Ruthenium(II)bis(2,2'-bipyridyl) Complexes of some 1,2,4-Triazoles**

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Received September 22, 1982

The first examples of ruthenium complexes of 1,2,4-triazoles are reported. Compounds of the type $[(bpy)_2RuL_2]^{2+}$ *(bpy = 2,2'-bipyridyl, L = 1,2,4-triazole (Htrz), 4-phenyl-1,2,4-triazole (Phtrz), 4-methyl-1,2,4-triazole (Metrz) and 4-allyl-1,2,4-triazole (Altrz) and of the type* $(bpy)_2RuL_2$ *(L = triazolato anion) have been prepared. The complexes are characterised by UV/VIS, infrared and* ^1H *NMR spectra and their redox chemistry has been investigated using cyclic-voltammetry. In all complexes reported the triazole ligands are acting as monodentate ligands.*

Introduction

Ruthenium bipyridyl complexes have attracted much attention because of their possible use as redox catalysts [1, 2]. Along with $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridyl), $Ru(bpy)_2$ complexes with additional ligands such as Cl^-, H_2O, CH_3CN, pyridine, poly(4-vinylpyridine), CO and NO have also been studied [2, 3] and dimeric species, with bridging ligands like pyrazine, 4,4'-bipyridyl, Cl^-, biimidazole and others have been reported [4]. Such complexes are of interest because they are useful materials for the study of electron transfer processes. Recently, pyrazole coordinated to the $(bpy)_2Ru$ moiety as a monodentate ligand, and in its deprotonated form as a bidentate ligand, was reported [5].

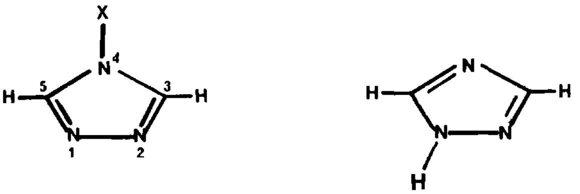

Fig. 1. Ligands (1) 4R-1,2,4-triazole. R = Methyl-, Phenyl-, Allyl- (2) 1,2,4-triazole.

We are currently investigating the coordinating behaviour of 1,2,4-triazoles towards transition metals. These triazoles usually act as bidentate ligands, resulting in polynuclear compounds [6a–c], but are also known to give mononuclear compounds with monodentate triazole ligands [6d–g]. Since the $(bpy)_2Ru$ moiety usually has a *cis*-geometry, bidentate coordination of 1,2,4-triazoles would lead to dimeric species, as in the corresponding pyrazolato complex [5]. Furthermore it was hoped that by binding such ligands to a $Ru(bpy)_2$ grouping information about their electron donor and acceptor properties could be obtained.

In this work we wish to report the first examples of ruthenium triazole complexes. 1,2,4-triazole (Htrz), 4-phenyl-1,2,4-triazole (Phtrz), 4-methyl-1,2,4-triazole (Metrz) and 4-allyl-1,2,4-triazole (Altrz) (see Fig. 1) have been coordinated to bis(bpy)Ru. The complexes obtained have been characterised by

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**This work is dedicated to Aart Vos on his retirement as a chemist.

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elemental analysis, infrared, ^{1}H NMR and electronic spectra. Their redox chemistry has been studied by cyclic voltammetry.

Experimental

Materials

Reagent grade solvents from Merck were used without further purification, unless otherwise stated. NMR solvents were obtained from Merck and Fluorochem. $RuCl_3 \cdot xH_2O$ was obtained from Johnson-Matthey. 1,2,4-triazole was obtained from Aldrich.

$Ru(bpy)_2Cl_2 \cdot 2H_2O$ was prepared as described by Whitten *et al.* [7]. 4-methyl-1,2,4-triazole was prepared according to Bayer [8]. The new compound 4-allyl-1,2,4-triazole was prepared in a similar manner, details of this synthesis will be described elsewhere [9]. 4-phenyl-1,2,4-triazole was prepared according to a method described by Wiley *et al.* [10].

