Dynamic NMR Conformational Studies of Ruthenium(II) Tetraazaporphyrinogen Complexes

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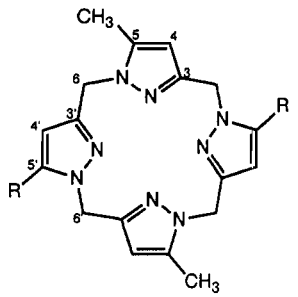
A series of Ru(II) tetraaazaporphyrinogen complexes with heteroaromatic axial ligands have been prepared in order to study their dynamic conformational behavior by variable-temperature NMR spectroscopy. Axial ligand rotation and macrocyclic interconversion proceed slowly at temperatures which depend mainly on the steric interactions occurring between the macrocycle and the axial ligands, both processes being concomitant. The free energies of activation increase in the following order: α-unsubstituted five-membered heterocycles < α-unsubstituted six-membered heterocycles < α-substituted five-membered heterocycles. The structure of the complexes when the dynamic processes are restricted on the NMR scale has been shown to be such that the macrocycle has a double saddle-shaped conformation. The axial heterocyclic ligands are perpendicular to the macrocycle and perpendicular to each other.

Introduction

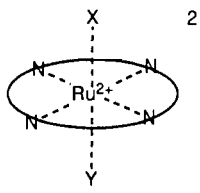
Coordination chemistry of macrocyclic ligands is a field which has received considerable interest in the past three decades.[1-4] However though an impressive number of sp^2 nitrogen-containing macrocycles are known, their ruthenium(II) complexes have not been widely investigated, in spite of their potential photochemical and photophysical properties: most of the studies concern porphyrin,[5] phthalocyanine,[6] and polypyridine[7] macrocycles. In our laboratory, we have developed a new series of polypyrazolic macrocycles which have the unique ability to form stable complexes with both alkali[8] and transition[9] metals.

In this paper we wish to report a special dynamic behavior of a series of trans Ru(II) complexes derived from the two tetraazaporphyrinogens **1** or **2**[10] and various axial ligands **a**–**j**.



1 R = CH_3

2 R = C_6H_5



a X = DMSO, Y = H_2O
b X = Y = CH_3CN
c X = Y = C_6H_5CN
d X = DMSO, Y = Py
e X = CH_3CN, Y = Py
f X = Y = Py
g X = Y = 4-OMePy
h X = Y = 3-MePyz
i X = Y = Pz
j X = Y = 3,5-diMePz

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC 250 spectrometer; chemical shifts are given in ppm, and coupling constants, in Hz. NOE-difference spectra were performed at 25 °C using the pulse program NOEMULT (acquisition time 5 s), on a degassed solution.

UV–visible spectra were recorded on a Philips PU8710 UV/vis spectrometer using standard 10-mm quartz cuvettes. The UV–visible data were stored on a personal computer and processed using Philips Falcon software.

IR spectra were obtained on a Philips PU 9700 IR spectrometer in KBr.

Cyclic voltammetry was carried out on a platinum disk electrode in dried acetonitrile with tetrabutylammonium hexafluorophosphate as supporting electrolyte; the potential of the working electrode, scanned at 200 mV/s between −2 and +2 V, was controlled by a Sirius potentiogalvanostat versus a saturated calomel electrode separated from the solution by a Tacussel bridge. The counter electrode was a platinum wire.

Materials. Macrocycles **1** and **2** were prepared as previously described.[10] $Ru(DMSO)_4Cl_2$ was purchased from Strem Chemicals. Heteroaromatic ligands were obtained from commercial sources and used as received [pyridine (Py), 2-methylpyrazine (2-MePyz), pyrazole (Pz), 3,5-dimethylpyrazole (3,5-diMePz)] or prepared as described in the literature [4-methoxypyridine (4-OMePy)].[11]

Synthesis of Ru(Mac)(DMSO)(H_2O)(PF_6)$_2$ (1a, 2a). Equimolar amounts of macrocycle **1** or **2** and of $Ru(DMSO)_4Cl_2$ were refluxed for 5 h in a $EtOH/H_2O$ mixture (75/25). The solvent was concentrated to dryness and the residue washed with ether. The chloride complex obtained was dissolved in water and precipitated as the hexafluorophosphate salt

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Table 1. Characterization Data for Ruthenium(II) Complexes

	yield, %	color	E_{ox}, V[a,b]	λ_{max}, nm[b]
1f	83	light brown	0.81	314, 387
2f	90	yellow	0.89	308.9 sh, 352.0, 385.8 sh
1g	85	pink beige	0.69	305.5 sh, 337.6
2g	87	pink beige	0.77	305.4 sh, 351.2
1h	75	light orange	0.97	301.6, 434.4
2h	95	dark yellow	1.14	310.4, 331.0, 428.0
1i	96	beige	0.72	306.4
2i	95	brown	0.83	311.9
1j	80	beige	0.66	309.1, 326.4
2j	75	light brown	0.73	314.8, 348.0

[a] Measured in acetonitrile with 0.1 M NBu_4PF_6; potentials *vs* SCE. [b] Measured in acetonitrile.

with a saturated solution of aqueous NH_4PF_6. The yellow solid was filtered out, thoroughly washed with ether, and dried in vacuum. Yield: 90%.

1a. ^{1}H NMR (CD_3CN): δ 2.48 and 2.50 (2 s, 6H, DMSO), 2.56 (s, 12H, CH_3), 5.42 and 5.51 (q, 8H, $4CH_2$, $\Delta\nu$ = 22.5 Hz), 6.50 (s, 4H, H-4). ^{13}C NMR (CD_3CN): δ 11.2 (CH_3), 44.7 and 45.6 (DMSO), 45.9 (C-6), 107.45 (C-4), 146.0 (C-5), 146.3 (C-3). λ_{max} (CH_3CN): 277.5 nm.

2a. ^{1}H NMR (CD_3CN): δ 2.58 (s, 6H, CH_3), 2.68 and 2.71 (2 s, 6H, DMSO), 5.61 (s, 4H, $2CH_2$), 5.42 and 5.59 (q, 4H, $2CH_2$, $\Delta\nu$ = 42.5 Hz), 6.54 (s, 2H, H-4), 6.82 (s, 2H, H-4′), 7.64 (m, 10H, C_6H_5). λ_{max} (CH_3CN): 286.4 nm.

Synthesis of Ru(Mac)(CH_3CN)$_2$(PF_6)$_2$ (1b, 2b). These complexes were obtained by refluxing complexes **1a** or **2a** in CH_3CN under nitrogen for 1 day. After evaporation of the solvent, the residue was taken up with ether, filtered, washed, and dried to give a yellow solid. Yield: 95% and 90%, respectively.

