Syntheses, Characterization, X-ray Crystal Structure, Redox and Photophysical Properties of Polypyridylruthenium(II) Complexes Containing Carboxylate-Substituted Pyridyltriazoles

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The syntheses and properties of two novel $[Ru(bpy)_2(L–L')]^{n+}$ complexes with **L–L′** = 3-carboxy-5-(pyrid-2′-yl)-1,2,4-triazole (**H$_2$cpt**) or 3-(ethoxycarbonyl)-5-(pyrid-2′-yl)-1,2,4-triazole (**Hcept**) ligands are described. Previous publications on Ru^{II} complexes containing (pyrid-2′-yl)-1,2,4-triazoles revealed that their coordination is possible via N1 and N4 of the triazole ring. ^{1}H NMR spectroscopic data and the crystal structure of $[Ru(bpy)_2(cept)]PF_6{\cdot}H_2O$ (**2**) indicate that the coordination of the **Hcpt**$^-$ and **cept**$^-$ occurs via N1 of the triazole ring. The crystals of **2** are monoclinic and belong to the space group $P2_1/n$ with $a = 12.339(7)$, $b = 16.512(7)$, $c = 16.802(8)$ Å, $\beta = 110.29(4)°$, and $Z = 4$. A water molecule is hydrogen-bonded to the carbonyl oxygen atom of the ethoxycarbonyl group with an O···O distance of 2.891 Å. Spectroscopic measurements reveal that **H$_2$cpt** and **Hcept** are strong σ-donor ligands. When coordinated to a ruthenium(II) centre, both triazole ligands reported in this study lost their acidic triazole hydrogen atoms and became negatively charged, resulting in even stronger σ-donor ligands, as demonstrated by a negative shift of their redox potentials compared to the complexes containing the neutral ligand. The complexes reported in this study showed ^{3}MLCT-based luminescence emission, both at room temperature and at 77 K.

Introduction

A considerable number of $[Ru(bpy)_2(L\text{-}L')]^{n+}$ systems with **L−L′** = substituted (pyrid-2′-yl)-1,2,4-triazole ligands have been reported by Hage et al.[1−14] Electrochemical, absorption, and emission measurements revealed that triazoles are strong σ-donor and weak π-acceptor ligands, thus lowering the oxidation potential of the metal ion. Additionally, due to a higher π* level of the triazole compared with the π* level of the **bpy** ligand, both the first reduction and the lowest exited states of these complexes are **bpy**-based.[1] Therefore, a study towards the related ligands with a variety of substituents is relevant.

In this paper the synthesis and properties of a Ru(bpy)$_2$ moiety with 3-carboxy-5-(pyrid-2′-yl)-1,2,4-triazole (**H$_2$cpt**) and 3-(ethoxycarbonyl)-5-(pyrid-2′-yl)-1,2,4-triazole (**Hcept**) ligands is described. The selection of the **H$_2$pct** and **Hpcet** ligands was made to study the effect of electron-withdrawing groups in the photophysical and electrochemical properties of the ruthenium(II) complexes. Previous publications, mainly from our laboratory[1−14] of a number of ruthenium(II) complexes containing (pyrid-2′-yl)-1,2,4-triazoles showed that coordination is possible via N1 and via N4 of the triazole ring. A crystal structure of the $Ru(bpy)_2(cept)](PF_6){\cdot}H_2O$ (**2**) revealed that the triazole ring is coordinated to ruthenium(II) via N1. This coordination mode was also observed for the 3-methyl-5-(pyrid-2′-yl)-1,2,4-triazole (**3Meptz**),[1] and is predicted for the **H$_2$cpt**-based complex. The structure and properties of the complexes were investigated with the use of ^{1}H NMR spectroscopy, ESI MS, CV measurements, UV/Vis absorption, and time-resolved emission spectroscopy.

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Results and Discussion

Ligand Syntheses

Synthesis of the ligands (structures given in Figure 1) was straightforward by starting from pyridylamidrazone and diethyl oxalate, in a ratio 1:4 to avoid possible formation of a dimer, and heating under reflux in absolute ethanol for 1 h (modified procedure[15]). However, contrary to the results reported in the literature, two different products were obtained. The ratio was found to be close to 1:1. The first fraction appeared to be a hydrolysed ester (acid), while the second fraction was the ester itself.