Preparation of $[(bpy)_2RuL_2](PF_6)_2$ Complexes. L = Phtrz, Metrz, Altrz, Htrz

1 mmol of $(bpy)_2RuCl_2 \cdot 2H_2O$ (520 mg) was refluxed in a water/acetone mixture (3:1 v/v) in the presence of 6 mmol of L for 3 hours. For L = Htrz 1 cm^3 1 *N* HCl was added to the reaction mixture to avoid deprotonation of the ligand. The compounds were precipitated as the PF_6^- salt by addition of excess of an aqueous NH_4PF_6 solution. The crude material was further purified by recrystallisation from acetone/water mixtures and dried *in vacuo.* The yields after purification were between 60 and 80%.

Anal. $[(bpy)_2Ru(Phtrz)_2](PF_6)_2$; Found: C, 42.80; H, 3.15; N, 13.87. Calculated: C, 43.48; H, 3.05; N 14.09%. $[(bpy)_2Ru(Metrz)_2](PF_6)_2 \cdot H_2O$ Found: C, 35.08; H, 2.76; N, 15.37. Calculated: C, 35.15; H, 3.15; N, 15.77%. $[(bpy)_2Ru(Altrz)_2](PF_6)_2$; Found: C, 38.88; H, 2.90; N, 15.44. Calculated: C, 39.18; H, 3.04; N, 15.22%. $[(bpy)_2Ru(Htrz)_2](PF_6)_2 \cdot \frac{1}{2}(CH_3)_2CO$; Found: C, 35.40; H, 2.83; N, 16.03. Calculated: C, 35.15; H, 2.87; N, 16.08%.

Preparation of $(bpy)_2Ru(trz)_2 \cdot H_2O$

This compound was prepared by the above method except that 1 *N* NaOH (10 cm^3) was used instead of NH_4PF_6. Upon cooling overnight purple crystals were formed. The precipitate was filtered and dried *in vacuo.* Yield 50%.

Anal. $(bpy)_2Ru(trz)_2 \cdot H_2O$; Found: C, 50.62; H, 3.43; N, 24.12. Calculated: C, 50.75; H, 3.87; N, 24.67%.

Equipment

Electronic spectra were recorded on a Pye-Unicam SP8-200 spectrophotometer. Peak positions are accurate to 1 nm and extinction coefficients have an accuracy of 5%. Emission spectra were obtained on a Perkin-Elmer 44B spectrophotometer. Spectra were recorded using a slitwidth of 5 nm. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer, the accuracy is ±4 cm^{-1} above 2000 cm^{-1} and ±2 cm^{-1} below 2000 cm^{-1}. The spectra were recorded both as KBr discs and as Nujol mulls. ^{1}H NMR spectra were obtained on a Bruker WP 80 or a Jeol-JNMX 60 NMR spectrometer. Peak positions were measured relative to an internal TMS standard. Electrochemical measurements were carried out at the University of North-Carolina, Chapel Hill and at the Eindhoven University of Technology. The measurements were carried out using standard equipment [5], using spectrograde solvents. 0.1 *M* tetraethylammonium perchlorate was used as a supporting electrolyte.

Results and Discussion

General

The compounds reported are apparently formed according to reaction (1):

$$cis\text{(bpy)}_2RuCl_2 + 2\ Phtrz \xrightarrow[\text{acetone/H}_2\text{O}]{\Delta\ 3h} cis\text{-}[(bpy)_2Ru(Phtrz)_2]^{2+} + 2Cl^- \qquad (1)$$

Triazoles were used in threefold excess. The cationic complexes were precipitated with NH_4PF_6 and could be recrystallised from water/acetone mixtures. The neutral $(bpy)_2Ru(trz)_2 \cdot H_2O$ was obtained by addition of NaOH to a solution of $[(bpy)_2Ru(Htrz)_2]^{2+}$ as in reaction (2):

$$[(bpy)_2Ru(Htrz)_2]^{2+} + NaOH \xrightarrow[\text{acetone/water}]{} (bpy)_2Ru(trz)_2 \qquad (2)$$

Different metal to ligand ratios were used to see whether dimeric species could be obtained. No such compounds could be isolated. The method used by Meyer *et al.* [5] for the preparation of binuclear species, reaction of $(bpy)_2Ru$ bis(pyrazole) complex with $[(bpy)_2Ru(acetone)_2]^{2+}$ failed to yield significant amounts of dimeric compounds. The characterisation of the different species is based on elemental analyses and spectroscopic data which are discussed below.

