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New ruthenium(II) heteroleptic complexes containing the 4-(2-pyridyl)pyrimidine ligand with amine and amino acid substituents

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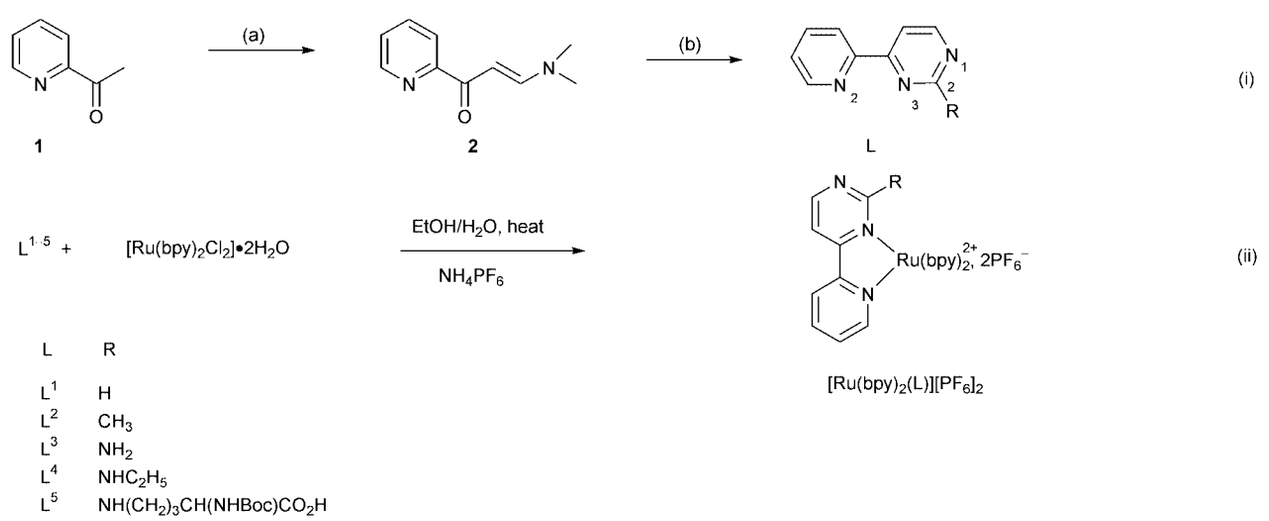
New 4-(2-pyridyl)pyrimidines (L) have been synthesized in high yields by condensing enaminones with the appropriate carboxamidine or guanidine under basic conditions. These asymmetric bidentate diimine ligands coming from a one-step functionalization of amine and amino acid groups were complexed to ruthenium to obtain new heteroleptic complexes of type $[Ru(bpy)_2(L)]^{2+}$. The ligands and complexes have been characterized by usual analytical methods, and the crystallographic study of one complex has been performed. Their spectroscopic and electrochemical properties have been investigated. ZINDO Calculations show that in the MLCT excited state the electron is mainly localized on the pyridylpyrimidine ligand. On the basis of electrochemical data, the first reduction potential of the complexes has been assigned to the redox couple involving this ligand.

Introduction

Polypyridine complexes of ruthenium(II) have stimulated considerable interest and activity as photosensitizers for photochemical and photoelectrochemical conversion of solar energy.[1] These complexes might also find application as components of molecular electronics devices[2] and as photoactive DNA cleavage agents for phototherapeutic purposes.[3] Symmetric polypyridine ligands such as 2,2′-bipyridine (bpy) have been extensively utilized as chelating agents,[4] but relatively little attention has been directed towards complexes that possess asymmetric bidentate diimine ligands.[5] It is clear that the replacement of one of the pyridine rings by other nitrogen-containing heterocycles offers the possibility of tuning the redox and photophysical properties of the complexes. As part of our programme of designing new nitrogen bidentate ligands,[6] we were interested by the synthesis of newly designed 4-(2-pyridyl)pyrimidine asymmetric ligands (L) and their heteroleptic ruthenium(II) complexes of type $[Ru(bpy)_2(L)]^{2+}$ (Scheme 1). On the other hand, it was interesting to introduce amine and amino acid groups at position 2 of the pyrimidine ring. Such substituents should increase the affinity of the corresponding complexes to DNA.[7] By the way, it should be emphasized that we herein report a one-step functionalization of an amino acid bearing an asymmetric bidentate diimine which was subsequently and successfully complexed to ruthenium. In this work the spectroscopic and electrochemical properties of this novel series of substituted pyridylpyrimidine ligands as well as the corresponding heteroleptic complexes have been investigated. ZINDO Calculations have been performed and support the assignment of electronic absorption spectra.



L	R
L^1	H
L^2	CH_3
L^3	NH_2
L^4	NHC_2H_5
L^5	$NH(CH_2)_3CH(NHBoc)CO_2H$

Scheme 1 Synthesis of the 4-(2-pyridyl)pyrimidines L^1–L^5 [(a) 1.25 equivalents of $(CH_3)_2NCH(OCH_3)_2$ at 100 °C, 16 h, 99%, (b) Guanidine or carboxamidine, 1 or 3 equivalents of sodium, EtOH, reflux] and the corresponding heteroleptic $[Ru(bpy)_2(L)]^{2+}$ complexes.