1b. ^{1}H NMR (CD_3CN): δ 2.54 (s, 12H, CH_3), 2.58 (s, 6H, CH_3CN), 5.40 (s, 8H, CH_2), 6.51 (s, 4H, H-4). ^{13}C NMR (CD_3CN): δ 11.0 (CH_3), 45.9 (C-6), 106.8 (C-4), 144.6 (C-5), 144.7 (C-3). λ_{max} (CH_3CN): 289.5 nm. E_{ox} (CH_3CN): 1.05 V.

2b. ^{1}H NMR (CD_3CN): δ 2.60 [s, 12H, CH_3CN and CH_3(Pz)], 5.50 and 5.55 (2s, 8H, CH_2), 6.52 (s, 2H, H-4), 6.84 (s, 2H, H-4′), 7.66 (m, 10H, C_6H_5). λ_{max} (CH_3CN): 304.8 nm. E_{ox} (CH_3CN): 1.13 V.

Synthesis of Ru(1)(C_6H_5CN)$_2$(PF_6)$_2$ (1c). This complex was prepared by refluxing complex **1a** in a large excess of benzonitrile for 2 days. After evaporation of the solvent, the residue is thoroughly washed with ether and dried to give a dark yellow powder. Yield: 60%. ^{1}H NMR (CD_3CN): δ 2.60 (s, 12H, CH_3), 5.50 (s, 8H, CH_2), 6.46 (s, 8H, H-4). ^{13}C NMR (CD_3COCD_3): δ 12.1 [CH_3(Pz)], 47.05 (C-6), 108.4 (C-4), 146.3 (C-5), 146.5 (C-3), 111.2 (CN), 127.0, 130.5, 134.2, 135.3(C_6H_5). λ_{max} (CH_3CN): 287.2, 298.3, 360.4 nm. E_{ox} (CH_3CN): 1.13 V.

Synthesis of Ru(1)(DMSO)Py(PF_6)$_2$ (1d) and Ru(1)(CH_3CN)Py(PF_6)$_2$ (1e). These complexes were prepared as described in a previous publication.[9]

Synthesis of Ru(Mac)(Het)$_2$(PF_6)$_2$ (1f–j, 2f–j). All the complexes containing heteroaromatic rings as axial ligands have been prepared using the same experimental conditions: a solution ($EtOH/H_2O$) of the complex Ru(Mac)(DMSO)(H_2O)Cl_2 obtained as described above was concentrated to half-volume and refluxed for 24 h with an excess (5 times) of the heterocyclic ligand. Solvents were evaporated to dryness; the hexafluorophosphate salt was obtained upon addition of water and a concentrated solution of NH_4PF_6. The precipitate was filtered out and washed with water. Yields, colors, $Ru^{2+/3+}$ potentials, and UV absorptions are given in Table 1.

Results and Discussion

Synthesis and Identification. The Ru(II) complexes **1a–j** and **2a–j** have been obtained either as described earlier[9] or by improved methods, all based on the axial ligand lability in the presence of more coordinating entities. Two points may be brought out:

Whatever are the experimental conditions, even drastic ones, it has been impossible to obtain complexes having α-substituted pyridines as axial ligands.

Complex **1a** had been described and used in a previous paper,[9] but at the time doubt was left about the nature of the two axial ligands. From a thorough NMR study done throughout this work, we may conclude unambiguously that, for complexes **1a** and **2a**, only one DMSO molecule is coordinated, the other axial trans position being occupied by a molecule of water. The presence of an $(AB)_4$ system for the macrocyclic methylene protons shows that the two axial ligands are different. Two singlets of equal intensity correspond only to one molecule of DMSO made dissymetric by the absence in the complex of a symmetry plane going through the DMSO ligand (two signals are also observed in ^{13}C NMR spectroscopy). This conclusion is corroborated by IR spectroscopic arguments: the presence of strong bands at 1060–1080 cm^{-1}, typical of $\nu_{S=O}$ due to S-bonded DMSO molecules,[12] and of medium-intensity broad bands around 440 cm^{-1}, which may be assigned to Ru–S and also Ru–OH_2 stretching modes.[13]

Redox Properties and Absorption Spectra. Each complex listed in Table 1 features a reversible wave corresponding to a one-electron oxidation of Ru(II) between 0.72 and 1.14 V. Two remarks may be made: (a) All complexes obtained from macrocycle **2** have oxidation potentials superior to those corresponding to macrocycle **1**, due to the presence of phenyl substituents; (b) potential values depend on the nature of the axial ligands considered as it has previously been described.[9] Reduction gives rise to ill-defined irreversible waves as already observed in some acyclic pyrazole–Ru(II) complexes.[14] The lowest-energy absorptions occur in the region 310–428 nm and may be attributed to MLCT transitions ($\epsilon \cong$ 10 000–15 000 M^{-1} cm^{-1}); the observation of several bands corresponds to the charge-transfer transitions from the metal d orbitals to the π^* orbitals of the different ligands present in the complex.[14]

NMR Studies. Chemical Shifts. ^{1}H NMR spectra of complexes **1c–j** and **2f–j**, in acetone-d_6 or DMF-d_7, are given in Tables 2 and 3. As far as chemical shifts are concerned, some remarks may be made concerning the coordination-induced effects which depend on the nature of the axial ligands. For all the complexes, normal lowfield shifts are observed for the protons belonging to the macrocyclic pyrazoles due to ligand to metal σ-donation,[14,15] but all the macrocyclic CH_2 protons appear at more upfield chemical shifts if the axial ligands are heteroaromatic rings (comparison of the **a–c** series with the **d–j** one). Furthermore it may be noticed that all the axial heteroaromatic protons (H and CH_3) α to the coordination sites undergo strong upfield shifts (from –1.1 to –1.8 ppm) which show the important mutual ring current effects of the heteroaromatic rings belonging to the macrocycle or to the axial ligands.

^{13}C NMR data are reported in Table 4. Signals have been assigned by comparison with reported values for pyrazole derivatives.[16] In the case of complexes with macrocycles **2**, pyrazole and methylene positions have been differentiated by a specific introduction of deuterium on the macrocyclic carbons in position 6.[17] The positive coordination-induced shifts observed in most cases are those expected from the contribution of the ligand-to-metal σ-donation essential effect in the ^{13}C NMR spectra of ruthenium(II) complexes.[14a,15] The negative or very low positive shifts which occur for carbons C-3(3′) and CH_2 belonging to the macrocyclic skeleton may be ascribed to conformational strain

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(17) The deuteriated macrocycle **2** has been obtained using the same method as for the nondeuteriated one,[10] except that the reduction of the intermediate (3-carbethoxy-3′(5′)-3-phenyl-5-methyl-1,3′(5′)-dipyrazoly)methane into the deuterated alcohol derivative has been done with $AlLiD_4$.