Electronic spectra

The electronic spectra of the compounds have been listed in Table I. All absorptions normally found for *cis*-$(bpy)_2Ru$ complexes are observed. The posi-

TABLE I. Electronic and Emission Spectra and Redox Potentials of $Ru(bpy)_2$ Complexes of 1,2,4-Triazoles and Related Compounds.

Compound	λ_{max} (log ϵ) in CH_3CN (nm)	λ_{max} (nm)[a] emission	Redox Potentials (V *vs.* SCE)[b]		
			$Ru^{III/II}$	ligand localised	
$[(bpy)_2Ru(Htrz)_2](PF_6)_2 \cdot \frac{1}{2}(CH_3)_2CO$	470(3.94); 330(3.89); 290(4.78)	660	+1.13	−1.49[c]	
$[(bpy)_2Ru(Phtrz)_2](PF_6)_2$	468(3.94); 330sh; 290(4.80)	645	+1.05	−1.48	−1.70
$[(bpy)_2Ru(Altrz)_2](PF_6)_2$	472(3.97); 328(3.93); 290(4.85)	660	+1.01	−1.47	−1.71
			+1.08	−1.44	−1.77[c]
$[(bpy)_2Ru(Metrz)_2](PF_6)_2 \cdot H_2O$	473(3.95); 330(3.90); 290(4.81)	660	+1.00	−1.46	−1.70
$(bpy)_2Ru(trz)_2 \cdot H_2O$	544(3.91); 367(3.94); 298(4.75)[d]	–	+0.45	−1.65[c]	
$[(bpy)_2Ru(pzH)_2](PF_6)_2$[e]	470(3.71); 323(3.69); 289(4.66)	627, 661[f]	+1.18	−1.52	−1.76
$(bpy)_2Ru(pz)_2 \cdot H_2O$[e]	581(3.66); 434(3.61)[d]		+0.30		
$[(bpy)_2Ru(py)_2](PF_6)_2$[e]	455(3.91); 338(4.20); 289(4.69)	615	+1.30	−1.32	−1.56
$(bpy)_2RuCl_2 \cdot 2H_2O$[e]	553(3.95); 380(3.94); 297(4.69)[d]		+0.32		

[a] Measured at room temperature in acetone solution. [b] Measured in CH_3CN with 0.1 *M* TEAP as supporting electrolyte scan rate 200 mV/sec, glassy-carbon electrode. [c] Measured in DMSO with 0.1 *M* TEAP as supporting electrolyte scan rate 500 mV/sec, glassy-carbon electrode. [d] Measured in DMF. [e] From reference 5. [f] In CH_3CN. pzH = pyrazole, py = pyridine.

tion of the lowest energy maximum in $[(bpy)_2RuL_2]^{n+}$ complexes is generally taken as a measure for the π-acceptor capacity of the ligand L [5]. As the $d\pi$-orbitals of the metal can be stabilised by metal to ligand back-bonding, the absorption is found at higher energy when L is a good π-acceptor. The position of the lowest $\pi^*(bpy) \leftarrow d\pi(Ru)$CT absorption in the cationic triazole complexes is very close to that observed in the corresponding pyrazole complex (see Table I), but is found at lower energy than for the corresponding pyridine complex. This suggests that in this type of complex 1,2,4-triazoles have similar π-acceptor capacities to pyrazole but are weaker π-acceptors than pyridine. The slight variation in band position with a change of substituent on the 4-position suggests that these groups influence the acceptor properties of the triazole to some extent.

The lowest energy absorption for the neutral $(bpy)_2Ru(trz)_2 \cdot H_2O$ is shifted considerably to lower energy. Its λ_{max} of 544 nm in DMF suggests that trz has similar π-donor properties to Cl^- (λ_{max} for $(bpy)_2RuCl_2$ is 540 nm) and is a weaker π-donor than the pyrazolato ion [5].