Experimental

General

All reactions were carried out under an argon atmosphere. Nuclear magnetic resonance spectra were recorded with Bruker AM-250 (250 MHz) and AC-200 (200 MHz) spectrometers for ^{1}H. Chemical shifts are reported in ppm and the solvent was used as internal reference. These instruments were also used for ^{13}C spectra. All melting points are uncorrected. The CI and FAB mass spectra (*m*-nitrobenzyl alcohol matrix) were recorded with a quadripolar Nermag R10-10H instrument. Elemental analyses were performed by the "Service de Microanalyse" of the LCC (Laboratoire de Chimie de Coordination). Column chromatography purifications were performed with Merck aluminium (deactivated with 8% water) or with silica gel (35–70 mesh). The complex $[Ru(bpy)_2Cl_2]\cdot 2H_2O$, 2-acetylpyridine and dimethylformamide dimethyl acetal were purchased from Fluka, 2,2′-bipyridine (99.5%) from Aldrich and $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (99%) from Strem Chemicals. The guanidines and carboxamides were purchased from Aldrich. For the preparation of compounds **2**, L^1 and L^3 see ref. 6. Spectroscopic grade ethanol (Carlo Erba) was used as supplied. For cyclic voltammetry, acetonitrile (Aldrich, spectrophotometric grade, 99.5%) was used as solvent and 0.1 mol l^{-1} tetrabutylammonium tetrafluoroborate (Janssen, 99%) as supporting electrolyte.

Synthesis of the 4-(2-pyridyl)pyrimidine ligands

2-Methyl-4-(2-pyridyl)pyrimidine L^2. A solution of acetamidinium chloride (2.14 g, 22.6 mmol) in absolute ethanol (75 ml) was added to a stirred solution of 2-[3-(dimethylamino)-1-oxoprop-2-en-1-yl]pyridine **2** (2.0 g, 11.3 mmol) in boiling absolute EtOH (50 ml) and stirring was continued for 20 min. To this mixture was added Na (0.78 g, 33.9 mmol, 3 equivalents) in absolute EtOH (50 ml) and the reaction mixture refluxed for 16 h. The solution was allowed to cool to room temperature and then concentrated under reduced pressure. The residue was dissolved in dichloromethane followed by removal of the precipitate by filtration. The filtrate was concentrated and the residue purified by column chromatography on flash silica gel (ethyl acetate) to give 1.88 g of L^2 as a white microcrystalline powder. Yield: 97%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.7 (d, 1 H, J = 4.45), 8.63 (m, 1 H), 8.43 (d, 1 H, J = 5.24), 8.1 (d, 1 H, J = 8.01), 7.8 (t, 1 H, J = 7.85 Hz), 7.35 (m, 1 H) and 2.8 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 167.87, 162.80, 157.82, 154.01, 149.44, 136.98, 125.20, 121.61, 114.22 and 26.08. MS (CI, NH_3): m/z = 172 (MH^+, 100%). Calc. for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.41; H, 5.62; N, 24.12%.

2-Ethylamino-4-(2-pyridyl)pyrimidine L^4. This compound was prepared in the same fashion as for L^2 by condensation of 3.0 g (16.95 mmol) of **2** with 1.23 g (16.95 mmol) of ethyl guanidine sulfate $\{[C_2H_5NHC(=NH)NH_2]_2\cdot H_2SO_4\}$ in the presence of 3 equivalents of sodium in absolute EtOH. The desired product was purified by column chromatography on silica gel (ethyl acetate–n-pentane, 80 : 20) to give 3.12 g of L^4 as a microcrystalline white powder. Yield: 92%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.64 (dd, 1 H, J = 6.33, 1.6), 8.38 (d, 1 H, J = 5.15), 8.34 (d, 1 H, J = 8.0), 7.77 (ddd, 1H, J = 7.78, 6.0, 1.76), 7.31 (m, 1 H), 5.48 (m, 1 H), 3.5 (m, 2 H) and 1.23 (t, 3 H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 163.0, 162.0, 158.5, 154.3, 148.8, 136.3, 124.4, 120.9, 106.0, 35.8 and 14.4. MS (CI, NH_3): m/z = 201 (MH^+, 100%). Calc. for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 66.21; H, 6.35; N, 27.64%.

2-(4-*tert*-Butoxycarbonylamino-4-carboxybutylamino)-4-(2-pyridyl)pyrimidine L^5. To a stirred solution of compound **2** (0.5 g, 2.8 mmol) in 5 mL of boiling absolute EtOH was added a solution of *N*α-Boc-L-Arg (0.77 g, 2.8 mmol; Boc = $COOC(CH_3)_3$) in 10 mL of absolute EtOH. After 10 min of stirring, 0.195 g (8.4 mmol, 3 equivalents) of sodium in 5 mL of absolute EtOH was added and the reflux maintained for 2 h. The solution was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography on deactivated aluminium (methanol–diethyl ether, 97 : 3) to give 1.1 g of L^5 as a yellow powder. Yield: 100%. $[\alpha]_{25}^{D}$ +13.5 deg. cm^3 g^{-1} dm^{-1} (c [g per 100 ml] 1.0, CH_3OH). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.6 (d, 1 H, J = 4.4), 8.27 (d, 1 H, J = 5.2), 7.7 (dd, 1 H, J = 7.7, 1.5), 7.4 (d, 1 H, J = 4.67 Hz), 7.3 (m, 1 H), 6.5 (m, 3 H), 5.9 (m, 1 H), 4.1 (s, 1 H), 3.4 (m, 2 H), 1.7 (m, 4 H) and 1.3 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 178.1, 163.9, 161.7, 157.3, 156.0, 154.2, 149.1, 136.8, 125.0, 121.6, 106.0, 79.1, 52.0, 50.3, 30.3, 28.3 and 25.8. MS (CI, NH_3): m/z = 388 (MH^+, 100%). Calc. for $C_{19}H_{25}N_5O_4$: C, 58.9; H, 6.5; N, 18.08. Found: C, 58.21; H, 6.35; N, 17.74%.

