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Ruthenium (II) complexes of a new tetrapyrazolic macrocycle

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Ruthenium (II) complexes of a new tetrapyrazolic macrocycle

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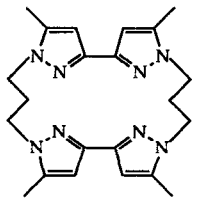
The new macrocycle L containing two bipyrazole subunits gives with $Ru(DMSO)_4Cl_2$ a stable trans complex in which the nature of the axial ligands has been established from ^1H and ^{13}C NMR, IR and UV experiments; the structure of the complexes obtained after axial ligand exchange has been mainly deduced from ^1H NMR data: a dynamic phenomenon has been observed in the case of pyridine axial ligands.

INTRODUCTION

Interest in the design of new macrocyclic receptors has become considerable in recent years[1-4] because of their encapsulating properties towards numerous guests making them remarkable molecules in the fields of molecular recognition, transport, selective catalysis or biological models.

For some time we have been interested in the properties of macrocycles incorporating pyrazole subunits[5] which give to the cavity the ability to complex hard and soft cations such as alkali and transition metals.

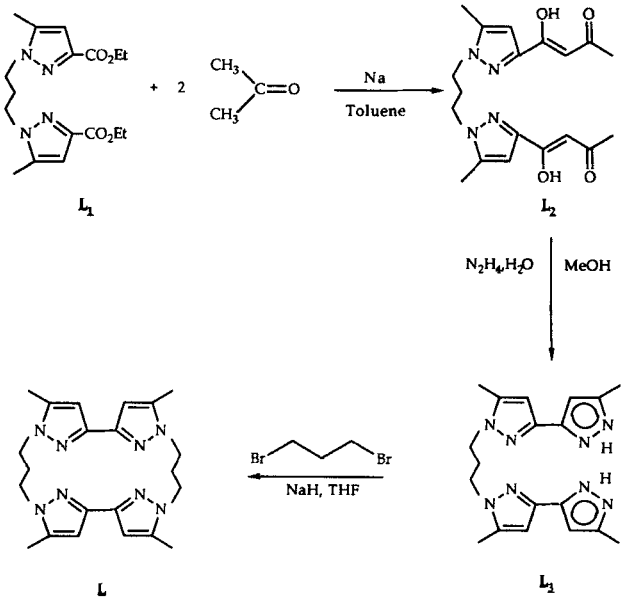
In this communication we are reporting the synthesis and Ru(II) coordination of a new tetrapyrazolic macrocycle L



L

RESULTS AND DISCUSSION

The macrocycle L has been prepared in three steps from bipyrazole L_1[5d] as shown in scheme 1:



Scheme 1

This synthesis follows a construction procedure different from that described for analogous macrocycles containing 2,2′-bipyridine or 1,10-phenantroline subunits.[6,7]

Condensation of the 1,3-bis(3′-carbethoxy-5′-methyl-1′-pyrazolyl) propane L_1 with acetone leads to compound L_2, in its di-(ketoenol) form (see ^1H NMR spectrum in the experimental part), and to a small amount of the diacid derived from L_1. It may be noticed that cyclisation of the tetrapyrazole L_3 (obtained by condensation of L_2 and hydrazine) with 1,3-dibromopropane in the operational conditions occurs predominantly (*>90%*) on the nitrogen atoms α to the methyl groups.

From the scarce known examples of macrocycles containing 2,2′-pyridine subunits,[6,7] it seems that such a cavity would not be appropriate for Ru(II) complexation.[8]

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On the contrary, in the case of macrocycle **L**, Ru(II) complexes are readily accessible.

The first Ru(II) complex **1a** has been obtained by reaction of equimolar amounts of **L** and $Ru(DMSO)_4Cl_2$ in a mixture H_2O/MeOH (20:80); the ^1H and ^{13}C NMR data in CD_3OD corresponding to this complex are reported in Table 1 and Table 2, and show that the macrocycle symmetry is kept, since the four pyrazolic rings are still equivalent, what is in favour of a trans structure for the complex. However the symmetric multiplet observed for the $N\text{-}CH_2$ protons in the complex (instead of a triplet in the macrocycle itself), shows the occurrence of a dissymmetry which may be ascribed to the presence of two different axial ligands [after irradiation of the central methylene protons, this multiplet becomes an $(AB)_4$ quartet]; this