Emission spectra were measured at room temperature in acetone and have been listed in Table I. No attempt was made to measure the emission quantum yield, but comparison of solutions with the same optical density revealed that the emission of the cationic compounds is at least as strong as that observed for *cis*-$[(bpy)_2Ru(py)_2]^{2+}$. The emission maxima for the triazole complexes are observed at lower energy than for $Ru(bpy)_3^{2+}$ (λ_{max} 615 nm) [11]. A maximum at 627 nm with a shoulder at 660 nm was observed for $[(bpy)_2Ru(pzH)_2](PF_6)_2$ (see Table I), but no evidence for a 620 nm emission was observed in our compounds. It is assumed that in these compounds the emitting state is the π^* (bpy) $\leftarrow d\pi$(Ru)MLCT excited state as has been proposed for other bis(bpy)Ru complexes [5]. The maximum for the Phtrz complex is found at slightly higher energy than for the other compounds, suggesting a somewhat more efficient back-donation from the metal to the triazole ligand in this complex. The intensity of the emission of the Htrz complex is only about 30% of that of the Phtrz complex and no emission was observed for $(bpy)_2Ru(trz)_2 \cdot H_2O$.

Redox-chemistry

In Table I the electrochemical data of the reported triazole compounds have been listed. The compounds were measured in CH_3CN to make comparison with related compounds possible. As $(bpy)_2Ru(bpy)_2Ru(trz)_2 \cdot H_2O$ is not soluble in acetonitrile this compound, together with the corrresponding Htrz complex, was measured in DMSO. The data obtained for the Altrz complex show that little difference in the position of the redox couples is found in the two solvents. However, the peak-to-peak separation found in CH_3CN is about 80 mV for all redox couples while in DMSO peak-to-peak separations up to 400 mV are observed.

For the cationic species $Ru^{III/II}$ waves at about 1.0 V *vs.* SCE are observed. Like in the corresponding pyrazole compound deprotonation of Htrz has a large influence on the position of this redox couple. The shift of the $Ru^{III/II}$ wave towards less positive

TABLE II. Infrared Absorptions between 600 and 700 cm^{-1} of $Ru(bpy)_2$ Complexes of 1,2,4-Triazoles.[a]

Compounds	Triazole Ring deform.	bpy vibration	Triazole Ring deform.	Other vibrations
$[(bpy)_2Ru(Htrz)_2](PF_6)_2 \cdot \frac{1}{2}(CH_3)_2CO$	690w, 682w	659w, 648w	630sh, 622m	
Htrz	681s		650s, 632sh	
$(bpy)_2Ru(trz)_2 \cdot H_2O$	686m	662m, 643sh	676s, 650m	
$[(bpy)_2Ru(Phtrz)_2](PF_6)_2$	687s	659w	645m	695m, 667w, 610w
Phtrz	685m		642m	695s, 670m, 609m
$[(bpy)_2Ru(Altrz)_2](PF_6)_2$	688w	659w, 645w	632m	
Altrz	688vw		640vs	
$[(bpy)_2Ru(Metrz)_2](PF_6)_2 \cdot H_2O$	690w	660w, 648w	630s	675w
Metrz	682vw		628vs	671m
$(bpy)_2RuCl_2 \cdot 2H_2O$		659w, 645w	–	

[a] w = weak; s = strong; m = medium; sh = shoulder, v = very.

voltage is possibly explained by the stronger electron donor properties of trz compared to Htrz.

In addition to the $Ru^{III/II}$ wave two more redox couples are found. At about −1.45 V and −1.70 V *vs.* SCE waves are observed, which are most likely due to a stepwise reduction of the bipyridyl ligands. Similar redox couples have been reported in other $Ru(bpy)_2$ complexes [2, 3]. All the redox couples observed appeared to be reversible, although the interpretation of the cyclic voltammograms obtained in DMSO was more difficult by the occurrence of solvent redox reactions.

Infrared Spectra

The infrared spectra show both bpy and triazole vibrations. The presence of acetone (ν_{CO}: 1710 cm^{-1}) in the Htrz complex and of water in the trz and Metrz compounds is confirmed by the IR data. Information about the coordination mode of 1,2,4-triazoles can often be obtained from the triazole out-of-plane deformation modes, which are found between 600 and 700 cm^{-1}. These vibrations are useful to deferentiate between monodentate and bidentate coordination [6]. They can also be used to investigate the nature of the coordination of Htrz and trz for which different coordination modes exist [12]. Furthermore, information about the position of the N–H proton in Htrz compounds can be obtained.