Table 2. ^{1}H NMR Chemical Shifts (ppm) and Coordination-Included Shifts (in Parentheses) of Complexes Ru(**1**)XY$(PF_6)_2$ at Variable Temperatures

			macrocycle			axial ligands				ΔG_c^*
compd	T, °C	X, Y	Me(Pz)	H(Pz)	CH_2	α	β	γ	other signals	(T_c, °C)
1[a]			2.31 s	5.88 s	4.98 bs					
1[b]			2.32 s	5.95 s	5.01 s					
1c[a]	RT	C_6H_5CN	2.69 s (+0.38)	6.72 s (+0.84)	5.89 s (+0.91)				C_6H_5, 7.5–7.7	~8.7 (–85)
	–95		2.68 s	6.69 s	5.66 b, 6.18; $\Delta\nu$ = 130 Hz				C_6H_5, 7.5–7.7	
1d[a]	RT	DMSO, Py	2.61 s	6.67 s	5.26, 5.87	7.59 d	7.20 t	7.83 t	DMSO, 2.69, 2.80	≪9 (–85)
	–100		2.64 s	6.76 s	5.26 b, 5.91	7.78 d	7.23 t	7.90 t		
1e[a,c]	RT	CH_3CN, Py	2.61 s (+0.30)	6.64 s (+0.76)	5.10 (+0.12), 5.67 (+0.69); $\Delta\nu$ = 165 Hz	7.58 d (–1.01)	7.10 t (–0.25)	7.75 t (–0.04)	CH_3CN, 2.29	9.3 (–60)
	–95		2.53 s, 2.64 s	6.58 s, 6.74 s	4.02, 6.20; $\Delta\nu$ = 654 Hz 5.54, 5.84; $\Delta\nu$ = 90 Hz	7.65 d	7.10 t	7.75 t		
1f[a,c]	RT	Py	2.56 s (+0,25)	6.60 s (+0.72)	5.06 s (+0.08)	7.66 d (–0.95)	7.08 t (–0.27)	7.70 t (–0.09)		10.5 (–35)
	–70		2.56 s	6.63 s	4.16, 5.92; $\Delta\nu$ = 534 Hz	7.76 d	7.09 t	7.75 t		
1g[a]	RT	4-OMePy	2.62 s (+0,31)	6.69 s (+0.81)	5.13 s (+0.15)	7.44 d (–1.17)	6.70 d (–0,39)		3.84 s (+0.1)	10.7 (–32)
	–80		2.60 s	6.69 s	4.26, 5.99; $\Delta\nu$ = 432 Hz	7.51 d	6.71 d		3.79 s	
1h[a]	RT	3-MePyz	2.61 s (+0.30)	6.68 s (+0.80)	5.20 bs (+0.22)	7.78 s (–0.79), 7.62 d (–0.76)	8.10 d (–0.35)		2.16 s (–0,41)	~11.2 (–30)
	–90		2.59 s	6.64 s, 6.65 s, 6.67 s (2H)	4.5, 5.9;[d] $\Delta\nu$ ~ 364 Hz	7.99 s, 8.01 s, 7.78 d, 7.80 d	8.10 d		2.02, 2.03	
1i[a]	RT	Pz	2.60 s (+0.29)	6.66 s (+0.78)	5.09 s (+0.11)	6.68 s (–0,68), 11.74 s (–0.90)	6.25 s (+0.08), 7.69 s (~+0.1)			~9.4 (–60)
	–98		2.59 s, 2.61 s	6.63 s, 6.64 s, 6.67 s (2H)	4.1, 6.0;[d] $\Delta\nu$ ~ 425 Hz	6.86 s, 12.38 s	6.39 s, 7.90 s			
1j[b]	RT	3,5-diMePz	2.59 s (2H), 2.65 s, 2.66 s	6.61 s, 6.65 s (2H), 6.68 s	4.2, 5.95;[d] $\Delta\nu$ ~ 427 Hz	11.01, 11.04	5.78 s		1.05 s (–1.17) (Me-3), 1.94 s (–0.23) (Me-5)	~16 (+80)
	+120		2.72 (+0.40)	6.72 s (+0.77)	5.18 bs (+0.17)	10.54 bs (–1.76)	5.80 s		1.13 s (Me-3), 2.08 s (Me-5)	

[a] In acetone-d_6. [b] In DMF-d_7. [c] Spectra recorded at 300 MHz. [d] Presence of four AB systems. [e] Activation free energies in kcal/mol (1 cal = 4.184 J) at the methylene coalescence temperature.

effects[15] within the complexes due either to the macrocyclic structure itself or to the presence of the four six-membered chelate rings.

However, the more characteristics spectral observation is the broadened appearance of the macrocyclic methylene protons or their unexpected high multiplicity in the case of most of the complexes. This peculiar behavior led us to undertake an NMR study at variable temperatures.

NMR Study as a Function of Temperature. The ^{1}H NMR spectra recorded in acetone-d_6 at low temperature and in DMF-d_7 at high temperature (see Tables 2 and 3) show that temperature variations lead to dramatic changes in the spectra. Such a behavior could find its origin in one or several of three dynamic processes which may occur in this kind of complex from variations of (i) the macrocyclic conformation, (ii) the position of the axial ligands with respect to each other or to the macrocycle, and (iii) the position of the metal in or out of the cavity.

We have studied first the simplest complex in the series, **1f**, in which the macrocycle has a C_4 symmetry and the axial ligands are identical and symmetric: at room temperature, the four pyrazole rings are equivalent as are the axial pyridines. The macrocyclic CH_2 protons appear as a singlet, showing the complete symmetry of the complex. At –70 °C, the only change is the transformation of this singlet into a quartet corresponding to a $(AB)_4$ system with a $\Delta\nu_{AB}$ greater than 500 Hz. The equivalence of the four pyrazoles at low temperature rules out the possibility of a dissymmetric position of the metal inside the cavity, and that of the axial pyridines shows that the metal is not out of the mean plane of the macrocycle. The diastereotopy of the CH_2 protons may arise from a slowing down of the interconversion process occurring between the axial and equatorial positions that these protons have in the four six-membered chelate rings. It has been shown that, in hexacoordinate non-macrocyclic structures $M(PzCH_2PyCH_2Pz)_2^{2+}$, the six-membered chelate rings exist in boat conformations in the solid state;[18] in solution, the CH_2 protons give rise at room temperature to an AB quartet, showing that they are not interchanging by boat–boat interconversion in the chelate ring.[14b,15] Furthermore, we may also consider the macrocyclic structure of the tetraazaporphyrinogen **1** as belonging to the heterocalixarene family. Such macrocycles with pyrrole subunits[19] though very close to our structure are stable only if the intercyclic meso carbons are disubstituted, preventing the presence of axial ligands in the corresponding metallic complexes; their solid-state structures[20] show that the pyrrolocalixarene macrocycles assume a double saddle-shaped conformation in which the six-membered chelate rings have a boat conformation tilting alternately up and down. Besides metal complexes of highly conjugated porphyrins, which behavior will be compared later to the complexes of this study, very few nitrogen-containing macrocyclic complexes with pyridines as axial ligands have been studied. In the only reported cases,[21,22] the structures in the solid state are such that the macrocycle is made nonplanar by undergoing a saddle-shaped[21] or ruffled[22] deformation to avoid steric interactions with the axial pyridines, perpendicular to each