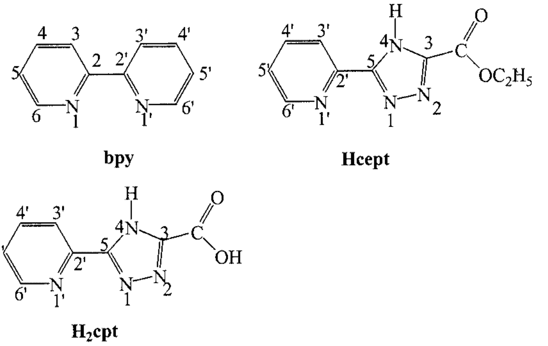
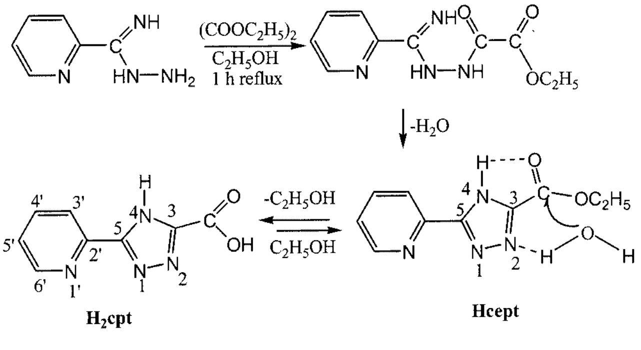


Figure 1. Structural formula of the ligands used in this study

The chemistry of amidrazones is diverse,[15–28] and offers the possibility of obtaining different products with a slight change in the experimental conditions. It is not clear how the reaction for obtaining the hydrolysed ligand may proceed. A possible reaction route is shown in Scheme 1. The triazole hydrogen atom forms a hydrogen bond to the free oxygen atom of the ethoxycarbonyl group, reducing the electron density in its carbon centre. The water molecule then attacks the partially positive carbon atom, followed by the hydrolysis of the ester. A supporting factor could be the activation of a water molecule by hydrogen-bonding to N2 of the triazole (see Scheme 1). In order to testify to these hypotheses, the same reaction was performed with an *N*-substituted triazole. The reaction was unsuccessful, and no products could be isolated. However, there are several possible routes for the hydrolysis of the ester, and more experiments would be needed to prove this mechanism.



Scheme 1. Reaction route and mechanism for the **H$_2$cpt** and **Hcept** ligand syntheses

Syntheses and Characterization of the Complexes

The synthesis of the metal complexes was achieved by using an excess of one of the ligands and *cis*-Ru(bpy)$_2$Cl$_2$. The **Hcept** ligand lost its triazole hydron and acquired a negative charge upon coordination to the ruthenium(II) centre. This phenomenon was known from previous studies[1,10,14] and has been attributed to the increased acidity of the coordinated triazole ligands. In the **H$_2$cpt**-based complex, both triazole and carboxylic hydrons were found to be ionised.

The mass of the complexes was determined using mass spectrometry. Both complexes reported showed mono-positively charged complex ions [M$^+$].

Another important technique for elucidating the structure of the ruthenium(II) complexes is ^{1}H NMR spectroscopy. The chemical shifts of complex **2** are shown in Table 1. For the sake of comparison the ^{1}H NMR chemical shifts of [Ru(bpy)$_2$(3Meptz)]$^+$ are also presented. The assignment of the ^{1}H NMR spectra of the complex presented in Table 1 was made based on literature data of the related pyridyltriazole complexes,[1,14] and the difference in coupling constants (^3J) of 3-H and 6-H of the pyridine ring.

The ^{1}H NMR spectrum of [Ru(bpy)$_2$(Hcpt)]$^+$ is rather complex and the assignment is difficult. There are two sets of peaks with the same coupling constants, but different intensities (approximately 3:1 for the ones with higher chemical shifts), which suggests that the **H$_2$cpt** ligand is partially dehydronated (higher chemical shift). Such a claim is also supported by CV data (see next section).

Description of the X-ray Structure of [Ru(bpy)$_2$(cept)]-(PF$_6$)·H$_2$O (2)

A projection of the structure of the title compound, the atom numbering, and the position of the hydrogen bonds is presented in Figure 2. Selected bond lengths and angles, and hydrogen-bond information are presented in Table 2. The ruthenium(II) ion coordinates to two **bpy** molecules in the *cis* configuration and one **cept$^-$** ion. The "bite angles" of the coordinated ligands are 78–79°, similar to the chelating angles observed for similar complexes.[1,10,12] The Ru–N distances, 2.04–2.06 Å, are in the normal range for this type of ruthenium(II) complexes.[1,13,29] The relatively long distance between the ruthenium(II) centre and the nitrogen atom of the pyridine ring of the **cept$^-$** ligand might be caused by the limited π backbonding of the pyridyltriazole-containing ruthenium(II) complexes. Steric factors might also play a role in these bond lengths. Similar distances were found for the analogous mononuclear **bpt$^-$**-containing ruthenium complex.[13]