For $[(bpy)_2Ru(Htrz)_2](PF_6)_2$, two sets of triazole ring torsion vibrations are observed, indicating the presence of two different triazole species (see Table II). The data suggest that in the main fraction, the N–H proton is located on the 4-position. This species shows a strong absorption at 622 cm^{-1} and a weak one at 682 cm^{-1}. In a smaller fraction, the proton is located at the 1-position, resulting in two vibrations (630 and 690 cm^{-1}) of equal intensity [12a]. A number of geometries for this compound are possible and these are given in Fig. 2. In combination with the NMR data species II and III are favoured.

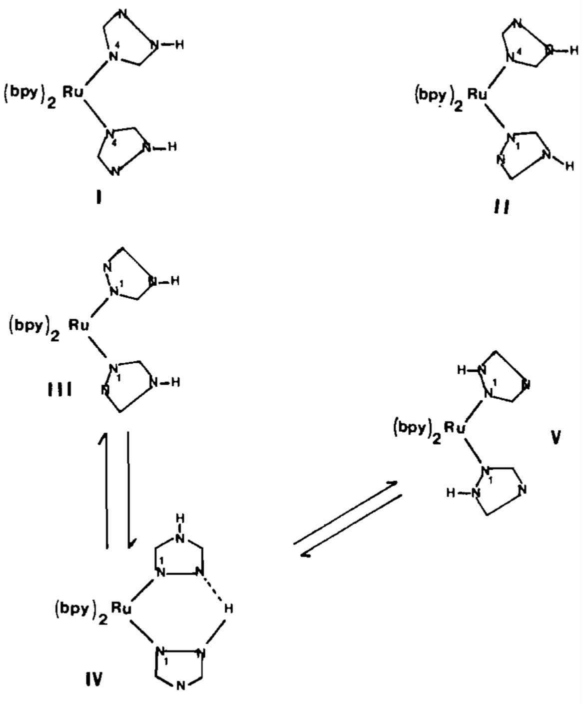


Fig. 2. Possible coordination modes of 1,2,4-triazole in $[(bpy)_2Ru(Htrz)_2](PF_6)_2$.

Deprotonation of Htrz strongly influences the position of the triazole deformation modes. The band found at 622 cm^{-1} in the Htrz complex shifts to 676

TABLE III. 80 MHz ^{1}H NMR Data of Ru(bpy)$_2$ Complexes of 1,2,4-Triazoles.

Compounds	Solvent	Chemical shift in ppm[a]		
		Triazole ring protons	6′-bpy protons	Other bpy protons
$[(bpy)_2Ru(Phtrz)_2](PF_6)_2$	CD_3CN	8.66; 8.64	9.32; 9.25	8.36–7.28
Phtrz	CD_3CN	8.62 (s, 2H)		
Phtrz	CD_3OD	8.96 (s, 2H)		
$[(bpy)_2Ru(Metrz)_2](PF_6)_2$	CD_3CN	8.15; 8.05	9.17; 9.08	8.36–7.13
Metrz	CD_3OD	8.50 (s, 2H)		
$[(bpy)_2Ru(Altrz)_2](PF_6)_2$	CD_3CN	8.23; 8.10	9.20; 9.14	8.46–7.22
Altrz	CD_3CN	8.36 (s, 2H)		
$[(bpy)_2Ru(Htrz)_2](PF_6)_2$	CD_3CN	8.35 broad	9.31; 9.25, 9.14; 9.08, 8.73; 8.67	8.40–7.15
$(bpy)_2Ru(trz)_2$	CD_3OD	7.82; 7.40	9.55; 9.47	8.43–7.20
Htrz	CD_3OD	8.36 (s, 2H)		
$[(bpy)_2Ru(Altrz)_2](PF_6)_2$	$CD_3CN + CF_3COOD$	8.66; 7.93	8.91; 8.82	8.50–7.00
$[(bpy)_2Ru(Htrz)_2](PF_6)_2$	$CD_3CN + CF_3COOD$	8.52; 8.00	9.22; 9.17, 9.01; 8.94 8.69; 8.63	8.52–7.18

