameters (×10^4) and Thermal Parameters.

Atom	x	y	z	B_{eq}/A^2
Ru(1)	−88.1(5)	1915.6(7)	1181.3(3)	3.2
Ru(2)	5209.5(5)	2364.0(7)	3605.6(3)	3.5
Cl(1)	−1197(2)	1127(2)	780(1)	4.4
Cl(2)	6269(2)	3076(2)	3166(1)	4.9
P(1)	1638(2)	2662(3)	2891(1)	4.7
P(2)	1127(2)	−4186(3)	828(1)	4.5
P(3)	6211(2)	1472(3)	6424(2)	6.3
P(4)	3265(2)	3459(3)	5417(2)	6.0
F(11)	959(4)	2066(5)	3190(3)	6.6
F(12)	908(4)	3159(6)	2567(3)	6.8
F(13)	2323(5)	3249(6)	2606(3)	7.6
F(14)	2356(4)	2153(6)	3225(3)	7.1
F(15)	1678(4)	1782(6)	2504(3)	7.0
F(16)	1589(5)	3531(6)	3287(3)	7.3
F(21)	1133(5)	−5071(5)	1212(3)	7.1
F(22)	1118(5)	−3287(6)	456(3)	7.1
F(23)	1869(4)	−3681(6)	1146(3)	6.5
F(24)	473(4)	−3625(6)	1151(3)	6.4
F(25)	393(5)	−4690(6)	520(3)	7.5
F(26)	1773(5)	−4754(8)	511(3)	9.0
F(31)	6960(5)	2025(6)	6186(3)	8.0
F(32)	6175(5)	2348(7)	6830(3)	8.8
F(33)	5568(5)	2091(6)	6099(3)	8.2
F(34)	5468(5)	964(6)	6708(4)	11.0
F(35)	6850(5)	883(8)	6759(4)	12.1
F(36)	6240(7)	627(8)	6053(5)	13.3
F(41)	3344(6)	4223(8)	5851(4)	10.9
F(42)	3997(6)	2836(8)	5644(5)	12.8
F(43)	2530(5)	4101(9)	5208(4)	10.9
F(44)	3194(8)	2720(12)	4998(5)	18.4
F(45)	2622(6)	2873(8)	5715(5)	13.5
F(46)	3916(7)	4079(9)	5133(5)	14.3
O(1)	1393(5)	2888(7)	1569(3)	6.1
O(2)	3875(6)	1536(7)	4171(3)	7.1
O(3)	5055(11)	3912(11)	78(5)	14.8
N(1)	797(5)	2514(7)	1447(3)	3.7
N(2)	4410(5)	1836(7)	3946(3)	4.2
N(11)	506(5)	524(6)	1262(3)	3.6
N(12)	−730(5)	2368(6)	1125(3)	3.4
N(13)	−715(5)	1686(6)	1844(3)	3.7
N(14)	414(5)	2102(6)	477(3)	3.6
N(25)	5867(5)	2792(6)	4256(3)	3.4
N(26)	4584(5)	1988(6)	2930(3)	3.8
N(27)	5876(5)	1016(6)	3582(4)	4.7
N(28)	4595(5)	3741(6)	3600(3)	3.7
C(11)	80(7)	−286(8)	1428(4)	4.0
C(12)	490(8)	−1196(9)	1495(5)	5.4
C(13)	1318(8)	−1277(10)	1405(6)	6.5
C(14)	1758(8)	−455(10)	1230(6)	6.6
C(15)	1348(7)	442(9)	1174(5)	5.0
C(21)	−1191(6)	3517(8)	708(4)	3.9
C(22)	−1649(7)	4394(9)	693(5)	4.9
C(23)	−1651(8)	4993(8)	1103(5)	5.4
C(24)	−1166(7)	4762(8)	1523(5)	5.0
C(25)	−706(7)	3890(8)	1523(4)	4.3
C(31)	−1544(6)	1893(9)	1866(4)	4.5
C(32)	−1971(7)	1724(11)	2297(5)	5.7
C(33)	−1563(8)	1312(11)	2715(5)	6.2
C(34)	−706(7)	1123(10)	2690(5)	5.5
C(35)	−284(7)	1306(9)	2248(4)	4.4
C(41)	464(7)	1331(9)	158(4)	4.7
C(42)	792(8)	1468(10)	−308(4)	5.2
C(43)	1057(7)	2400(10)	−456(4)	5.2
C(44)	1010(7)	3174(9)	−123(4)	4.7
C(45)	697(6)	3022(8)	347(4)	3.8
C(51)	6711(8)	2653(9)	4307(4)	4.8
C(52)	7149(7)	2955(10)	4722(5)	5.6
C(53)	6756(7)	3422(11)	5098(5)	6.0
C(54)	5882(8)	3450(11)	5052(5)	5.8
C(55)	5464(7)	3233(8)	4623(4)	4.2
C(61)	4599(7)	2572(9)	2520(4)	4.7
C(62)	4195(7)	2306(9)	2083(4)	5.0
C(63)	3745(8)	1428(10)	2062(5)	5.6
C(64)	3721(7)	828(9)	2476(5)	5.2
C(65)	4148(7)	1117(9)	2913(4)	4.7
C(71)	6191(7)	694(9)	3150(5)	6.0
C(72)	6640(8)	−193(10)	3125(6)	7.9
C(73)	6765(8)	−702(12)	3557(7)	9.1
C(74)	6454(9)	−416(10)	4011(7)	8.4
C(75)	5977(8)	494(9)	4012(5)	6.3
C(81)	5021(7)	4610(8)	3693(4)	4.1
C(82)	4609(7)	5506(8)	3712(4)	4.6
C(83)	3756(8)	5533(9)	3631(5)	5.6
C(84)	3313(8)	4658(10)	3533(5)	6.0
C(85)	3753(7)	3769(9)	3516(5)	5.4