As can be seen in Figure 2, the **cept$^-$** ligand is coordinated to ruthenium(II) via N111 and N121. This coordination mode was observed for other pyridyltriazoles containing bulky groups bound to the remaining carbon atom of the triazole ring.[1] A water molecule is relatively strongly hydrogen-bonded via H1 to O2 with an O1···O2 distance of 2.89 Å, and via H2 to F1 and F2 of a neighbouring PF$_6^-$ ion with an O1···F1 distance of 2.91 Å (see Table 2). No

Table 1. The ^{1}H NMR chemical shifts versus TMS of the **Hcept** and **3Meptz** ligands in $[Ru(bpy)_2(L-L')]^+$ complexes; values between parentheses present the difference in chemical shift of the pyridyltriazole ligands upon coordination

Compound[a]	3′-H	4′-H	5′-H	6′-H	CH_2	CH_3
$[Ru(bpy)_2(cept)]^+$	8.01 (−0.11)	7.49 (−0.07)	7.35 (−0.66)	7.79 (−0.93)	4.25 (−0.05)	1.28 (−0.05)
$[Ru(bpy)_2(3Meptr)]^+$	8.02 (+0.00)	7.99 (+0.09)	7.23 (−0.20)	7.67 (−0.96)		2.20 (−0.16)

[a] From ref.[14]

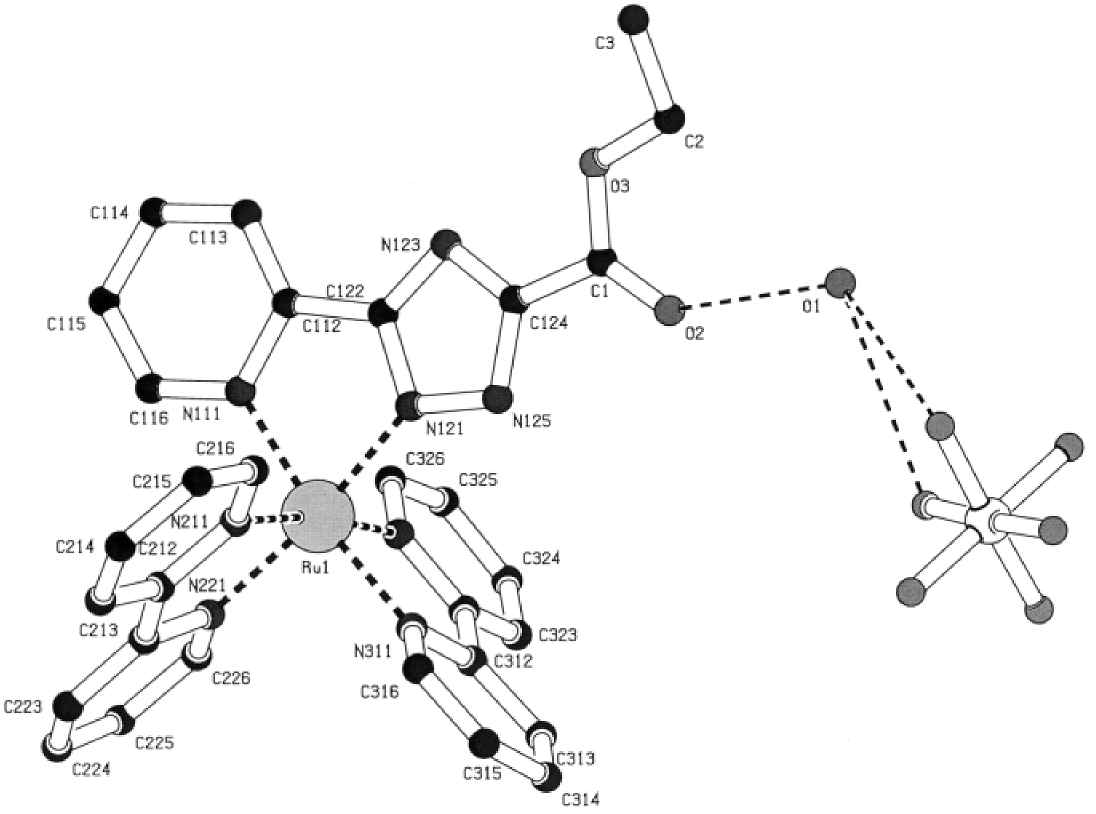


Figure 2. PLUTON drawing and numbering system of the $[Ru(bpy)_2(cept)](PF_6)\cdot H_2O$; the hydrogen atoms were omitted for reasons of clarity; hydrogen bonds from the water molecule to carboxylate and PF_6 are indicated by dashed lines

hydrogen bonds were found in which N123 and N125 of the triazolate ring were involved.