Table 1 ^1H NMR[a] and UV spectral data for complexes **1** to **3**

	Solvent	*Me (Pz)*	*H (Pz)*	*N-CH₂*	*-CH₂-*	*Axial ligands*	*λ (nm) (CH₃CN)*	*ε M⁻¹ cm⁻¹*
L	$CDCl_3$	2.38 s	6.08 s	4.22 t	2.60 m			
	CD_3OD	2.55 s	6.21 s	4.44 t	2.79 m			
	CD_3CN	2.40 s	5.88 s	4.19 t	mask.			
RuL(DMSO)ClX	CD_3OD	2.78 s	7.00 s	4.68 m and 4.89 m	~2.60 m	DMSO: 2.62 s	343.2	6860
X = Cl **1a**		(+0.23)	(+0.89)	(+0.24) (+0.45)	(−0.19)		357.3	7260
RuL(DMSO)ClX	CD_3CN	2.54 s	6.74 s	4.30 m and 4.68 m	~2.38 m	DMSO: 2.34 s		
X = PF_6 **1a'**		(+0.14)	(+0.86)	(+0.11) (+0.49)				
RuL(DMSO)(H_2O)	CD_3CN	2.60 s	6.80 s	4.28 m and 4.41 m	~2.40 m	DMSO: 2.35 s	324.7	7600
$(PF_6)_2$ **1b**		(+0.20)	(+0.92)	(+0.09) (+0.22)	(−0.20)		339.7	7620
	CD_3OD	2.84 s	7.16 s	4.51 m and 4.78 m	~2.70 m	DMSO: 2.65 s		
		(+0.29)	(+0.95)	(+0.07) (+0.34)	(−0.09)			
RuL$(CH_3CN)_2$	CD_3CN	2.59 s	6.73 s	4.36 t	2.39 m	CH_3CN: 2.02	341.6	7360
$(PF_6)_2$ **2**		(+0.19)	(+0.85)	(+0.17)	(−0.20)		356.0	9020
RuL$(Py)_2(PF_6)_2$	CD_3CN	2.45 s	7.00 s	3.76b (t at +40 °C)	2.19 m	7.35 d (H_α) (−1.26)	376.0 sh	7640
3		(+0.05)	(+1.12)	(−0.43)	(−0.40)	7.0 t (H_β) (−0.35)	3.96.8	10860
						7.61 t (H_γ) (−0.18)		
	$(CD_3)_2CO$ RT	2.60 s	7.22 s	4.09 b	2.44 m	7.57 d (H_α); 7.18 t (H_β); 7.75 t (H_γ)		
	−90 °C[b]	2.58 s	7.29 s	3.72 m and 4.38 d	2.40 m	7.58 d (H_α); 7.23 t (H_β); 7.80 t (H_γ)		
				$\Delta\gamma = 159.2$ Hz				

[a] Coordination induced shifts are given in parentheses. Abbreviations: s = singlet; d = doublet; t = triplet; b = broad; sh = shoulder; Py = pyridine; Pz = pyrazole.
[b] Activation free energy at the coalescence temperature: $T_c = 0$ °C; $\Delta G_c^* = 12.7$ Kcal·mol.

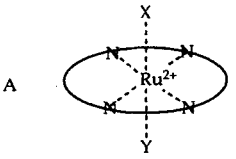
Table 2 ^{13}C NMR[a] data for macrocycle **L**[b] and complexes **1** to **3**

	Solvent	C_3 *(Pz)*	C_4 *(Pz)*	C_5 *(Pz)*	CH_3 *(Pz)*	*N-CH₂*	*-CH₂-*	*Axial ligands*
L	CD_3OD	145.74	103.97	140.16	11.41	48.53	29.70	–
RuL(DMSO)ClX	CD_3OD	150.51	105.27	148.90	12.05	47.03	30.97	DMSO: 45.58
X = Cl **1a**		(+4.77)	(+1.3)	(+8.74)	(+0.64)	(−1.50)	(+1.27)	(+6.08)
RuL(DMSO)ClX	CD_3CN	148.79	103.79	147.24	11.30	45.72	29.38	DMSO: 44.64
X = PF_6 **1a'**								
RuL(DMSO)(H_2O)	CD_3CN	148.90	104.50	148.69	11.39	46.38	29.01	DMSO: 43.59
$(PF_6)_2$ **1b**		(+3.16)	(+0.53)	(+8.53)	(−0.02)	(−2.15)	(−0.69)	(+4.09)
RuL$(CH_3CN)_2$	CD_3CN	148.41	103.63	146.88	11.33	45.77	29.79	CH_3CN: 3.22 (+2.92)
$(PF_6)_2$ **2**		(+2.67)	(−0.34)	(+6.72)	(−0.08)	(−2.76)	(+0.09)	126.16 (+8.96)
RuL$(Py)_2(PF_6)_2$	CD_3CN	148.03	104.69	147.48	11.39	44.66	29.77	C_α 152.44 (+2.54)
3		(+2.29)	(+0.72)	(+7.32)	(−0.02)	(−3.87)	(+0.07)	Py: C_β 125.42 (+1.62)
								C_γ 137.28 (+1.28)