atoms. The C–C distances in adjacent pyridines of 3.161(16)–3.284(17) Å are less than the van der Waals contact of the aromatic ring (about 3.4 Å). This will cause the mutual repulsion between the adjacent pyridines and would tend to increase the dihedral angle between the RuN$_4$ and pyridine best planes (this repulsion will become a minimum at 90°).

Fig. 2 and 3 show that the axially coordinated nitrosyl and chloride are held above and below the cage of the four pyridine rings and thus are in a fairly crowded situation. The distances between pyridine carbon and axial chloride of 3.184(12)–3.270(11) Å are less than the sum of the van der Waals radii of the aromatic ring and the chloride (about 3.5 Å). The distance between pyridine carbon and axial nitrosyl nitrogen of 3.038(15)–3.258(14) Å is also slightly less than the sum of the van der Waals radii of the aromatic ring and nitrogen (about 3.2 Å). The environment of complex "2" is similar to that of complex "1" described above (see Table V). These two kinds of repulsion between the equatorial pyridine and the axial ligands, on the other hand, would tend to decrease the dihedral angles between the RuN$_4$ and the pyridine best planes.

The dihedral angles in this complex are determined so as to reduce these contrary repulsions; consequently, this complex comes to have a propeller-like arrangement of the four equatorial pyridines. These

TABLE II. Selected Intramolecular Distances (Å) and Angles (°) for the $[RuClpy_4NO]^{2+}$ Ions, with e.s.d.s in Parentheses.