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Table 3. ^{1}H NMR Chemical Shifts (ppm) and Coordination-Included Shifts (in Parentheses) of Complexes Ru(**2**)(XY)$(PF_6)_2$ at Variable Temperatures

			macrocycle						axial ligands				
compd	T, °C	X, Y	Me(Pz)	H-4	H-4′	CH_2-6	CH_2-6′	C_6H_5(Pz)	α	β	γ	R	ΔG_c^{*} [c] (T_c, °C)
2[a]			2.35 s	5.75 s	6.31 s	5.18 bs	5.18 bs	7.55 m					
2[b]			2.36 s	5.81 s	6.40 s	5.19 s	5.20 s	7.58 m					
2f[a]	RT	Py	2.66 s (+0.31)	6.57 s (+0.1)	7.00 s (+0.69)	5.28 s (+0.1)	5.18 s	7.64 m	7.90 d (−0.71)	7.20 t (+0.15)	7.83 t (+0.04)		10.8 (−30)
	−70		2.58 s	6.84 s	7.00 s	4.48 d, 6.13 d; Δν = 413 Hz	4.38 d, 6.02 d; Δν = 410 Hz	7.64 (6H), 7.70 (4H)	7.98 d, 8.08 d	7.18 t, 7.21 t	~7.8 m		
2g[a]	RT	4-OMePy	2.68 s (+0.33)	6.74 s (+0.99)	7.01 s (+0.70)	5.29 s (+0.11)	5.19 s (+0.01)	7.62 m	7.61 d (−1.00)	6.78 d (−0.31)		3.85 s (−0.09)	11.0 (−25)
	−60		2.68 s	6.81 s	7.0 s	4.50 d, 6.13 d; Δν = 408 Hz	4.42 d, 6.0 d; Δν = 395 Hz	7.64 (6H), 7.70 (4H)				3.78 b, 3.80 b	
2h[a]	RT	3-MePyz	2.67 s (+0.32)	6.79 s (+1.04)	7.01 s (+0.70)	5.39 s (+0.21)	5.28 s (+0.1)	7.64 m	7.87 s (−0.70), 7.81 d (−0.57)	8.17 d (−0.28)		2.23 s (−0.34)	~11 (−25)
	−90		2.56 s, 2.58 s	6.82–6.86, 4 s	6.98 s, 7.0 s	~4.7 m, ~6.0 m Δν = 325 Hz		7.68, 7.78	8.2, 8.22, 8.29 s, 8.0 t, 8.11 t	~8.2		2.16 sb	
2i[a]	RT	Pz	2.52 s (+0.17)	6.70 s (+0.95)	6.98 s (+0.67)	5.25 s (+0.07)	5.17 s (−0.01)	7.62 m	6.90 s (−0.66), 11.98 s (−0.66)	6.31 s (+0.14), 7.75 s (+0.15)			~9.8 (−50)
	−90		2.62 bs	6.74–6.85, 4 s	6.95–7.01, 2 s	4.38 m, 6.09 m 4.59 m, 6.0 m		7.66 (6H), 7.70 (4H)	7.10, 7.20	6.41 b, 7.92, 7.98			
2j[b]	RT	3,5-di-MePz	2.62 s, 2.63 s, 2.68 s, 2.70 s	6.70–6.81, 4 s	7.04 b	4.40 m, 5.94 m, 4.48 m, 6.14 m		7.69 (6H), 7.76 (4H)	11.3 b	5.86 s		1.10, 1.12 (Me-3), 2.01 (Me-5)	~16.5 (+90)
	+120		2.62 s (+0.26)	6.68 s (+0.87)	6.99 s (+0.59)	5.18 b	5.18 b	7.61 s	10.69 s (−1.61)	5.80 (+0.02)		1.19 (−0.98) (Me-3), 2.20 (+0.03) (Me-5)	

[a] In acetone-d_6. [b] In DMF-d_7. [c] Activation free energies in kcal/mol (1 cal = 4.184 J) at the methylene coalescence temperature.

Table 4. ^{13}C NMR Chemical Shifts (ppm) and Coordination-Included Shifts (in Parentheses) of Complexes Ru(**1**)XY$(PF_6)_2$ and Ru(**2**)XY$(PF_6)_2$

compd	X, Y	C-3	C-4	C-5	CH_3	CH_2-6	axial ligands
1[a]		147.6	104.9	139.5	10.3	46.0	
1[b]		147.0	104.4	139.0	10.9	46.1	
1a[a]	DMSO, H_2O	145.8 (−1.8)	108.45 (+3.55)	146.0 (+6.5)	11.8 (+1.5)	46.5 (+0.5)	DMSO, 44.7 (+4.7), 45.6 (+5.6)
1b[a]	CH_3CN	146.1 (−1.5)	108.1 (+3.2)	145.6 (+6.1)	12.0 (+1.7)	46.7 (+0.7)	CH3CN, 3.2 (+2.9), 125.8 (+8.1)
1f[a]	Py	146.5 (−1.1)	108.7 (+3.8)	146.5 (+7.0)	12.0 (+1.7)	46.7 (+0.7)	C-α, 154.2 (+4.2); C-β, 126.5 (+2.2); C-γ, 138.2 (+1.7)
1i[a]	Pz	146.6 (−1.0)	108.8 (+3.9)	145.8 (+6.3)	12.0 (+1.7)	46.6 (+0.6)	C-3″, 143.6 (+4.6); C-4″, 108.1 (+2.7); C-5″, 133.4 (+3.6)
1j[b,d]	3,5-diMePz	146.5 (−0.5)	107.7 (+3.3)	145.2 (+6.2)	11.4 (+0.5)	46.5 (+0.4)	C-3″, 155.6 (+8.1); C-4″, 108.2 (+2.8); C-5″, 144.2 (+4.4)