Electrochemical Properties

The highest occupied molecular orbitals (HOMOs) of most of the polypyridylruthenium(II) complexes are metal-centred, while their lowest unoccupied molecular orbitals (LUMOs) are known to be ligand-centred.[30] The oxidation of these complexes leads to the formation of the low-spin ruthenium(III) complexes $[\pi_M\ (t_{2g})^5]$, while the reduction primarily takes place in the π* orbital of the polypyridine ligands.[30]

The redox potentials of the studied complexes and of some similar complexes taken from the literature are reported in Table 3. The complexes were hydronated by addition of a drop of 1 M $HClO_4$ solution in acetonitrile. The oxidation potentials of the hydronated species occurred at higher potentials. This increase in the oxidation potential was caused by the decreased σ-donor capacity of the hydronated triazoles, which led to the stabilisation of the dπ metal orbitals.

The redox behaviour of **2** is similar to complexes of analogous pyridyltriazoles reported in the literature,[1,14] with a small shift to higher values. The reason for that is a decreased σ-donor ability of the **Hcept** ligand. This is due to the presence of an electron-withdrawing group ($COOC_2H_5$) at C-3 of the triazole ring. The cyclic voltammogram of **2** is shown in Figure 3 (**2** and **2a**). The first reduction potentials are attributed to **bpy** ligands.

The redox behaviour of **1** is rather complicated. Both, triazole ring and acid hydrons of the **H$_2$cpt** ligand are partially dehydronated (see **1** in Figure 3). When a drop of 1 M $HClO_4$ was added to a solution, the first oxidation peak disappeared (see **1a** in Figure 3) and the carboxy group be-

Table 2. Selected bond lengths [Å], angles [°], and hydrogen-bond information for complex $[Ru(bpy)_2cept](PF_6)\cdot H_2O$

Bond lengths [Å]					
Ru(1)−N(111)	2.104(6)	C(112)−C(113)	1.375(10)	N(123)−C(124)	1.348(9)
Ru(1)−N(121)	2.039(5)	C(112)−C(122)	1.465(10)	C(124)−N(125)	1.348(9)
Ru(1)−N(211)	2.063(5)	C(113)−C(114)	1.379(11)	C(124)−C(1)	1.473(10)
Ru(1)−N(221)	2.052(6)	C(114)−C(115)	1.392(11)	C(1)−O(2)	1.202(9)
Ru(1)−N(311)	2.061(6)	C(115)−C(116)	1.398(11)	C(1)−O(3)	1.343(9)
Ru(1)−N(321)	2.051(6)	N(121)−C(122)	1.347(8)	O(3)−C(2)	1.452(9)
N(111)−C(116)	1.338(9)	N(121)−N(125)	1.351(8)	C(2)−C(3)	1.489(13)
N(111)−C(112)	1.367(8)	C(122)−N(123)	1.324(9)		
Bond angles [°]					
N(121)−Ru(1)−N(321)	90.1(2)	N(221)−Ru(1)−N(311)	91.6(2)	N(121)−Ru(1)−N(111)	78.3(2)
N(121)−Ru(1)−N(221)	172.3(2)	N(121)−Ru(1)−N(211)	96.7(2)	N(321)−Ru(1)−N(111)	96.4(2)
N(321)−Ru(1)−N(221)	94.9(2	N(321)−Ru(1)−N(211)	171.1(2)	N(221)−Ru(1)−N(111)	95.3(2)
N(121)−Ru(1)−N(311)	95.1(2)	N(221)−Ru(1)−N(211)	78.9(2)	N(311)−Ru(1)−N(111)	172.0(2)
N(321)−Ru(1)−N(311)	78.9(2)	N(311)−Ru(1)−N(211)	94.8(2)	N(211)−Ru(1)−N(111)	90.6(2)
Hydrogen bond information D−H	*d*(D−H)	*d*(H···A)	DHA [°]	*d*(D···A)	A
O1−H1	0.840	2.105	155.59	2.891	O2
O1−H2[a]	0.840	2.134	153.01	2.908	F1[b]
		2.498	149.4	3.250	F2[b]

[a] Bifurcated H bond. [b] Symmetry operation: 3/2 − *x*, −1/2 + *y*, 1/2 − *z*.