Synthesis of $[Ru(bpy)_2(L)][PF_6]_2$ complexes

$[Ru(bpy)_2(L^1)]^{2+}$. The complex *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.21 g, 0.4 mmol) was suspended in a mixture of ethanol and water (50 mL, 75 : 25) and heated under argon for 30 min. Ligand L^1 (0.075 g, 0.48 mmol, 1.2 equivalent) was added, and the mixture refluxed for 16 h. The resulting solution was cooled to room temperature and the ethanol removed under pressure. After filtration, a saturated solution of ammonium hexafluorophosphate was added dropwise to the filtrate to complete precipitation. The precipitate was collected by filtration, washed by water and diethyl ether, and dried to give 0.292 g of the desired complex. TLC (alumina, acetone–water–saturated aqueous potassium nitrate, 90 : 10 : 1) showed the material to be pure. Yield: 85%. ^{1}H NMR (CD_3CN): δ 9.18 (1 H, d, J = 5.28), 8.9 (1 H, d, J = 8.06), 8.7 (5H, m), 8.55 (1 H, s), 8.3 (5 H, m), 7.99 (1 H, d, J = 5.43), 7.97 (1 H, d, J = 5.44), 7.87 (1 H, d, J = 5.33 Hz), 7.82 (2 H, m), 7.5 (4 H, m) and 7.2 (1 H, m). ^{13}C NMR (CD_3CN): δ 161.5, 159.24, 158.5, 153.7, 153.2, 152.8, 139.5, 130.9, 129.2, 129.1, 127.8, 125.9, 125.8 and 120.6. FAB MS: m/z = 716 (100, M − PF_6^+), 571 (47%, M − 2PF_6^+). Calc. for $C_{29}H_{23}F_{12}N_7P_2Ru$: C, 40.48; H, 2.69; N, 11.39. Found: C, 40.75; H, 2.54; N, 11.51%.

$[Ru(bpy)_2(L^2)]^{2+}$. This complex was obtained by reaction of 0.168 g (0.32 mmol) of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ with 1.2 equivalents of L^2 using the procedure described for $[Ru(bpy)_2(L^1)]^{2+}$. The complex was purified as a hexafluorophosphate salt, 0.258 g. Yield: 92%. ^{1}H NMR (CD_3CN): δ 9.05 (2 H, m), 8.84 (4 H, m), 8.72 (1 H, d, J = 7.85), 8.55 (1 H, d, J = 7.3), 8.25 (6 H, m), 8.02 (1 H, d, J = 8.1), 7.96 (1 H, d, J = 5.54), 7.85 (1 H, d, J = 7.36 Hz), 7.65 (5 H, m) and 2.35 (3H, s). ^{13}C NMR (CD_3CN): δ 174.13, 165.41, 158.75, 157.94, 157.70, 157.45, 157.19, 154.32, 152.94, 152.56, 152.21, 139.05, 138.80, 138.60, 129.68, 128.76, 128.52, 127.35, 125.37, 125.16, 117.04 and 27.79. FAB MS: m/z = 730 (56.95, M − PF_6^+) and 585 (100%, M − 2PF_6^+). Calc. for $C_{30}H_{25}F_{12}N_7P_2Ru$: C, 41.20; H, 2.88; N, 11.21. Found: C, 40.85; H, 3.04; N, 11.35%.

$[Ru(bpy)_2(L^3)]^{2+}$. This complex was obtained by reaction of 0.084 g (0.16 mmol) of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ with 1.2 equivalents of L^3 using the procedure described for $[Ru(bpy)_2(L^1)]^{2+}$. The complex was purified as a hexafluorophosphate salt, 0.126 g. Yield: 90%. ^{1}H NMR (CD_3CN): δ 9.08 (1 H, dd, J = 7.22, 1.12), 8.9 (1 H, d, J = 8.18), 8.8 (1 H, d, J = 8.12), 8.65 (3 H, m), 8.55 (1 H, t, J = 7.95 Hz), 8.25 (5 H, m), 8.05 (2 H, m), 7.8 (3 H, m) and 7.55 (5 H, m). ^{13}C NMR (CD_3CN): δ 162.9, 160.9, 159.0, 158.8, 158.7, 158.2, 157.7, 155.1, 153.9, 153.7, 153.1, 151.9, 141.2, 140.0, 139.9, 139.7, 129.9, 129.6, 129.1, 128.6, 128.1, 127.1, 126.5, 126.3, 125.9, 125.8, 125.6 and 125.1. FAB MS: m/z = 731 (56.95, M − PF_6^+) and 585 (100%, M − 2PF_6^+). Calc. for $C_{29}H_{24}F_{12}N_8P_2Ru + 4H_2O$: C, 36.76; H, 3.40; N, 11.82. Found: C, 36.39; H, 3.51; N, 12.11%.

$[Ru(bpy)_2(L^4)]^{2+}$. This complex was obtained by reaction of 0.150 g (0.286 mmol) of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ with 1.2 equivalents of L^4 using the procedure described for $[Ru(bpy)_2(L^1)]^{2+}$. The complex was purified as a hexafluorophosphate salt, 0.219 g. Yield: 85%. ^{1}HMR (CD_3CN): δ 8.75 (6 H, m), 8.45 (1 H, d, J = 5.3), 8.2 (5 H, m), 8.0 (1 H, d, J = 5.58), 7.9 (1 H, d, J = 5.06), 7.65 (8 H, m), 5.25 (1 H, m, NH), 3.15 (2 H, m) and 0.63 (3 H, t, J = 7.25 Hz). ^{13}C NMR (CD_3CN): δ 165.8, 165.3, 161.3, 159.1, 158.8, 158.6, 158.5, 155.1, 153.2, 153.0, 152.7, 152.6, 130.0, 129.9, 129.4, 129.3, 129.2, 127.6, 126.5, 126.0, 125.9, 109.8, 38.0 and 13.1. FAB MS: m/z = 759 (30.29, M − PF_6^+) and 613 (73.53%, M − $2PF_6^+$). Calc. for $C_{31}H_{28}F_{12}N_7P_2Ru$: C, 41.21; H, 3.12; N, 12.40. Found: C, 41.28; H, 3.25; N, 12.56%.