Ru(1)–Cl(1)	2.315(3)	Ru(2)–Cl(2)	2.313(3)
Ru(1)–N(1)	1.766(8)	Ru(2)–N(2)	1.753(9)
Ru(1)–N(11)	2.118(8)	Ru(2)–N(25)	2.105(8)
Ru(1)–N(12)	2.103(8)	Ru(2)–N(26)	2.122(8)
Ru(1)–N(13)	2.107(8)	Ru(2)–N(27)	2.115(9)
Ru(1)–N(14)	2.109(8)	Ru(2)–N(28)	2.107(8)
N(1)–O(1)	1.123(11)	N(2)–O(2)	1.141(12)
Cl(1)–Ru(1)–N(1)	175.8(3)	Cl(2)–Ru(2)–N(2)	179.2(3)
Cl(1)–Ru(1)–N(11)	88.5(2)	Cl(2)–Ru(2)–N(25)	87.7(2)
Cl(1)–Ru(1)–N(12)	90.0(2)	Cl(2)–Ru(2)–N(26)	89.4(2)
Cl(1)–Ru(1)–N(13)	87.3(2)	Cl(2)–Ru(2)–N(27)	87.9(3)
Cl(1)–Ru(1)–N(14)	86.5(2)	Cl(2)–Ru(2)–N(28)	88.7.(2)
N(1)–Ru(1)–N(11)	90.7(4)	N(2)–Ru(2)–N(25)	91.5(4)
N(1)–Ru(1)–N(12)	90.9(4)	N(2)–Ru(2)–N(26)	91.3(4)
N(1)–Ru(1)–N(13)	96.8(3)	N(2)–Ru(2)–N(27)	92.4(4)
N(1)–Ru(1)–N(14)	89.4(3)	N(2)–Ru(2)–N(28)	90.9(4)
N(11)–Ru(1)–N(12)	176.9(3)	N(25)–Ru(2)–N(26)	177.0(3)
N(11)–Ru(1)–N(13)	90.3(3)	N(25)–Ru(2)–N(27)	91.3(3)
N(11)–Ru(1)–N(14)	91.0(3)	N(25)–Ru(2)–(N(28)	89.1(3)
N(12)–Ru(1)–N(13)	86.9(3)	N(26)–Ru(2)–N(27)	89.6(3)
N(12)–Ru(1)–N(14)	91.7(3)	N(26)–Ru(2)–N(28)	89.9(3)
N(13)–Ru(1)–N(14)	173.7(3)	N(27)–Ru(2)–N(28)	176.6(3)
Ru(1)–N(1)–O(1)	172.9(8)	Ru(2)–N(2)–O(2)	176.7(9)
Ru(1)–N(12)–C(21)	121.6(7)	Ru(2)–N(26)–C(61)	122.9(7)
Ru(1)–N(12)–C(25)	118.4(7)	Ru(2)–N(26)–C(65)	117.4(7)
Ru(1)–N(13)–C(31)	119.9(7)	Ru(2)–N(27)–C(71)	120.2(8)
Ru(1)–N(13)–C(35)	119.5(7)	Ru(2)–N(27)–C(75)	117.8(8)
Ru(1)–N(14)–C(41)	121.0(7)	Ru(2)–N(28)–C(81)	121.7(7)
Ru(1)–N(14)–C(45)	118.6(7)	Ru(2)–N(28)–C(85)	119.1(7)
Ru(1)–N(11)–C(11)	121.1(7)	Ru(1)–N(25)–C(51)	120.9(7)
Ru(1)–N(11)–C(15)	119.4(7)	Ru(1)–N(25)–C(55)	120.2(7)

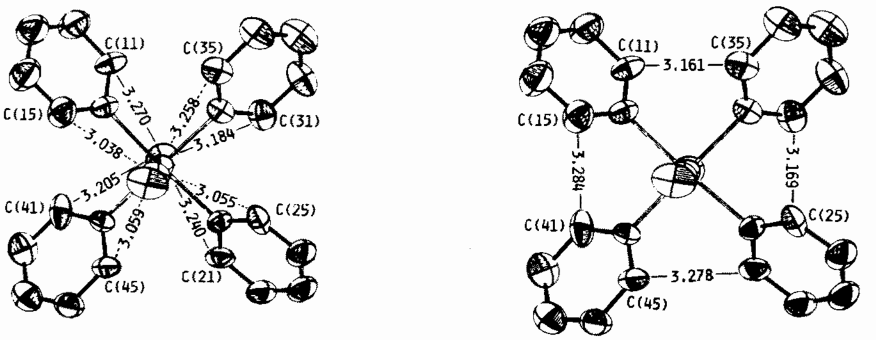
TABLE III. Significant Structural Parameters for Linear RuNO Complexes.

Complex	Ru–N	N–O	Ru–N–O	Ru–Cl		Ref.
				trans to NO	*cis* to NO	
$(NH_4)_2[RuCl_5NO]$	1.738(2) Å	1.131(3) Å	176.7(5) Å	2.357(1) Å	2.376(1) Å	15
$K_2[RuCl_5NO]$	1.747(6)	1.112(7)	176.8(9)	2.359(2)	2.372(8)	16
$[RuCl_3(CH_3(C_6H_5)_2P)_2NO]$	1.744(6)	1.132(6)	176.4(6)	2.357(2)	2.398(7)	17
$[RuCl_3((C_6H_5)_3P)_2NO]$	1.737(7)	1.142(8)	180.0(0)	2.353(2)	2.394(2)	18
$[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$	1.770(9)	1.172(14)	172.8(9)			19
trans-$[RuOH(NH_3)_4NO]Cl_2$	1.735(3)	1.159(5)	173.8(3)			19
trans-$[RuCl(C_5H_5N)_4NO] \cdot 1/2H_2O$	1.760(9)	1.132(13)	174.8(1.9)	2.314(1)		This work[a]

[a] Average value of two complex cations, complex "1" and complex "2".

angles range from about 40–45°, as was stated above. This range denotes the flexibility of the Ru–N bond and the importance of the crystal packing effect in determining the final dihedral angles in the crystalline state.