[a] As the spectra are very complex, an exact integration of the peaks is not possible. Triazole ring protons appear as singlets and 6′-bpy protons as doublets.

cm^{-1} upon deprotonation. This is in agreement with spectra obtained for other triazolato complexes [12]. The infrared activity of the second triazole deformation vibration as 686 cm^{-1} points to a rather unusual monodentate coordination of the triazolato anions. The presence of the triazole vibration at 650 cm^{-1} is not fully understood. A possible explanation could be the presence of hydrogen bonding between triazole and water. The presence of a band at 686 cm^{-1} points to a 1-coordination for the triazolato anion.

With 4R-1,2,4-triazoles, the symmetry of the triazole ring is mainly determined by the substituent [6b, 13]. Monodentate coordination causes, in most cases, only a small distortion of the local C_{2v} symmetry of the triazole ring [6d]. Distortion of the C_{2v} symmetry of the triazole nucleus should also in these cases result in the infrared activity of a second out-of-plane ring vibration, which is located around 690 cm^{-1}. On close examination of the infrared data (see Table II), it is observed that this absorption indeed gains intensity upon coordination. This strongly suggests monodentate coordination of the 4R-1,2,4-triazole ligands.

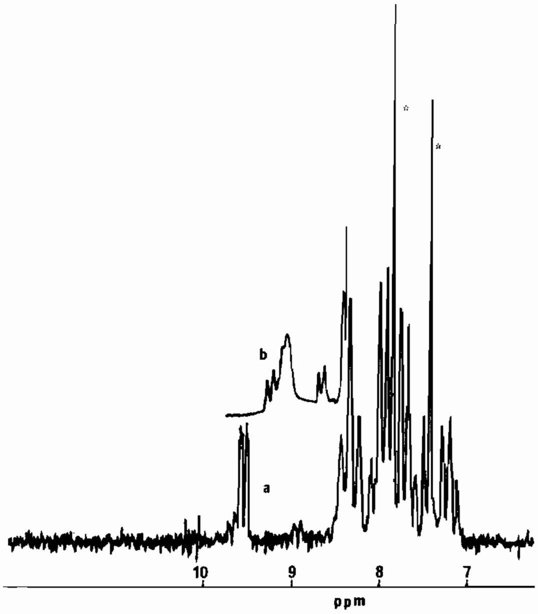


Fig. 3. 80 MHz ^{1}H NMR spectra of a) $(bpy)_2Ru(trz)_2 \cdot H_2O$ in CD_3OD *triazole protons. b) 6′-bpy protons in $[(bpy)_2Ru(Htrz)_2](PF_6)_2$ measured in CD_3CN.

^{1}*H NMR Spectra*

We have shown recently that proton NMR spectra can be a useful tool for the study of triazole complexes in solution [6d]. It was shown that unambiguous information about the coordination mode of the ligands can be obtained. NMR spectra can also be used to determine the *cis*- or *trans*-orientation of the bipyridyl ligands [3j, 14]. Spectral data, obtained in CH_3CN, have been listed in Table III.