compd	C-3	C-3′	C-4	C-4′	C-5	C-5′	CH_3	CH_2-6	CH_2-6′	axial ligands
2[c]	146.9	147.2	104.5	105.1	139.4	144.9	11.7	46.4	47.1	
2[b]	147.2	147.8	104.5	105.4	139.5	144.6	11.0	46.1	47.05	
2f[a]	146.7 (−0.2)	147.7 (+0.5)	109.1 (+4.6)	109.7 (+4.6)	146.5 (+7.1)	150.3 (+5.4)	12.3 (+0.6)	47.9 (+1.5)	46.9 (−0.2)	C-α, 154.3 (+4.4); C-β, 126.8 (+3.0); C-γ, 138.5 (+2.5)
2j[b,d]	145.4 (−1.8)	148.1 (+0.3)	108.5 (+4.0)	108.7 (+3.3)	147.2 (+7.7)	149.2 (+4.6)	11.5 (+0.5)	47.5 (+1.4)	48.2 (+1.15)	C-3″, 155.8 (+8.3); C-4″, 108.3 (+2.9); C-5″, 144.6 (+4.8)

[a] In acetone-d_6. [b] In DMF-d_7. [c] In $CDCl_3$ (insoluble in acetone-d_6). [d] Spectra recorded at +120 °C.

other. In the case of complex **1f**, the occurrence of a double saddle shape conformation with noninterconverting CH_2 axial and equatorial protons explains the NMR spectrum observed at low temperature. With such a conformation of the macrocycle, only two possibilities are left for the position of the two axial pyridines: they may rotate freely or take a mutually perpendicular orientation (a parallel position would lead to two kinds of AB systems for the CH_2 protons, and an intermediate orientation would induce more dissymmetry in the NMR spectrum). In order to get more insight into the structure of this complex in solution, we have studied the NMR spectra of several Ru(II) complexes in the same series, with a lower symmetry due to changes in the axial ligands or in the macrocyclic substituents. Complex **1e** contains two different axial ligands, acetonitrile and pyridine; at room temperature, the four macrocyclic pyrazole rings are equivalent and the four CH_2 groups give rise to an $(AB)_4$ system due to the nonequivalence of the two sides of the macrocycle. At −90 °C (see Figure 1 and Table 2), two kinds of pyrazoles and of CH_2 protons are present; such an observation is only compatible with a double saddle-shaped conformation in which, because of the axial dissymmetry, two sets of six-membered chelate rings exist leading to two sets of axial–equatorial protons. The very large $\Delta\nu_{AB}$ observed for one of these sets is due to the strong upfield shift undergone by the axial protons facing an axial pyridine ring prevented from rotation at low temperature.

These strong presumptions of a noninterconversion of the macrocycle and of a restricted rotation of the axial ligands on the NMR scale have been corroborated by studying complexes in

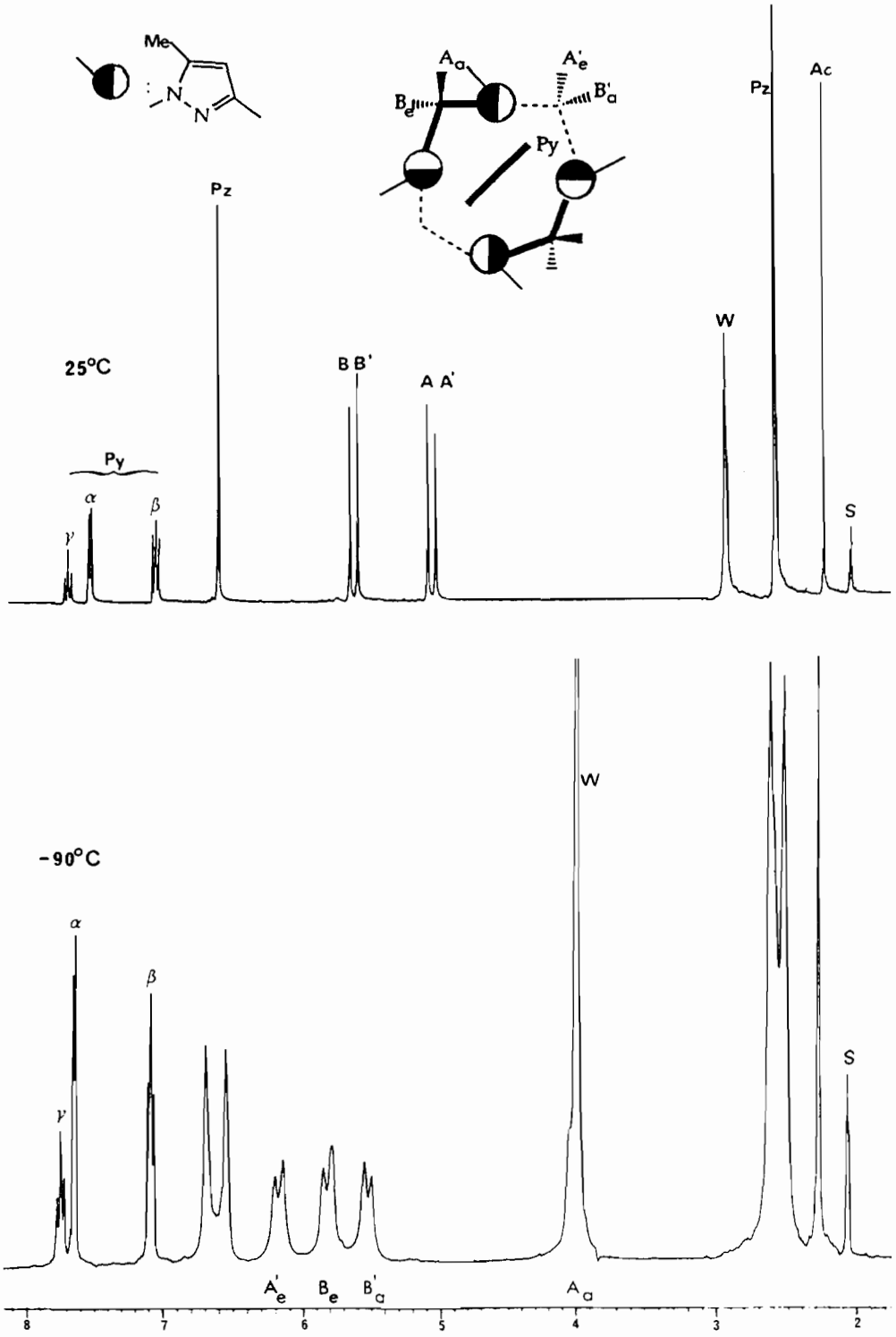


Figure 1. ^{1}H NMR spectra of complex **1e** in acetone-d_6 (S), (W, water; Ac, acetonitrile).

which unsymmetrically substituted axial ligands are introduced, as is the case for compounds **1h–j**. For instance, in the case of complex **1h** at −90 °C, we have observed four different pyrazolic rings, four sets of AB systems for the CH_2 protons, and two nonequivalent 2-methylpyrazine ligands (see Table 2 and Figure 2), what is only compatible with a hindered rotation of the axially coordinated ligands lowering the symmetry of the macrocycle.