The same propeller-like structure was also found in trans-$[Ni(ClO_4)_2(3,5\text{-}dpy)_4]$ (dpy = dimethylpyridine) [13]. It is interesting, however, that $[Ni(3,4\text{-}dpy)_4](ClO_4)_2$ exhibits square-planar coordination around the Ni atom and that the planes of the ligand are perpendicular to the molecular plane [14]. This complex has no axially coordinated ligand and so no repulsion between the equatorial and axial ligands. This would lead the substituted pyridine rings to



Complex "1" ..... C-N(NO)
—— C-Cl

Complex "1"

Fig. 2. Intramolecular non-bonded atomic distances in complex "1".

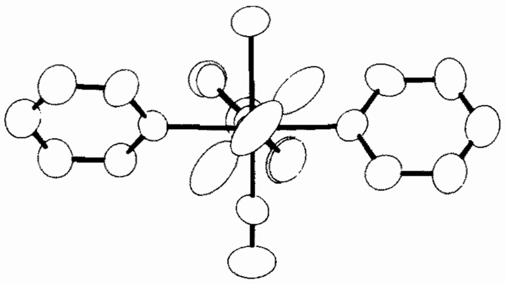


Fig. 3. Structure of complex "2" viewed along the equatorial pyridine–Ru–pyridine.

TABLE IV. Dihedral Angles (°) between Planes.

Ru(1)N_4–N(11)py	45.0(4)	Ru(2)–N(25)py	44.3(4)
Ru(1)N_4–N(12)py	48.9(3)	Ru(2)–N(26)py	55.3(3)
Ru(1)N_4–(N13)py	43.8(3)	Ru(2)–N(27)py	43.6(4)
Ru(1)N_4–N(15)py	40.4(3)	Ru(2)–N(28)py	46.5(3)
N(11)py–N(12)py	93.4(4)	N(25)–N(26)py	99.6(4)
N(13)py–N(14)py	84.2(4)	N(27)–N(28)py	90.0(5)

TABLE V. Significant Intramolecular Non-bonded Distances (Å) for Complex "2".

Distances between adjacent pyridines			
C(51)–C(75)	3.240(17)	C(61)–C(85)	3.459(17)
C(55)–C(81)	3.196(15)	C(65)–C(71)	3.364(16)
Distances between Cl and pyridine			
Cl(2)–C(51)	3.200(12)	Cl(2)–C(71)	3.225(13)
Cl(2)–C(61)	3.224(12)	Cl(2)–C(81)	3.244(11)
Distances between NO and pyridine			
N(2)–C(55)	3.099(14)	N(2)–C(75)	3.098(16)
N(2)–C(65)	2.978(15)	N(2)–C(85)	3.038(15)

rotate perpendicular to the molecular plane so as to minimize the adjacent pyridine–pyridine repulsion.

The differences between the structures of these two substituted pyridine complexes clearly show the important role of the axial ligands in determining the structure and the dihedral angles.

Hydrogen atoms bonded to C(11) and C(15) or to the corresponding carbon atoms in each pyridine occupy crowded positions. The repulsions between the pyridine hydrogens and the other atoms within the molecule are estimated by using the calculated coordinates for the pyridine hydrogens. The distances are as follows: Cl(1)–H, 2.757(3)–2.826(3); Cl(2)–H, 2.690(3)–2.783(3); N(1)–H, 2.641(9)–2.882(8); N(2)–H, 2.509(9)–2.706(9); C-(adjacent ring)–H, 2.975(11)–3.369(13) Å. Some of these distances seem short. Their repulsions may not be so important in determining the molecular structure.

The four molecules of PF_6^- anion have an ordinary octahedral geometry with an average P–F bond length of 1.57(2) Å. Their large temperature factors, especially those of two groups defined by P(3) and P(4), may imply a fairly large disorder in the crystal.