$[Ru(bpy)_2(L^5)]^{2+}$. This complex was obtained by reaction of 0.150 g (0.286 mmol) of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ with 1.2 equivalents of L^5 using the procedure described for $[Ru(bpy)_2(L^1)]^{2+}$. The complex was purified as a hexafluorophosphate salt, 0.219 g. Yield: 85%. ^{1}H NMR(CD_3CN): δ 8.75 (6 H, m), 8.45 (1 H, m), 8.2 (5 H, m), 8.0 (2 H, m), 7.65 (8 H, m), 5.25 (1 H, m, NH), 4.1 (1 H, m), 3.15 (2 H, m), 1.8 (1 H, m), 1.51 (1 H, m), 1.45 (9 H, s) and 1.05 (2 H, m). ^{13}C NMR (CD_3CN): δ 177.5, 165.9, 165.6, 161.5, 159.3, 158.9, 158.7, 158.6, 155.3, 155.0, 153.3, 153.0, 152.8, 152.6, 150.8, 140.5, 140.0, 139.7, 139.4, 139.2, 130.1, 129.6, 128.8, 128.3, 127.8, 126.9, 126.2, 125.8, 125.2, 124.8, 110.0, 80.2, 65.2, 45.0, 43.0, 26.4 and 25.9. FAB MS: m/z = 946 (9.16, M − PF_6^+) and 800 (13.79%, M − $2PF_6^+$). Calc. for $C_{39}H_{41}F_{12}N_9O_4P_2Ru + 2H_2O$: C, 41.57; H, 4.03; N, 11.19. Found: C, 41.68; H, 4.21; N, 11.26%.

Absorption spectroscopy and cyclic voltammetry

The UV-visible electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammetry curves were recorded with a Wenking system (model 81 potentiostat) using a platinum button (Solea Tacussel EDI 101T) as the working electrode and a platinum wire of 1 mm diameter as the counter electrode. The working electrode was carefully polished with diamond sprays (Struers) and rinsed with ethanol before each potential run. Experiments were performed at a scan rate of 0.2 V s^{-1} on Ar-purged acetonitrile solutions, containing 0.1 mol l^{-1} tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Concentrations of 10^{-3} and 5×10^{-4} mol l^{-1} were used for ligands and complexes respectively.

Structure determination of $[Ru(bpy)_2(L^2)]^{2+}$, $2PF_6^-$

The data were collected on a Stoe IPDS (Imaging Plate Diffraction System) equipped with an Oxford Cryosystems cooler device. Coverage of the unique set was over 96% complete to at least 24.1°. Crystal decay was monitored by measuring 200 reflections per image. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. Owing to the rather low μx value, 0.24 (μx is the product of the mid size of the crystal and the absorption coefficient), no absorption correction was considered.

On the basis of the systematic absences, the space group ($P2_1/c$ or $P2_1$) could not be unambiguously defined. Indeed if the absences corresponding to the twofold screw axis 2_1 were verified, the systematic absences related to the c glide plane ($h0l$, $l = 2n + 1$) were not fully satisfied. The structure could be solved by direct methods (SIR 92)[8] in $P2_1/c$ but the refinement was unstable with large discrepancies between the anisotropic thermal parameters. A much better refinement was obtained in $P2_1$ with two molecules in the asymmetric unit. Although these two molecules are closely related by a pseudo inversion centre, no unusual parameter correlations were observed. Considering Flack's enantiopole parameter, 0.50, its rather good standard deviation (0.04), and the agreement between related distances in two molecules, the occurrence of a racemic twin might be considered. The structure was refined by least-squares procedures on F^2. The H atoms were introduced as a riding model and given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Details of data collection and refinement are given in Table 2. Selected bond lengths and angles for the two molecules are listed in Table 3.

The calculations were carried out with the help of the SHELXL 97 programs[9] running on a PC. The drawing of the molecule was realized with the help of CAMERON.[10]

CCDC reference number 186/1571.

See http://www.rsc.org/suppdata/dt/1999/3095/ for crystallographic files in .cif format.

ZINDO calculations

The optical absorption spectra of the ligands and of the $[Ru(bpy)_2(L^2)]^{2+}$ complex were calculated by using the ZINDO semiempirical program.[11] This Intermediate Neglect of Differential Overlap (INDO) model, adapted for spectroscopy and extended to second transition metal series, has been used for some time for studying the spectroscopy of large complexes.[12] The SCF calculation is followed by a configuration interaction (CI) calculation; a Rumer diagram is used to generate the CI matrix. The CI contains all singly excited configurations generated by removing electrons from the ten highest occupied MOs and placing them into the ten lowest unoccupied MOs. The geometries of the *cis* and *trans* conformers of all the ligands were optimized by using the AM1 method. Concerning the complex $[Ru(bpy)_2(L^2)]^{2+}$, the crystallographic data determined in this paper for N, C and Ru atoms were used for the ZINDO calculation. Hydrogen atoms were placed at a distance of 1.09 Å from their bonding partner.

Results and discussion

Ligands

Synthesis. The synthesis of ligands L^1–L^5 is outlined in Scheme 1 (i). The enaminone **2**[6a] was obtained with quantitative yield by reaction of 2-acetylpyridine **1** with 1.2 equivalents of the dimethylformamide dimethyl acetal at 100 °C.[13] The condensation of **2** with the appropriate guanidine or carboxamidine under basic conditions yielded the 4-(2-pyridyl)-pyrimidine ligands L^1–L^5 in good to excellent yields. The functionalized amino acids with metal-binding sites such as L^5 are attractive building blocks for the construction of synthetic peptides.[14] Since only a few examples of functionalized amino acids with bidentate metal-binding sites have been described, it was interesting to use this straightforward procedure in the preparation of new functionalized amino acids using the *N*α-Boc-L-Arg as the guanidine reagent. Thus, the reaction of **2** with 1 equivalent of *N*α-Boc-L-Arg in hot absolute ethanol in the presence of 2 equivalents of sodium ethoxide yielded L^5 without loss of the *tert*-butoxycarbonyl group, in quantitative yield.[15]