[a] Coordination induced shifts are given in parentheses.
[b] L is not soluble enough in CD_3CN to perform ^{13}C NMR analysis.

is confirmed by the observation of one singlet at 2.62 ppm corresponding to only one DMSO molecule. The equivalence of the two DMSO methyl groups in ^1H and ^{13}C NMR spectroscopy shows the presence of at least one symmetry plane going through DMSO in the complex. This DMSO ligand is S-bonded to ruthenium as shown by the S=O stretching bands observed at 1057 and 1078 cm^{-1};[9] the unusual high field shift for an S-bonded DMSO (3.2 to 3.5 ppm[9b,10] for non-macrocyclic complexes), may be explained by its position above the aromatic pyrazole rings of the macrocycle.

At this stage, a doubt was left about the nature of the second axial ligand for two reasons: first, this complex **1a** is unexpectedly soluble in CH_3CN and second the anion exchange with NH_4PF_6 is not as easy as usual, leading to two compounds; one **1a'** gives an ^1H NMR spectrum (see Table 1) in CD_3CN identical to **1a** and must just correspond to an anion exchange which has no influence on the complex behaviour; the other complex **1b** (see Table 1), obtained pure after several washings with water, gives completely different ^1H and ^{13}C NMR spectra still showing the presence of one DMSO ligand but in which the other axial ligand has been exchanged: this complex, **1b**, has the usual ligand exchange behaviour[11] in CH_3CN and pyridine (see below) and must correspond to the complex $RuL(DMSO)(H_2O)(PF_6)_2$ as generally obtained.[11] The elemental analysis and mass spectrum of **1a** show that the complex has the formula $RuL(DMSO)(H_2O)Cl_2$; in its UV spectrum in CH_3CN compared to that of **1b**, bathochromic shifts (see Table 1) are observed, which cannot be due to simple anion exchanges but are well explained if a chloride is present as an axial ligand;[12] such a structure accounts also for the solubility of **1b** in organic solvents and for the difficulty to exchange the chloride anions.



A

1a : X=DMSO, Y=Cl^-, A=Cl^-
1b : X=DMSO, Y=H_2O, A=$(PF_6^-)_2$
2 : X=Y=CH_3CN, A=$(PF_6^-)_2$
3 : X=Y=pyridine, A=$(PF_6^-)_2$

The complex **2** obtained from **1b** in CH_3CN has ^1H and ^{13}C NMR spectra which show that the complex has a higher degree of symmetry than **1a** and contains two CH_3CN molecules; the equivalence of the four pyrazolic rings and of the two acetonitrile ligands is a proof of a trans structure.

The same conclusion holds for complex **3** containing two pyridine ligands at room temperature; however its ^1H NMR spectra show coordination effects different from the two previous complexes: first, at room temperature, the N-CH_2 protons are strongly upfield shifted as well as the H_α pyridinic protons, though the expected Ru(II) coordination induced shifts are towards lowfield[13,14] because of predominant ligand to metal σ-donation; such an unusual behaviour may be assigned to mutual important anisotropy effects from the heteroaromatic rings belonging to the macrocycle or to the axial ligands. However one may notice on the ^1H NMR spectrum at +25 °C, a broadening of the signal corresponding to the N-CH_2 protons which becomes sharp at +40 °C. When the temperature decreases, this same signal broadens to split into two multiplets: the free activation energy of this dynamic process has been calculated to be 13 kcal/mol at the coalescence temperature. The origin of this phenomenon may be found in steric interactions taking place between the macrocyclic ring and the pyridine ligands. We have thoroughly studied[11] an analogous process in the case of Ru(II) complexes of tetraazaporphyrinogens and found that the occurrence of such interactions leads to a restricted rotation of their axial ligands which take a mutual perpendicular position.