The same phenomenon is observed in ^{13}C NMR spectroscopy. For instance in the case of complex **1j** (see Figure 3), for which the dynamic process is slow at room temperature, the dissymmetry introduced by the hindered rotation of the axial ligands is obvious upon carbons C-3, C-5, and C-6 of the macrocycle. It has been necessary to raise the temperature to +120 °C in DMF-d_7 to observe only one signal for each type of carbon, as expected for a complex with a symmetry C_4. At +50 °C, only signals belonging to axial ligands remain sharp, but all the macrocyclic signals are broad.

We have also observed that a lowered symmetry of the macrocycle is reflected in the resonances of the axial ligands. This is the case for complexes **2f** and **2g** in which macrocycle **2** has a symmetry C_2. At room temperature (see Table 3), the CH_2 protons give rise to two singlets due to the presence of two differently substituted pyrazoles, but both axial ligands are equivalent. At low temperature, we have observed two sets of AB systems for the methylene protons and also two sets of α and β pyridinic protons due to the inequivalence of the two axial ligands (in the case of complex **2g** two signals appear for the OCH_3 protons). In the case of unsymmetric axial ligands as in

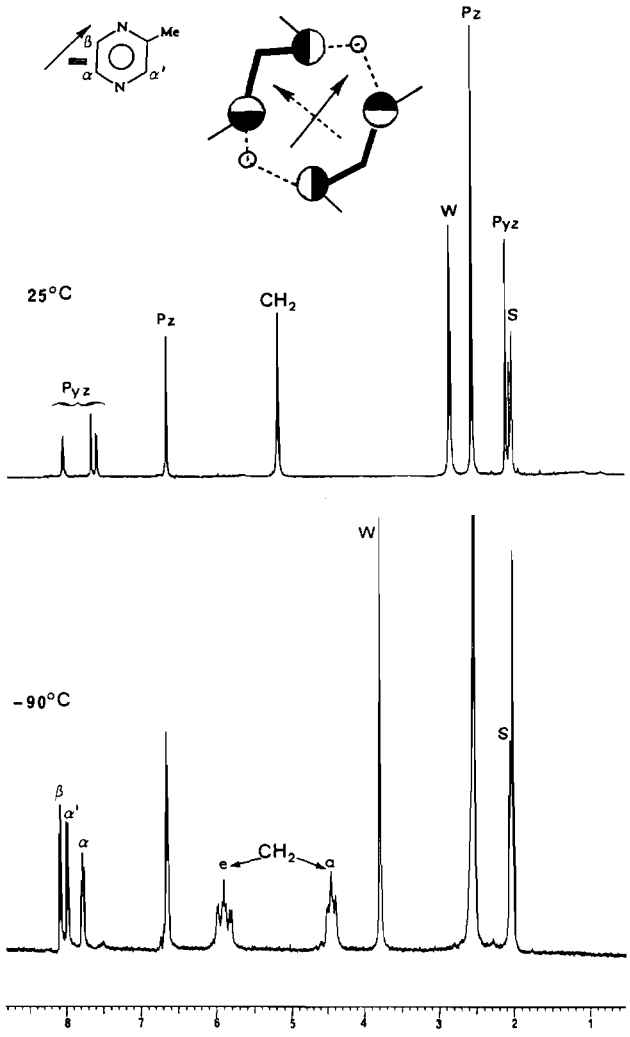
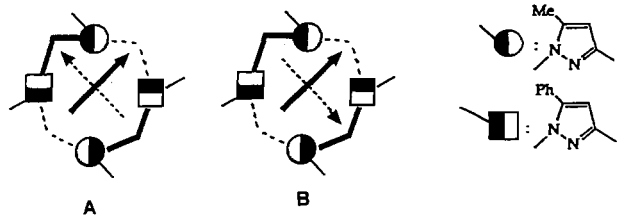


Figure 2. ^{1}H NMR spectra of complex **1h** in acetone-d_6 (S) (W, water).

complexes **2h–2j**, the presence of four singlets for the H-4 as well as CH_3 pyrazole protons shows that two complexes, **A** and **B**, exist, which differ only by the relative position of the axial ligands with respect to the two types of pyrazole rings.



This whole series of experiments is consistent with the previously assumed structure of our Ru(II) tetraazaporphyrinogen complexes when conformational motions are restricted on the NMR time scale. Such a structure is confirmed by comparing the chemical shifts of the axial and equatorial protons (see Tables 2 and 3): as the temperature decreases, axial protons undergo shifts depending greatly on the nature of the axial ligand (chemical shifts appear between 4.0 and 5.7 ppm), while equatorial ones vary only from 5.8 to 6.2 ppm. Such an observation shows the strong influence of the axial ligands on the axial methylene protons facing them and thus confirms the double saddle-shaped structure of the macrocycle as well as the hindered rotation of the heteroaromatic axial ligands.

In order to get complete knowledge of the frozen conformational structure of our complexes, one point remains to be clarified: the relative position of the axial ligands toward the macrocyclic core. NMR experiments bring some answers to this question; it can be seen in Tables 2 and 3 that all the protons α to the coordination sites of the heteroaromatic axial ligands are downfield shifted when their rotation is restricted. This means that, as the temperature is lowered, the axial ligands avoid lying over the macrocyclic pyrazole rings. Using ^{1}H NOE-difference spectroscopy, which provides information about nuclei in close steric proximity,[23] we choose to study complex **1j**, for which the dynamic process is slow at room temperature; we made a series of experiments (see Figure 4) saturating successively protons belonging to the axial ligands. Saturation of the methyl α to the coordination site leads to a direct NOE effect on its neighboring pyrazolic proton but also to a clear cross polarization effect on the macrocyclic H-4 pyrazolic protons and weaker ones on the macrocyclic CH_2 and CH_3 protons. Small NOE effects are also observed when the NH proton is saturated. In absence of T_1 measurements no quantitative evaluation may be done. These experiments are in agreement with the previously assumed intereferences between the macrocycle and the axial ligands within complexes such as **1j**; the only further result which may be suggested from this study is that the axial ligands would have a preferential position over the CH_2–C(Pz) bond rather than over the CH_2–N(Pz) one reflecting their different nature as already reported for a series of related macrocycles.[8]

From simple molecular modeling,[24] it appears that for complex **1f** the structure with the lowest energy has conformational features close to those deduced from NMR arguments as shown in Figure 5: double saddle-shaped macrocycle and pyridines in mutual perpendicular orientation, lying over the CH_2–C(Pz) bond.