Spectroscopy. Electronic absorption spectra of ligands L^1, L^3, L^4 and L^5 are shown in Fig. 1. The corresponding experimental and calculated absorption maxima for all ligands are presented in Table 1. The geometries of *cis* and *trans* conformers of bpy have been determined at the MP2/6-31G**//HF/6-31G** level by Howard.[16] The *trans* conformer is predicted to be lower in energy but the *cis*–*trans* interconversion barrier is only of 6 kJ mol^{-1}. In organic solvents, dipole measurements indicate a *trans* non-planar configuration.[16] The calculated spectra are in good agreement with previous INDO/S CI calculations[17] and with experimental results if we assume that bpy is in the *trans*

Table 1 Experimental and calculated absorption maxima in ethanol and redox potentials in acetonitrile for the different ligands at 298 K

Ligand	λ_{max}/nm (ε/l mol^{-1} cm^{-1}) calculated *a*	calculated *b*	experimental	E_{red}/V *vs.* SCE
bpy	273	284	283 (14480)	−2.18
	235		244 (sh) (9950)	
	229	240	236 (12240)	
L^1		278	279 (12820)	−1.78
			242 (sh) (6880)	
		234	235 (7620)	
L^2		280	280 (15240)	−1.85
			244 (sh) (7360)	
		235	237 (8710)	
L^3		296	324 (7660)	−1.90
		289	286 (sh) (7280)	
			276 (9380)	
		235	241 (23010)	
L^{4c}		296	352 (sh) (2110)	−1.98
		290	338 (2430)	
			287 (sh) (2550)	
			273 (sh) (4760)	
			253 (13100)	
		237	242 (sh) (11390)	
L^5			342 (3730)	−1.95
			288 (sh) (4440)	
			277 (sh) (7260)	
			253 (19830)	

[a] *cis* Conformer. [b] *trans* Conformer. [c] Calculation performed on $NHCH_3$ instead of $NHCH_2CH_3$.

conformation. The experimental and calculated absorption spectra of L^1 and L^2 are similar to the bpy spectrum. From ZINDO calculations we have attributed the absorption bands to strong $\pi \longrightarrow \pi^*$ transitions. Absorption spectra of L^3, L^4 and L^5 present a supplementary band at wavelengths above 320 nm. For L^4 and L^5 this band is very large and is characterized by a molar absorption coefficient ε less intense than that of the π–π^* bands. It can be attributed to a n–π^* transition implying a lone pair of electrons located on one of the nitrogen atoms. For L^3, the band at 324 nm is relatively fine and it seems difficult with the present data to conclude about its nature (n–π^* or π–π^* transition). The absence of any calculated absorption band at a wavelength longer than 300 nm does not agree with experimental data. A possible explanation would be the presence of a species due to hydrogen-bonded interactions with ethanol in the first solvation shell of 2-aminopyrimidine compounds.[18]

Redox properties. Peak potentials of the "free" ligands are given in Table 1. We observed that L^1 is easier to reduce than bpy. In fact, the mesomeric donor effect of the nitrogen atom at the 1 position of the pyrimidine induces an electronic depletion around this nitrogen. This increases the electron attractor power of L^1. The reduction potentials of ligands L^3, L^4 and L^5 are similar and more negative than that of L^1. Indeed, the lone pair of the nitrogen atom of the substituent at the 2 position to the pyrimidine increases the electron density *via* a donor mesomeric effect making the reduction of the ligands more difficult. The reduction potential of L^2 is intermediate (−1.85 V) between those of L^1 and L^3. This is in line with the well known inductive effect of a methyl group which is less intense than the mesomeric effect.

Complexes

Synthesis. Ruthenium(II) complexes containing the novel ligands were synthesized by utilizing $[Ru(bpy)_2Cl_2]$ as the source of the metal fragment as shown in Scheme 1 (ii). The complex $[Ru(bpy)_2Cl_2]$ reacted for 16 h with the respective ligands in a boiling 75:25 solution of EtOH–water.[19] After removal of ethanol under reduced pressure and filtration of the aqueous solution, the complexes were precipitated with an excess of NH_4PF_6. They were obtained in excellent yield with high purity as their hexafluorophosphate salts and characterized by NMR spectroscopy, mass spectrometry, electrochemistry and absorption spectroscopy. An X-ray structural analysis of $[Ru(bpy)_2(L^2)]^{2+}$ was carried out.

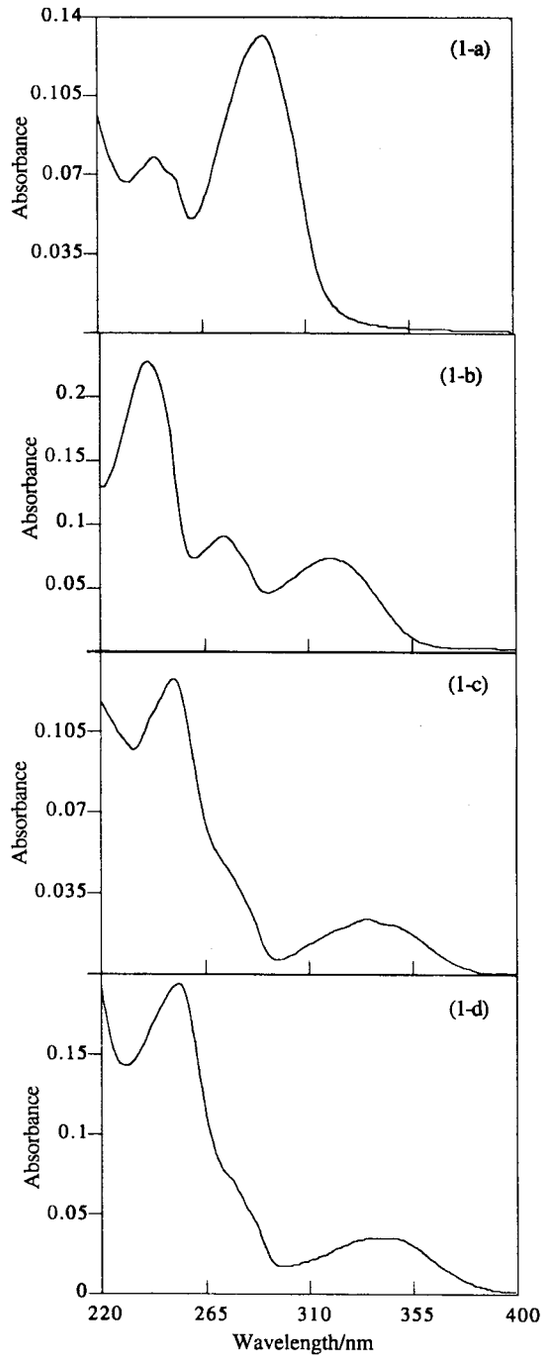


Fig. 1 Absorption spectra of ligands L^1 (a), L^3 (b), L^4 (c) and L^5 (d), in ethanol (10^{-5} mol l^{-1}).