As we have already noticed, the doublet given by the H_α pyridine protons undergoes an important upfield shift in the complex ($\Delta\nu > 1$ ppm); this signal does not move as the temperature decreases and does not split even at −90 °C; this may occur only for two relative positions of the pyridine ligands in the frozen state: they may be parallel to each other lying over or between the bipyrazole rings (over the C-C bond) or they may be mutually perpendicular but in this case they must lie over two opposite pyrazole nitrogens.

The upfield shift observed for the N-CH_2 macrocyclic protons may be explained by both hypotheses.

A simple molecular modeling[15] leads to lowest energy structures when the pyridine ligands take a mutual parallel alignment over the interpyrazolic C-C bonds.

The UV absorption in the region 320–400 nm given in Table 1 correspond to MLCT transitions; they appear at lower energies than in the case of the corresponding tetraazaporphyrinogen Ru(II) complexes:[5a] the main reason for this difference of behaviour should be the presence of two bipyrazole chelates giving more rigidity and better π-acceptor properties to the macrocycle.

Cyclic voltammetry in acetonitrile of complexes **1b**, **2** and **3**, gave oxidation waves at 1.53 V, 1.18 V, 1.07 V respectively. This indicates that in all complexes ruthenium(II) is oxidized in one step. Moreover, cyclic voltammograms showed a reversible oxidation process.

Upon reduction, no waves were observed up to −2 V; usually in polyheterocyclic Ru(II) complexes, the reduction process takes place on a ligand Π^* orbital;[12] as the reduction of a pyrazolic group is

expected to occur at -2.1 to -2.5 Volts,[16] this result is normal.

EXPERIMENTAL SECTION

Measurements

^1H and ^{13}C NMR spectra have been obtained with a Bruker AC 250 spectrometer using Me_4Si as internal reference; chemical shifts are reported in ppm.

UV-visible absorption spectra have been determined on a Philips PU 8710 UV/vis. spectrometer using 10 mm quartz cuvettes.

IR spectra have been recorded on Philips PU 9700 infrared spectrophotometer.

FAB-mass spectra have been taken on a JEOL JMX DX-333 mass spectrometer.

Elemental analyses have been performed by the Microanalytical Laboratory, Ecole Nationale Supérieure de Chimie, Montpellier, France.

Melting points have been taken on a Büchi apparatus and are uncorrected.

Cyclic voltammetry was performed on a platinum disk electrode in dried acetonitrile with tetrabutylammoniumhexafluorophosphate as supporting electrolyte; the potential of the working electrode, scanned at 200 mV/s between -2 V 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.

Synthesis

The 1,3-bis(3'-carbethoxy-5'-methyl-1'-pyrazolyl)propane, $\underline{L_1}$, has been prepared as reported earlier.[5d]

$Ru(DMSO)_4Cl_2$ was used as purchased from Strem Chemicals.

All compounds have been characterized by elemental analyses and NMR spectroscopy.

-1,3-bis[3'-(butan-1'',3''-dionyl)-5'-methyl-1'-pyrazolyl]-propane, $\underline{L_2}$. The diester $\underline{L_1}$ (28,7 mM) in anhydrous toluene (100 ml) is slowly added to a suspension of sodium (72 mM) in toluene (100 ml); then acetone (72 mM) in toluene (100 ml) is added at 0 °C. The mixture is left two days at room temperature. The precipitate which is formed is filtered, washed with toluene, dissolved in H_2O and neutralized with acetic acid to pH 5. After extraction with CH_2Cl_2, the organic layer is dried over Na_2SO_4 and concentrated *in vacuo* to give an oil which becomes a light beige powder in anhydrous ether (70% yield); mp 127 °C; MS, m/z 373 $[L_2+H]^+$; *Anal.* Calculated for $C_{19}H_{24}N_4O_4$: C, 61.29%; H, 6.45%; N, 15.05%. Found: C, 61.09%; H, 6.76%; N, 15.05%. ^1H NMR ($CDCl_3$): δ 2.28 [s, $\underline{CH_3}$ (Pz) and $\underline{CH_3}(CH_3C=O)$, 12H]; 2.53 [q, $CH_2\underline{CH_2}CH_2$, 2H]; 4.18 [t, $N\underline{CH_2}$, 4H]; 6.29 [s, $=\underline{CH}$, 2H]; 6.54 [s, $\underline{H}$(Pz), 2H].