As was described above, the crystal structure determination confirmed that four pyridine rings are arranged in a propeller fashion with pitch of 46°. NMR spectra, however, suggest that rapid cogwheel rotation of the pyridine rings about Ru–N(py) axis is occurring in solution, since essentially the same NMR pattern was observed for both the nitrosyl complex (8.6(ppm)d, 8.3t, 7.7t in $CHCl_3$) and trans-$RuCl_2py_4$] (8.5d, 7.5t, 7.0t in $CHCl_3$) [15], in spite of the fact that 2 and 6, 3 and 5 proton of the pyridine rings should be inequivalent in the former complex. An additional evidence for this surmise was obtained from the temperature dependence of the NMR spectra in the nitrosyl

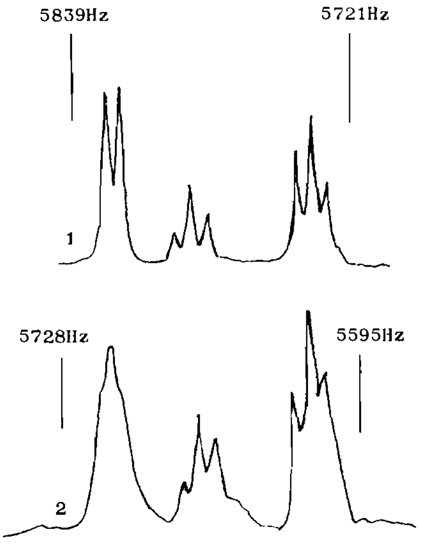


Fig. 4. The temperature dependence of the pmr spectra of $[RuCl(py)_4NO](PF_6)_2$ in $CHCl_3$. 1; 27 °C, 2; –57 °C.

complex. As is shown in Fig. 4, the doublet line which is assignable to 2 and 6 pyridine protons changes at –57 °C to a singlet broadened line with shoulders. The spectral change observed could be explained as a result of slowing down of the cogwheel rotation.

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References

1 F. Bottomley and M. Mukaida, *J. C. S. Dalton* (in press).
2 R. D. Feltham and J. H. Enemark, 'Topics in Stereochemistry' in 'Inorganic and Organometallic Stereochemistry', ed. by G. L. Geoffroy, Wiley, Vol. 12 (1981).
3 F. Bottomley, *Coord. Chem. Rev.*, *26*, 7 (1978).
4 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, *55*, 69.
5 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, *13*, 339 (1974), where 6 is the number of d electrons of Ru atom when the nitrosyl group is formally considered to be coordinated as NO^+.
6 C. G. Pierpont, D. G. Van Derveer, W. Durland and R. Eisenberg, *J. Am. Chem. Soc.*, *92*, 4760 (1970).
7 P. T. Cheng, B. R. Loescher and S. C. Nyburg, *Inorg. Chem.*, *10*, 1275 (1971).
8 Best planes and their dihedral angles are calculated according to BP70; T. Ito, *Sci. Papers Inst. Phys. Chem. Rev.*, 1981, *75*, 55.
9 I. Sotofte and S. E. Rasmussen, *Acta Chem. Scand.*, *21*, 2028 (1967).
10 D. J. Hamm, J. Bordner and A. F. Schriner, *Inorg. Chim. Acta*, *7*, 637 (1975).
11 G. J. Long and P. J. Clark, *Inorg. Chem.*, *17*, 1394 (1978).
12 J. L. Templeton, *J. Am. Chem. Soc.*, *101*, 4906 (1979).
13 Madaule-Aubry and G. M. Brown, *Acta Cryst.*, 1968, *B24*, 745.
14 Madaule-Aubry, W. R. Busing and G. M. Brown, *Acta Cryst.*, 1968, *B24*, 754.
15 T. Veal and D. J. Hodgson, *Inorg. Chem.*, *11*, 1420 (1972).
16 T. Veal and D. J. Hodgson, *Acta Cryst.*, 1972, *B28*, 3525.
17 A. J. Schultz, R. L. Henry, J. Reed and R. Eisenberg, *Inorg. Chem.*, *13*, 732 (1974).
18 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, *14*, 3060 (1975).
19 F. Bottomley, *J. Chem. Soc. Dalton*, 1974, 1600.