Structure of $[Ru(bpy)_2(L^2)]^{2+}$, $2PF_6^-$. The asymmetric unit contains two cations and four anions. The two cations are nearly identical; only one (molecule 1) is shown on Fig. 2 with the atom labelling scheme. The ruthenium–nitrogen bond lengths range from 2.022(7) to 2.137(6) (Table 3). The longest is observed for the pyrimidine ring 2.137(6) Å [2.109(7) Å]. Similar lengthening were observed in related complexes with α substituted bpy or related ligands.[6b,20] As suggested by the

Table 2 Crystallographic data for $[Ru(bpy)_2(L^2)][PF_6]_2$ recorded at 160 K

Empirical formula	$C_{30}H_{25}F_{12}N_7P_2Ru$
M	874.58
Shape (color)	Box (dark red)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	12.2871(17)
b/Å	10.5692(12)
c/Å	25.100(4)
β/°	95.266(17)
V/Å^3	3245.9(8)
Z	4
R(int)	0.0285
R	0.0348
$wR2$	0.0841
Goodness of fit	1.024

short contact between one H of the methyl substituent and the nitrogen N(16), 2.563 Å [2.558 Å], this increase in bond length might result from the steric interaction between this methyl substituent on the pyrimidine ring and the bpy ring 5. It is indeed this bpy ligand which exhibits the larger twisting 8.4(4) [8.9(5)]° about the interannular C–C bond. The other bpy ligand displays an inter-ring angle of only 5.6(1) [5.6(2)]°, whereas the two rings of the (pyridyl) pyrimidine are almost planar, interplanar angle 1.2(5) [2.7(5)]°. However, an electronic influence of the pyrimidine ring itself could not be ruled out.

Spectroscopy. The absorption data for all the complexes are summarized in Table 4. The absorption spectra of $[Ru(bpy)_2(L^1)]^{2+}$ and $[Ru(bpy)_2(L^5)]^{2+}$ determined in ethanol solutions are presented in Fig. 3. By comparison with the reference product, *i.e.* $[Ru(bpy)_3]^{2+}$, the absorption band in the visible region has been assigned to a metal-to-ligand charge transfer (MLCT)

Table 3 Selected interatomic distances [Å] and bond angles [°] for $[Ru(bpy)_2(L^2)][PF_6]_2$