Table 3. Electrochemical properties of ruthenium(II) complexes containing **H_2cpt** and **Hcept** ligands; values in V, derived from CV measurements in CH_3CN versus Ag/AgCl reference; the scan rate was 100 mV/s

Compound	Oxidation potentials	Reduction potentials (site)	Ref.
$[Ru(bpy)_2(cpt)]$	0.90	−1.51 (bpy), −1.84 (bpy, cpt)	this work
$[Ru(bpy)_2(cept)]^+$	1.09	−1.43 (bpy), −1.69 (bpy)	this work
$[Ru(bpy)_2(Hcpt)]^+$	1.04	−1.51 (bpy), −1.84 (bpy, cpt)	this work
$[Ru(bpy)_2(Hcept)]^{2+}$	1.26	−1.43 (bpy), −1.69 (bpy)	this work
$[Ru(bpy)_2(H_2cpt)]^{2+}$	1.33	not observable	this work
$[Ru(bpy)_2(3Meptr)]^+$	0.8	−1.46 (bpy), −1.72 (bpy), −2.25 (3Meptr)	[1]
$[Ru(bpy)_2(H3Meptr)]^{2+}$	1.2	−1.53 (bpy), −1.86 (bpy),	[1]

came hydronated. Due to the presence of an electron-withdrawing group (COOH) at C-3 of the triazole ring, the remaining triazole hydrogen atom will only be partially ionized (see **1a** in Figure 3, the smaller peak at 1.33 V). The reduction parts of the voltammograms are not clear and an accurate assignment is quite difficult and was not attempted.

The fine-tuning of the electrochemical properties of **1** was possible by changing the pH of the solution. It is anticipated that in a strong acidic environment **H_2cpt** becomes a stronger π-acceptor than **bpy**, and the first reduction poten-

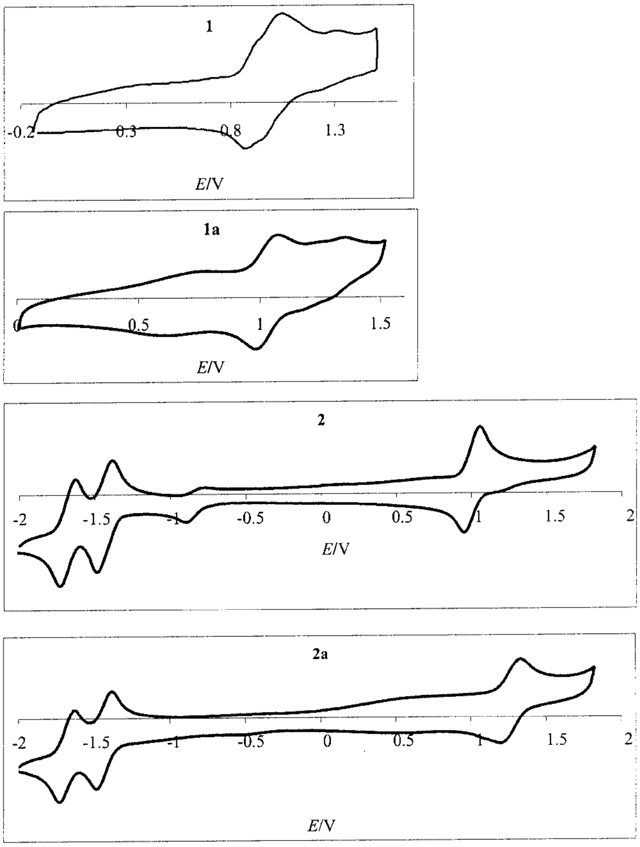


Figure 3. Cyclic voltammograms of the $[Ru(bpy)_2(cpt)]^+$ (**1**), $[Ru(bpy)_2(Hcpt)]^+$ (**1a**) $[Ru(bpy)_2(cept)]^+$ (**2**), and $[Ru(bpy)_2(Hcept)]^{2+}$ (**2a**) referenced against Ag/AgCl

tial, as well as the lowest exited state of **1** could be located at the **H_2cpt** ligand.

Absorption and Emission Spectra

The absorption and emission spectra of **1** and **2** in acetonitrile at room temperature are shown in Figure 4. The wavelengths and extinction coefficients of the lowest energy absorption maxima at 298 K, the wavelengths of the emission maxima at 77 K and 298 K, the luminescence lifetimes at 77 K and 298 K and the luminescence quantum yields at 298 K are summarized in Table 4, where the luminescence properties of the $[Ru(bpt)(bpy)_2]^+$ complex,[7] taken as model compound, are also displayed for comparison.