-1,3-bis[3'-(3''-methyl-5''-pyrazolyl)-5'-methyl-1'-pyrazolyl]propane, $\underline{L_3}$. A solution of compound $\underline{L_2}$ (18 mM) and hydrazine monohydrate (36 mM) in anhydrous methanol (100 ml) is magnetically stirred for one night at room temperature. The precipitate which appears is filtered and thoroughly washed with ether; (38% yield); mp 153 °C; MS, m/z 365 $[\underline{L_3}+H]^+$; *Anal.* Calculated for $C_{19}H_{24}N_8$: C, 62.64%; H, 6.59%; N, 30.77%. Found: C, 62.49%; H, 6.86%; N, 30.55%. ^1H NMR (DMSO d_6): δ 2.22 and 2.25 [s, CH_3(Pz), 12H]; 2.5 [q, CH_2-$\underline{CH_2}$-CH_2, 2H]; 4.05 [t, NCH_2, 4H]; 6.21 [s, H(Pz N-subst), 6H]; 6.29 [s, H(Pz NH), 6H].

-Macrocycle $\underline{L}$. A solution of HNa (1.65 mM) in anhydrous THF (200 ml) is dropped into a solution of tetrapyrazole $\underline{L_3}$ (0.5 mM) and 1,3-dibromopropane in anhydrous THF (180 ml). The mixture is refluxed for three days. The precipitate obtained is filtered and purified by chromatography on alumina eluting with CH_2Cl_2/C_2H_5OH (99:1); (33% yield); mp > 250 °C; MS, m/z 405 $[L+H]^+$; ^1H NMR and ^{13}C NMR: see Tables 1 and 2. *Anal.* Calculated for $C_{22}H_{28}N_8$: C, 65.35%; H, 6.93%; N, 27.72%. Found: C, 65.18%; H, 6.77%; N, 27.84%.

-RuL(DMSO)Cl_2 1a. Equimolar amounts of the macrocycle $\underline{L}$ and of $Ru(DMSO)_4Cl_2$ are refluxed for six days under nitrogen in a mixture H_2O/CH_3OH (20:80). The solution is concentrated to dryness; the residue is taken up with anhydrous ether, filtered, washed with ether and dried *in vacuo* to give a greenish-beige solid; (80% yield); MS, m/z 619 $[LRu(DMSO)Cl]^+$, 541 $[LRuCl]^+$; ^1H NMR and ^{13}C NMR: see Tables 1 and 2. *Anal.* Calculated for $C_{24}H_{34}N_8OSCl_2Ru$, H_2O: C, 42.86%; H, 5.36%; N, 16.67%. Found: C, 42.82%; H, 5.59%; N, 16.49%.

-RuL(DMSO)$(H_2O)(PF_6)_2$ 1b. This complex is precipitated in H_2O from the chloride complex **1a** with a concentrated NH_4PF_6 solution. The solid is filtered, thoroughly washed with water then with ether and dried *in vacuo*; (80% yield); MS, m/z 602 $[LRu(DMSO)(H_2O)]^+$, 524 $[LRuH_2O]^+$; ^1H NMR and ^{13}C NMR: see Tables 1 and 2. *Anal.* Calculated for $C_{24}H_{36}N_8O_2SP_2F_{12}Ru$: C, 32.32%; H, 4.04%; N, 12.57%. Found: C, 32.09%; H, 4.26%; N, 12.25%.

-RuL$(CH_3CN)_2(PF_6)_2$ 2. This complex is obtained by refluxing complex **1b** for four hours in CH_3CN under nitrogen. After evaporation of the solvent, the residue

is taken up with ether, filtered, washed and dried; a mustard solid is obtained; (93% yield); MS, m/z 733 $[LRu(CH_3CN)_2PF_6]^+$, 506 $[LRu]^+$; ^1H NMR and ^{13}C NMR: see Tables 1 and 2. *Anal.* Calculated for $C_{26}H_{34}N_{10}P_2F_{12}Ru$: C, 35.58%; H, 3.88%; N, 15.96%. Found: C, 35.29%; H, 3.76%; N, 15.75%.

-RuL(Py)$_2$(PF$_6$)$_2$ 3. A solution of complex **1b** in pyridine is refluxed for six hours under nitrogen and concentred *in vacuo*; the residue is taken up with ether, filtered and dried to give a yellow solid; (88% yield); MS, m/z 954 $[LRu(Py)_2(PF_6)_2]^+$, 809 $[LRu(Py)_2(PF_6)]^+$, 506 $[LRu]^+$; ^1H NMR and ^{13}C NMR: see Tables 1 and 2. *Anal.* Calculated for $C_{32}H_{38}N_{10}P_2F_{12}Ru$: C, 40.29%; H, 3.99%; N, 14.69%. Found: C, 40.08%; H, 3.74%; N, 14.43%.

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