Molecule 1		Molecule 2	
Ru(1)–N(11)	2.137(6)	Ru(2)–N(21)	2.109(7)
Ru(1)–N(12)	2.060(4)	Ru(2)–N(22)	2.050(5)
Ru(1)–N(13)	2.051(6)	Ru(2)–N(23)	2.061(7)
Ru(1)–N(14)	2.022(7)	Ru(2)–N(24)	2.054(8)
Ru(1)–N(15)	2.088(7)	Ru(2)–N(25)	2.038(8)
Ru(1)–N(16)	2.051(5)	Ru(2)–N(26)	2.060(5)
N(11)–C(111)	1.356(8)	N(21)–C(211)	1.349(10)
N(11)–C(115)	1.372(10)	N(21)–C(215)	1.337(11)
N(12)–C(121)	1.321(9)	N(22)–C(221)	1.398(9)
N(12)–C(125)	1.369(10)	N(22)–C(225)	1.328(10)
N(13)–C(131)	1.355(10)	N(23)–C(231)	1.372(10)
N(13)–C(135)	1.354(9)	N(23)–C(235)	1.344(9)
N(14)–C(141)	1.318(10)	N(24)–C(241)	1.400(11)
N(14)–C(145)	1.375(9)	N(24)–C(245)	1.308(10)
N(15)–C(151)	1.356(10)	N(25)–C(251)	1.340(11)
N(15)–C(155)	1.315(10)	N(25)–C(255)	1.396(11)
N(16)–C(161)	1.377(8)	N(26)–C(261)	1.347(9)
N(16)–C(165)	1.333(8)	N(26)–C(265)	1.362(8)
N(114)–C(113)	1.301(11)	N(214)–C(213)	1.341(13)
N(114)–C(115)	1.353(10)	N(214)–C(215)	1.331(13)
N(14)–Ru(1)–N(13)	78.5(3)	N(24)–Ru(2)–N(23)	80.1(3)
N(14)–Ru(1)–N(16)	84.8(3)	N(24)–Ru(2)–N(26)	87.7(3)
N(13)–Ru(1)–N(16)	96.2(2)	N(26)–Ru(2)–N(23)	96.7(2)
N(14)–Ru(1)–N(12)	93.9(3)	N(22)–Ru(2)–N(24)	92.3(3)
N(13)–Ru(1)–N(12)	88.3(3)	N(22)–Ru(2)–N(23)	87.8(3)
N(16)–Ru(1)–N(12)	174.91(19)	N(22)–Ru(2)–N(26)	175.5(2)
N(14)–Ru(1)–N(15)	96.05(17)	N(25)–Ru(2)–N(24)	95.09(19)
N(13)–Ru(1)–N(15)	173.4(3)	N(25)–Ru(2)–N(23)	173.1(3)
N(16)–Ru(1)–N(15)	79.5(3)	N(25)–Ru(2)–N(26)	78.1(3)
N(12)–Ru(1)–N(15)	95.8(3)	N(25)–Ru(2)–N(22)	97.4(3)
N(14)–Ru(1)–N(11)	170.4(3)	N(24)–Ru(2)–N(21)	170.5(3)
N(13)–Ru(1)–N(11)	96.4(2)	N(23)–Ru(2)–N(21)	96.3(2)
N(16)–Ru(1)–N(11)	103.9(2)	N(26)–Ru(2)–N(21)	101.5(2)
N(12)–Ru(1)–N(11)	77.8(2)	N(22)–Ru(2)–N(21)	78.8(3)
N(15)–Ru(1)–N(11)	89.5(3)	N(25)–Ru(2)–N(21)	89.1(3)
C(111)–N(11)–C(115)	117.4(6)	C(215)–N(21)–C(211)	114.4(7)
C(111)–N(11)–Ru(1)	113.1(4)	C(211)–N(21)–Ru(2)	114.5(5)
C(115)–N(11)–Ru(1)	129.5(5)	C(215)–N(21)–Ru(2)	131.1(6)
C(121)–N(12)–C(125)	117.2(5)	C(225)–N(22)–C(221)	117.7(5)
C(121)–N(12)–Ru(1)	117.6(5)	C(221)–N(22)–Ru(2)	115.8(5)
C(125)–N(12)–Ru(1)	125.1(5)	C(225)–N(22)–Ru(2)	126.4(5)
C(135)–N(13)–C(131)	117.2(7)	C(235)–N(23)–C(231)	119.2(7)
C(135)–N(13)–Ru(1)	126.5(5)	C(235)–N(23)–Ru(2)	127.0(6)
C(131)–N(13)–Ru(1)	116.3(4)	C(231)–N(23)–Ru(2)	113.8(5)
C(141)–N(14)–C(145)	118.4(6)	C(245)–N(24)–C(241)	118.5(7)
C(141)–N(14)–Ru(1)	117.3(5)	C(241)–N(24)–Ru(2)	113.7(5)
C(145)–N(14)–Ru(1)	123.8(5)	C(245)–N(24)–Ru(2)	127.5(6)
C(155)–N(15)–C(151)	121.3(7)	C(251)–N(25)–C(255)	116.2(8)
C(155)–N(15)–Ru(1)	124.6(6)	C(255)–N(25)–Ru(2)	126.2(7)
C(151)–N(15)–Ru(1)	113.8(5)	C(251)–N(25)–Ru(2)	117.5(6)
C(165)–N(16)–C(161)	118.4(5)	C(261)–N(26)–C(265)	117.9(6)
C(165)–N(16)–Ru(1)	126.3(4)	C(265)–N(26)–Ru(2)	125.3(4)
C(161)–N(16)–Ru(1)	115.2(4)	C(261)–N(26)–Ru(2)	116.8(5)
C(113)–N(114)–C(115)	118.2(7)	C(215)–N(214)–C(213)	117.2(8)

Table 4 Absorption parameters in ethanol solution for ruthenium(II) complexes (10^{-5} mol l^{-1})

Complex	λ_{max}/nm (ε/l mol^{-1} cm^{-1})			
$[Ru(bpy)_3]^{2+}$		450 (13700)	287 (80290)	245 (25620)
$[Ru(bpy)_2(L^1)]^{2+}$	482 (sh) (5310)	441 (7210)	286 (52260)	245 (15960)
$[Ru(bpy)_2(L^2)]^{2+}$	480 (sh) (3620)	442 (5140)	286 (44940)	243 (20870)
$[Ru(bpy)_2(L^3)]^{2+}$		449 (6610)	289 (31390)	236 (13210)
$[Ru(bpy)_2(L^4)]^{2+}$	483 (sh) (11250)	447 (17290)	288 (85500)	244 (47300)
$[Ru(bpy)_2(L^5)]^{2+}$	487 (sh) (7950)	448 (10950)	289 (61890)	245 (29500)

Table 5 Redox potentials in acetonitrile for ruthenium(II) complexes

	$E_{1/2}$/V *vs.* SCE				
		Reduction			
Complex	Oxidation				$\Delta E_{1/2}$/V
$[Ru(bpy)_3]^{2+}$	1.30	−1.30	−1.48	−1.73	2.60
$[Ru(bpy)_2(L^1)]^{2+}$	1.33	−1.01	−1.40	−1.70	2.34
$[Ru(bpy)_2(L^2)]^{2+}$	1.38	−1.12	−1.45	−1.70	2.50
$[Ru(bpy)_2(L^3)]^{2+}$	1.34	−1.11	−1.43	−1.67	2.45
$[Ru(bpy)_2(L^4)]^{2+}$	1.34	−1.08	−1.32	−1.55	2.42
$[Ru(bpy)_2(L^5)]^{2+}$	1.34	−1.10	−1.42	−1.65	2.44

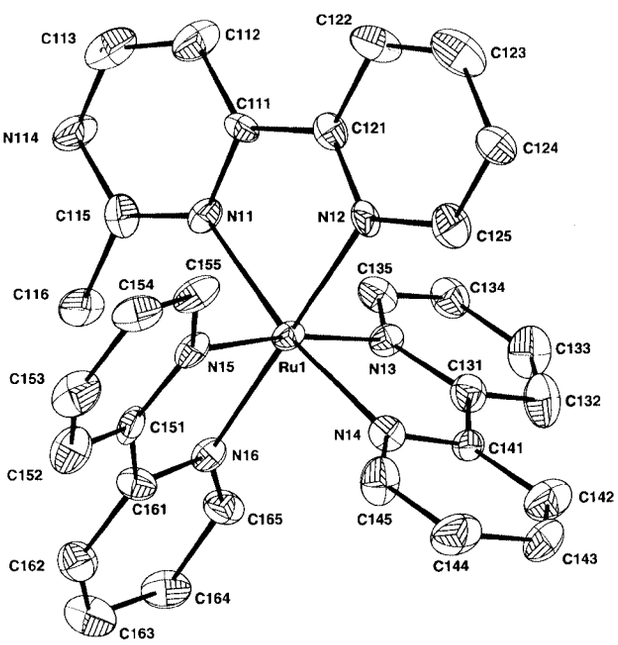


Fig. 2 Molecular view of the cation $[Ru(bpy)_2(L^2)]^{2+}$ (molecule 1). Ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