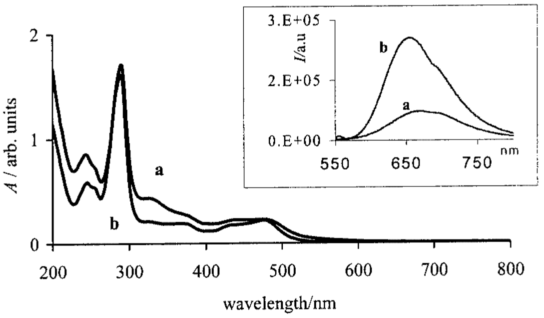


Figure 4. Absorption spectra in acetonitrile solutions at 298 K of $[Ru(bpy)_2(Hcpt)]^+$ (**a**) and $[Ru(bpy)_2(cept)]^+$ (**b**); inset: emission spectra measured at room temperature in acetonitrile approximately 2 10^{-5} M

For the complexes examined, the intense absorption bands in the UV region are due to ligand−centre transitions, and the moderately intense broad bands in the visible region (Figure 4) can be assigned to metal-to-ligand charge-transfer (^{1}MLCT) transitions. When deprotonated, both **H_2cpt** and **Hcept** are expected to be better donors and worse acceptors than **bpy**. The absorption and emission spectra of the two complexes are in agreement with this expectation. Replacement of a **bpy** ligand of $[Ru(bpy)_3]^{2+}$ by an **L−L′** ligand to give $[Ru(L{-}L')(bpy)_2]^+$ caused an increase in the electronic charge of the metal atom with a consequent red shift of the metal-to-ligand charge-transfer (Ru→bpy) absorption and emission band (Figure 4 and inset). A similar behaviour has been observed for complexes containing imidazole-type bridging ligands.[1,7,10,14]

The luminescence intensity was found to exhibit a monoexponential decay in all cases. The state responsible for luminescence is likely the lowest ^{3}MLCT excited state, which corresponds to a spin-forbidden (Ru→bpy) transition. Experiments have also been performed in butyronitrile rigid matrix at 77 K and the results obtained are also summarized in Table 4.

All the photophysical properties for the reported compounds are pH-sensitive, and can be tuned by hydronation and dehydronation of the ligands.

Conclusion

In this paper ruthenium(II) mixed-ligand complexes with the newly synthesized ligands **H_2cpt** and **Hcept** are described. The crystal structure of $[Ru(bpy)_2(cept)](PF_6)\cdot H_2O$ has revealed that the **cept$^-$** ligand is coordinated to ruthenium(II) via N1 of the triazole ring. The coordination mode of the related **Hcpt$^-$** ligand is likely to take place via N1 as well. Such a coordination mode results from the presence of the bulky groups at C-3 of the triazole ring, generating steric hindrance to the N4 binding site of the triazole ring.

The CV measurements revealed that the redox potentials for the complexes discussed in this paper are altered with changing pH. The redox potentials of the complexes shift to lower values after dehydronation, which is attributed to the increased σ-donor capacity of the negatively charged ligands. Both photophysical and electrochemical data for the above-mentioned complexes suggest that **Hcpt$^-$** and **cept$^-$** are stronger σ-donor ligands than **bpy**, and that the first reduction processes involve the late ligands. **Hcpt$^-$** and **cept$^-$** play a role of spectator ligands. Both complexes show a moderate emission, which occurs from the lowest-lying triplet excited state ^{3}MLCT.

Experimental Section

Synthesis of the Ligands: A mixture of diethyl oxalate (43 g, 0.29 mol) and 2-pyridylamidrazone (10 g, 0.07 mol) in ethanol (50 mL), prepared as reported by Hage,[1] was heated under reflux for 1 h (modified procedure[15]). Two fractions were obtained in an approximate 1:1 ratio. The first fraction, 3-carboxy-5-(pyrid-2′-yl)-1,2,4-triazole (**H_2cpt**), precipitated immediately, while the second, 3-(ethoxycarbonyl)-5-(pyrid-2′-yl)-1,2,4-triazole (**Hcept**), precipitated after standing for one night at −20 °C. The second fraction was purified by recrystallisation from a acetone/methanol mixture (2:1, v/v). The yield (including both fractions) based on 2-pyridylamidrazone was 4.8 g, 30%.