To bring some elements of comparison between our structural determination and literature results, we may only refer to studies concerning hexacoordinated porphyrin complexes with axial heteroaromatic ligands. Some of their physical properties have been found to depend on the axial ligand orientation.[25,26] Most of the work on this subject concerns solid-state studies of iron porphyrins. The more striking result is the great influence of steric effects between axial ligands and bulky meso substitutions on the metalloporphyrins.[25-27] It is now well established that encumbered systems favor a perpendicular relative orientation of the two axial ligands. In order to avoid steric hindrance with the axial ligands the porphyrin core undergoes substantial nonplanar deformations to take an S_4 ruffled conformation in which the meso carbon atoms are alternatively above and below the mean plane of the macrocycle. Furthermore the orientation of the axial ligands toward the porphyrinic ring is such that they adopt a position between the two extreme ones (above the macrocyclic opposite N atoms, $\Phi = 0°$, or above the opposite meso carbons, $\Phi = 45°$) which give rise to opposite electronic and steric effects: the orientation is a balance of these factors. Generally it has been observed that in hindered low-spin porphyrin systems with a perpendicular orientation of the axial ligands the Φ angle is near 45° except in the case of a Co(III) porphyrin complex in which perpendicular axial imidazole planes are oriented at small Φ angles.[28]

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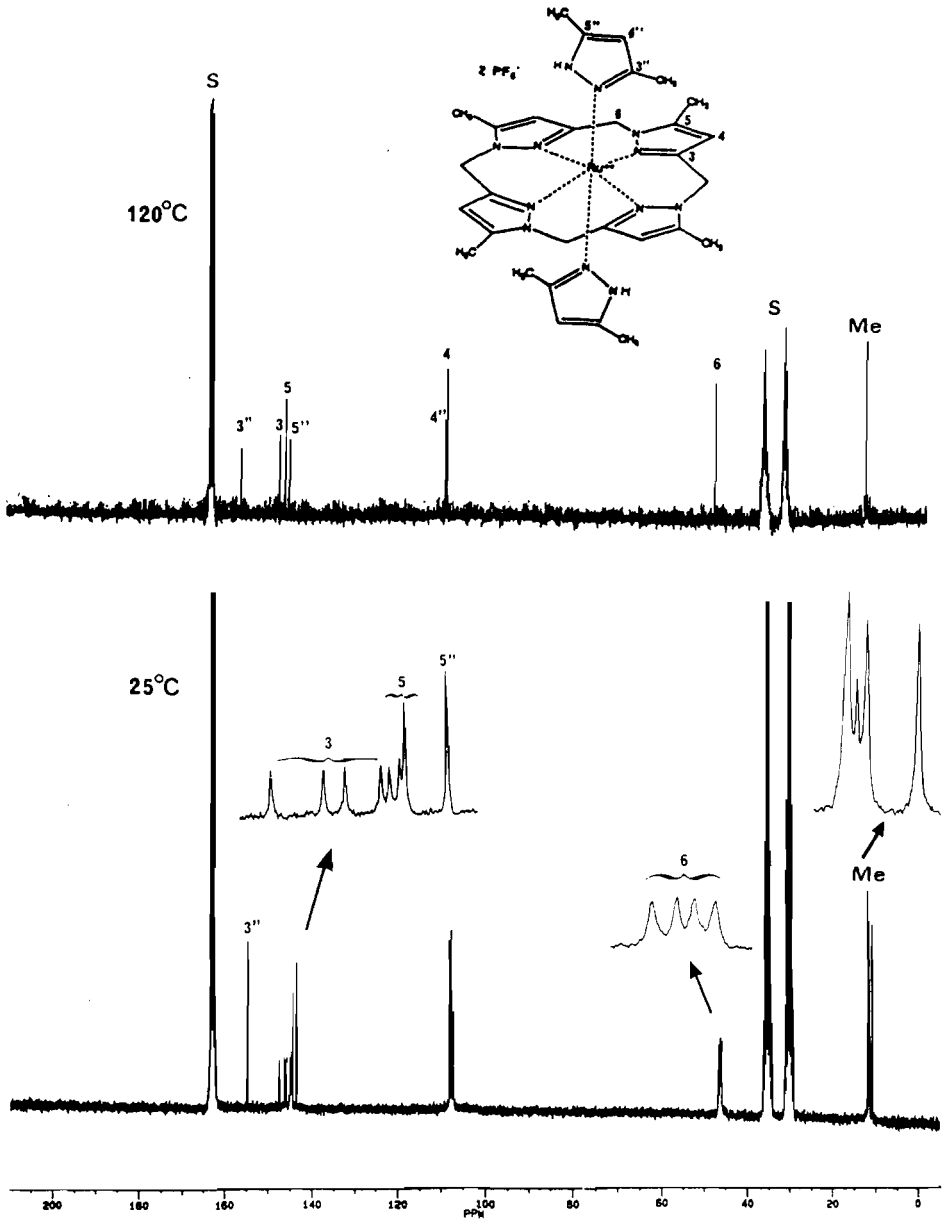

Figure 3. ^{13}C NMR spectra of complex **1j** in DMF-d_7 (S).

Recently it has been shown in the porphyrin series[26b,29-32] that the conformations observed in the solid state are retained in solution, though the position of the axial ligands toward the macrocycle has been subject to controversy. These results are difficult to compare as they have been obtained from different metalloporphyrins using various methods based on NMR spectroscopy (^{59}Co NMR spectroscopy,[28] calculations based on ring current effects,[30] low-temperature ^1H NMR spectroscopy,[26b,29] NOESY or ROESY low-temperature experiments[32]). Our system differs from the porphyrin complexes first in its higher flexibility; it has been shown that metallohydroporphyrins reduced at two meso carbons have enhanced flexibility and higher affinity for axial ligands than porphyrins.[33] This, together with the different complexing ability of macrocycles **1** and **2**, which have only neutral nitrogen donor atoms and no macrocyclic aromaticity, may explain why, in the case of the 2-substituted azole axial ligand, their rotation is frozen at room temperature, which has never been observed in porphyrin derivatives.