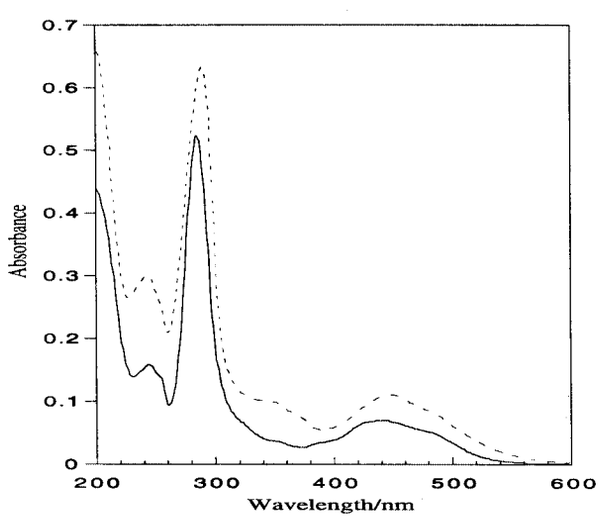


Fig. 3 Absorption spectra of complexes $[Ru(bpy)_2(L^1)]^{2+}$ (full line) and $[Ru(bpy)_2(L^5)]^{2+}$ (dotted line) in ethanol (10^{-5} mol l^{-1}).

transition.[21] The ZINDO calculation performed on $[Ru(bpy)_2(L^2)]^{2+}$ suggests several bands (from 446 to 400 nm) in the visible region which can be assigned to a metal-to-ligand charge transfer associated with the promotion of a ruthenium d electron into a π* orbital of bpy and (or) pyridylpyrimidine ligands. In the concerned excited state the electron is mainly localized on the pyridylpyrimidine ligand.

A more intense band appears in the region 280–320 nm which can be associated with a $\pi \longrightarrow \pi^*$ ligand-centred (LC) transition[22] in agreement with the ZINDO calculation. Moreover the calculation results in this region lead to the attribution of several bands to $d \longrightarrow d^*$ transitions (MC). A third absorption band appearing in the 230–260 nm region of the experimental spectra can be assigned to MLCT transitions according to ZINDO calculations.

Redox properties. The redox potentials of all the complexes as determined by cyclic voltammetry in acetonitrile are in Table 5. The voltammograms exhibit, in each case, one reversible oxidation wave and three reversible reduction waves. By comparison with the oxidation potential of the reference complex, we attribute the potentials in the range +1.33 to +1.38 V *vs.* SCE to the redox couple Ru^{3+}–Ru^{2+} of the heteroleptic complexes. These potentials are related to the energy of the HOMO orbital of the metal.[23] The potentials of the second and third reduction of the heteroleptic complexes are similar to the corresponding potentials of the reference complex. This indicates that these two reductions take place on the bpy ligands of the heteroleptic complexes. The first reduction potentials ranging from −1.01 to −1.12 V *vs.* SCE are less negative than that of $[Ru(bpy)_3]^{2+}$ (−1.30 V *vs.* SCE). Consequently, it is clear that the first reduction can only be attributed to the redox couple involving the pyridylpyrimidine ligand. The corresponding potential is related to the energy of the π* (LUMO) ligand orbital. The successive reductions of the heteroleptic complexes take place according to eqns. (1)–(3).

$$[Ru^{II}(bpy)_2(L)]^{2+} + e^- \longrightarrow [Ru^{II}(bpy)_2(L^-)]^+ \quad (1)$$

$$[Ru^{II}(bpy)_2(L^-)]^+ + e^- \longrightarrow [Ru^{II}(bpy)(bpy^-)(L^-)] \quad (2)$$

$$[Ru^{II}(bpy)(bpy^{-})(L^{-})] + e^{-} \longrightarrow [Ru^{II}(bpy^{-})(bpy^{-})(L^{-})]^{-} \quad (3)$$

The comparison between the first reduction potential values shows that the non-substituted ligand L^1 in the complex is easier to reduce than the substituted one (by about 100 mV). Consequently, the π* antibonding orbital (LUMO) of L^1 is that of lowest energy. This result is in agreement with those obtained for the "free" ligand. The ZINDO calculated levels of the orbitals for the "free" ligands in their *trans* conformations are correlated with the electrochemical data. The difference $\Delta E_{1/2}$ between the oxidation potential E_{ox} and the first reduction E_{red1} of the heteroleptic complexes is correlated with the difference between the HOMO and LUMO energy, *i.e.* to the energy at the maximum of the absorption band located in the visible region. This result reinforces the attribution of this band mainly to the transition $S_0 \longrightarrow {}^1MLCT(L)$. Thus, the optical and redox orbitals are of similar nature, and the MLCT excited state of the heteroleptic complexes $[Ru(bpy)_2(L)]^{2+}$ corresponds essentially to the Ru→L transition.

In summary, we have prepared, characterized and studied the spectroscopic and electrochemical properties of 4-(2-pyridyl)pyrimidine asymmetric ligands (L) and their heteroleptic ruthenium(II) complexes $[Ru(bpy)_2(L)]^{2+}$. The presence of amine and/or amino acid functions on the 4-(2-pyridyl)-pyrimidine ligand makes the corresponding complexes interesting candidates for immobilization on solid supports or incorporation into dendrimers. It is interesting that ligand L^5 which is a functionalized amino acid with metal-binding sites provides new opportunities for the construction of synthetic peptides. The synthesis of such new peptides containing L^5 or its corresponding complex $[Ru(bpy)_2(L^5)]^{2+}$ is currently under investigation.

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