Table 4. Photophysical properties of ruthenium(II) complexes containing **Hcpt$^-$**, **cept$^-$**, and **bpt$^-$** ligands compared with $[Ru(bpy)_3]^{2+}$

Compound	Absorption λ/nm ($\varepsilon/10^4$ M^{-1}cm^{-1})[a]	Emission (room temp.) λ/nm (τ/ns)[a]	$\varphi_{em(room\ temp.)} \times 10^3$	Emission (77 K) λ/nm (τ/μs)[b]
$[Ru(bpy)_2(Hcpt)]^+$	480 (1.3)	670 (55)	0.83	620 (2.97)
$[Ru(bpy)_2(cept)]^+$	476 (1.1)	656 (93)	2.6	610 (4.00)
$[Ru(bpy)_2(bpt)]^+$	475 (1.13)	678 (160)[c]	3[d]	628 (2.80)
$[Ru(bpy)_3]^{2+}$ [d]	452 (1.30)	620 (0.17)		582 (4.8)

[a] Measured in an aerated acetonitrile solution. [b] Measured in a butyronitrile solution. [c] Measured in a de-aerated acetonitrile solution. [d] Taken from ref.[7]

I. 3-Carboxy-5-(pyrid-2′-yl)-1,2,4-triazole (H_2cpt): M.p. 292 °C. MS: *m/z* = 191 [MH$^+$]. $C_8H_6N_4O_2$ (190.2): calcd. C 50.53, H 3.20, N 29.46; found C 49.57, H 3.30, N 28.52. IR: ṽ = 3271.1 (νN−H, sharp), 3128.2 (νO−H, broad), 1700.2 cm^{-1} (νC=O). ^{1}H NMR (300 MHz, DMSO): δ = 7.97 (d, 3′-H), 7.54 (m, 4′-H), 8.00 (t, 5′-H), 8.66 (d, 6′-H).

II. 3-(Ethoxycarbonyl)-5-(pyrid-2′-yl)-1,2,4-triazole (Hcept): M.p. 164 °C. MS: *m/z* = 219 [MH$^+$]. $C_{10}H_{10}N_4O_2$ (218.2): calcd. C 55.04, H 4.62, N 25.67; found C 54.93, H 4.53, N 25.63. IR: ṽ = 3161.1 (νN−H, broad), 1733.8 cm^{-1} (νC=O). ^{1}H NMR (300 MHz, DMSO): δ = 1.33 (t, CH_3), 4.30 (q, CH_2), 8.12 (d, 3′-H), 7.56 (t, 4′-H), 8.01 (t, 5′-H), 8.72 (d, 6′-H).

Synthesis of the Ruthenium Complexes

[Ru(bpy)$_2$(Hcpt)]PF$_6$ (1): *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (520 mg, 1 mmol), prepared as reported in the literature,[31] and **H$_2$cpt** (380 mg) were added to a 50 mL ethanol/water (1:1, v/v) mixture. The mixture was heated under reflux for 4 h. After cooling, the solvent was removed by rotary evaporation. The remaining solid was dissolved in 10 mL of water and added to a saturated NH_4PF_6 (4 mmol) solution. The precipitate was filtered off and dried. The solid was recrystallised from a 50 mL acetone/water (1:1, v/v) mixture. The yield based on *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O was 0.5 g (65%). The complex was purified further by column chromatography using neutral alumina and acetone followed by ethanol as eluents. MS: *m/z* = 603 [M$^+$].

[Ru(bpy)$_2$(cept)](PF$_6$)·H$_2$O (2): This complex was prepared and purified as with **1**, except that for column chromatography acetone was used as eluent. The yield based on *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O was 0.75 g (90%). Crystals of [Ru(bpy)$_2$(cept)](PF$_6$)·H$_2$O, suitable for X-ray structural determination, were obtained by slow concentration at room temperature of a diluted solution of **2** in a mixture of methanol/water (1:1, v/v). MS: *m/z* = 632 [M$^+$].