The free energies of activation corresponding to the macrocyclic interconversion and/or the axial ligand rotation, calculated at the coalescence temperature T_c of the macrocyclic methylene protons, are given in Tables 2 and 3.[34] All the complexes described here may be classified in four categories depending on the nature of the axial ligands: (i) In the case of two α-unsubstituted six-membered azines, the free energies are found around 11 kcal/mol; (ii) for two α-unsubstituted five-membered azoles, these energies are less than 10 kcal/mol; (iii) in the case of two α-methyl-substituted five-membered azoles the free energies are greater than 16 kcal/mol; (iv) if one or two nonheteroaromatic axial ligands are present, the barriers are equal to 9 kcal/mol as it is the case for complexes **1c,e** or less than this value as estimated

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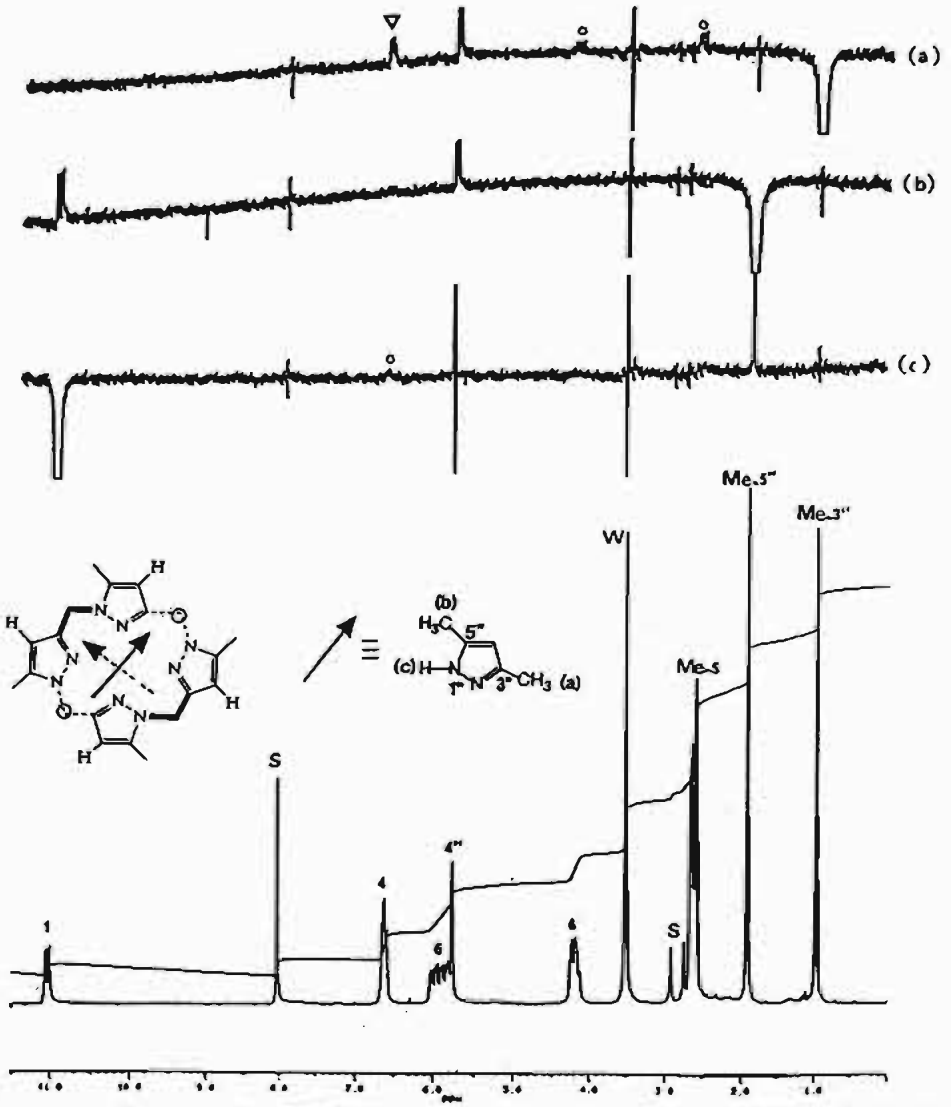

Figure 4. NOE-difference spectra for complex **1j** in DMF-d_7 (S) at +25 °C after saturation of protons: (a) Me-3", (b) Me-5", (c) NH-1 (W, water).

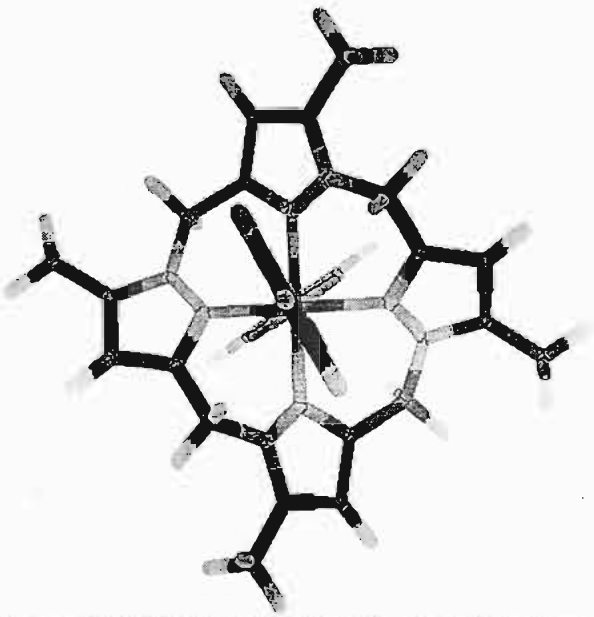

Figure 5. Stick molecular model after energy minimizing, illustrating the disposition of the pyridine axial ligands and the conformation of macrocycle **1f**.

for complexes **1a,b** (their NMR spectra do not show any broadening at low temperature) or for complex **1d** (a slowing of the dynamic phenomenon started to appear at −90 °C). If we add to these results that complexes with α-methyl-substituted pyridines as axial ligands were impossible to prepare, it becomes obvious that steric interactions must be the predominant factors which control the dynamic process. Another observation corroborates this conclusion: all the free energies measured for the complexes implicating macrocycle **2**, more sterically demanding with its two phenyl substituents, are higher than those corresponding to the analogous complexes from macrocycle **1**. In the low-temperature NMR studies of porphyrin complexes, the activation free energies determined[29] are lower than those measured in our series but follow the same trend. The authors[29] generally attribute the observed dynamic process to the hindered rotation of the axial ligands, but it has been suggested that it could be a combination of ligand rotation and fluxional porphyrin distorsion.[32] The higher barriers obtained in the more flexible azaporphyrinogens show that, in this series, the dynamic phenomenon observed corresponds to two concomitant processes: in order to avoid steric interactions, not only restricted is the rotation of the axial ligands but also restricted is the interconversion of the double saddle-shaped macrocycle.