Physical Measurements: Infrared spectra of the compounds in the region 4000−200 cm^{-1} were measured with a Perkin−Elmer Paragon 1000 FTIR spectrophotometer using pressed KBr pellets. ^{1}H NMR spectra were recorded with a Bruker WM 300 MHz NMR spectrometer. The ^{1}H NMR spectra of the ligands were obtained in $(CD_3)_2SO$ solvent, while those of the ruthenium(II) complexes were recorded in $(CD_3)_2CO$. The peak positions are relative to TMS. Mass spectra were obtained with a Finnigan MAT TSQ-70 equipped with a custom-made electrospray interface (ESI). Spectra were collected by constant infusion of the analyte, dissolved in a methanol/water (80:20) solution with 1% acetic acid. Elemental C, H, N analyses were carried out with a Perkin−Elmer 2400 Series II analyser. Cyclic voltammograms were recorded using an Autolab PG Stat10 potentiostat controlled by a GPES4 software. A home-made three-compartment cell was used, containing an Ag/AgCl electrode as a reference electrode, a platinum wire as counter electrode, and a glassy carbon electrode as working electrode. All the CV measurements were carried out in spectroscopic grade acetonitrile, using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The scan rate was 100 mV/s. Prior to each run the solution was purged with argon for 30 s. Absorption and emission spectra at room temperature were performed in air-equilibrated spectroscopic grade acetonitrile solutions in 1-cm quartz cells using a Perkin−Elmer Lambda 900 spectrophotometer and Fluorolog equipment, respectively. The standard compound used for determining the emission quantum yields of the complexes was [Ru(bpy)$_3$]$^{2+}$ in an aerated water solution (φ_{em} = 0.028).[32] The quantum yields were calculated according to Equation (1).[33,34]

$$\phi_{em} = \phi'_{em} * \left(\frac{I}{I'}\right) * \left(\frac{A'}{A}\right) * \left(\frac{\eta}{\eta'}\right)^2 \tag{1}$$

In Equation (1), *I* (sample) and *I′* (standard) are the integrated emission intensities, *A* and *A′* the absorptions at the excitation wavelength, and η and η′ the refractive indices of the solvents. Time-resolved emission spectra were obtained using a HamamatsuC-5680 streak camera equipped with an M 5677 sweep unit. Excitation at 337 nm was achieved by a pulsed (fwhm 600 ps) nitrogen laser (LTB, MGS 405 TD) operating at a repetition rate of 20 Hz. The time resolution of this set was ca. 200 ps, as limited by the laser pulse width. For measurements at 77 K in a rigid matrix, freshly distilled butyronitrile as a solvent was used. All the values for emission maxima are uncorrected for the phototube response. Estimated errors are as follows: band maxima, ±2 nm; relative luminescence intensity ±20%; lifetimes, ±10%.

X-ray Crystallographic Study of [Ru(bpy)$_2$(cept)](PF$_6$)·H$_2$O (2): A red needle-shaped crystal was selected and mounted on a glass fibre using the oil-drop method.[35] X-ray data were collected with a Rigaku AFC-7S diffractometer (graphite-monochromated Mo-K_α radiation, λ =0.71073 Å, ω-2θ scans). The intensity data were corrected for Lorentz and polarisation effects, for absorption (ψ-scan absorption correction) and extinction. All non-H atoms were refined anisotropically. The water H atoms were located from a Fourier-difference map. All other H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The structure was solved by direct methods. The programs TEXSAN,[36] SHELXS-97,[37] and SHELXL-97[38] were used for data reduction, structure solution, and structure refinement, respectively. Refinement of F^2 was done against all reflections. The weighted *R* factor, *wR*, and goodness of fit, *S*, are based on F^2. Conventional *R* factors, *R*, are based on *F*, with *F* set to zero for negative F^2. Selected crystal data and numerical details of the structure determination are given in Table 5. The supple-

Table 5. Crystal data and details of the structure determination for [Ru(bpy)$_2$(cept)](PF$_6$)·H$_2$O {weighting schemes: $w = 1.0/[\sigma^2(F_o^2) + (0.0871P)^2 + 4.0317P]$}

Crystal data:	
Empirical formula	$RuC_{30}H_{27}F_6N_8O_3P$
Formula mass	793.64
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	12.339(7)
b [Å]	16.512(7)
c [Å]	16.802(8)
β [°]	110.29(4)
V [Å^3]	3211(3)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.642
F(000)	1600
μ [cm^{-1}]	0.620
Crystal size [mm]	0.50 × 0.20 × 0.15
Data collection/refinement:	
Temperature [K]	193(2)
$\theta_{min.}$, $\theta_{max.}$ [°]	2.52, 26.49
Total data collected	5303
Observed refl. [$I > 2\sigma(I)$]	3861
Independent refl. (R_{int})	5053 (0.0539)
No.of refined params.	445
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0657, 0.1544
Goodness-of-fit on F^2	1.042
Min. and max. residual electron density [e·Å^{-3}]	0.878, −0.629

mentary crystallographic data for this paper is contained within publication CCDC-164043. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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