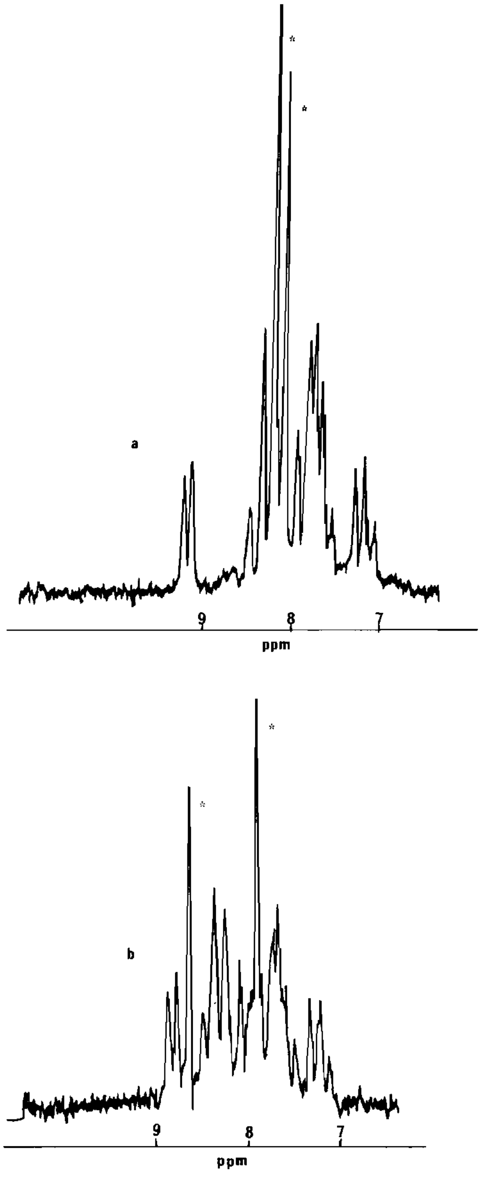
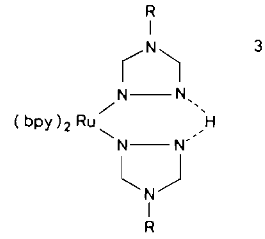


Fig. 4. 80 MHz ^{1}H NMR spectrum of [$(bpy)_2Ru(Altrz)_2$]-$(PF_6)_2$ in: a) CD_3CN; b) CD_3CN + CF_3COOD. *triazole ring protons.

The compounds show all the resonances which are expected for triazole complexes of bis(bpy)Ru-(II). A series of multiplets is observed between 7.4 and 8.4 ppm and a doublet at about 9.2 ppm. The patterns observed are characteristic for *cis*-$(bpy)_2$-Ru(II) complexes [3j, 14]. A typical spectrum has been given in Fig. 3.

For most compounds two distinct singlets are observed between 8.5 and 7.5 ppm, depending on the nature of the triazole ligand (see Fig. 3). These resonances have been assigned to the two protons of the triazole ring. Resonances which can be attributed to methyl-, allyl- and phenyl-groups are observed in the usual positions [6d] and only small shifts are observed upon coordination. The presence of two singlets for the triazole ring protons indicates a monodentate coordination of the triazole ligands, as in this case the protons will be inequivalent. This was confirmed earlier by the ^{1}H NMR data and crystal structure of $Cr(CO)_5Metrz$ and related compounds [6d, e].

Experiments with acidified CD_3CN were carried out to investigate whether a protonation of thr coordinated triazole ligands is taking place under these conditions. Fig. 4a,b shows that upon addition of CF_3COOD protonation is indeed taking place, as evidenced by large shifts of the triazole protons. Probably a species like VI is formed under these conditions.



VI

Infrared spectra already showed that different species are present in the solid state in the Htrz complex. It was hoped that additional information about the nature of these species could be obtained from the NMR spectra. The pattern of the bipyridyl resonances is often indicative for the nature of a particular complex. On coordination, one of the 6-protons of each bpy ligand is found at higher field than in the free ligand, while the other is deshielded and shifted to low field. The position of the low field doublet in bis(bpy) complexes is extremely sensitive to the nature of the fifth and sixth ligand [3j, 14]. The presence of three resonances between 9 and 10 ppm, which are attributed to 6-protons of the bpy ring, suggest that also in solution two species are present. The doublet observed at 9.14 and 9.08 ppm (see Fig. 3b) points to a [$(bpy)_2RuX_2$] species and doublets centred at 9.28 and 8.70 ppm are typical for [$(bpy)_2$-RuXY] species. From the integration we assume a 3:1 ratio for these two compounds. Because of the complexity of the spectrum in the bpy region, no unambiguous assignment of the different compounds can be made. But in combination with the infrared data species I and II in Fig. 2 are favoured.

Acid-Base Behaviour

UV/VIS and NMR spectra suggest that the nature of the 1,2,4-triazole complex depends strongly on the solvent and on the pH of the solution. Without the presence of base a partial deprotonation of

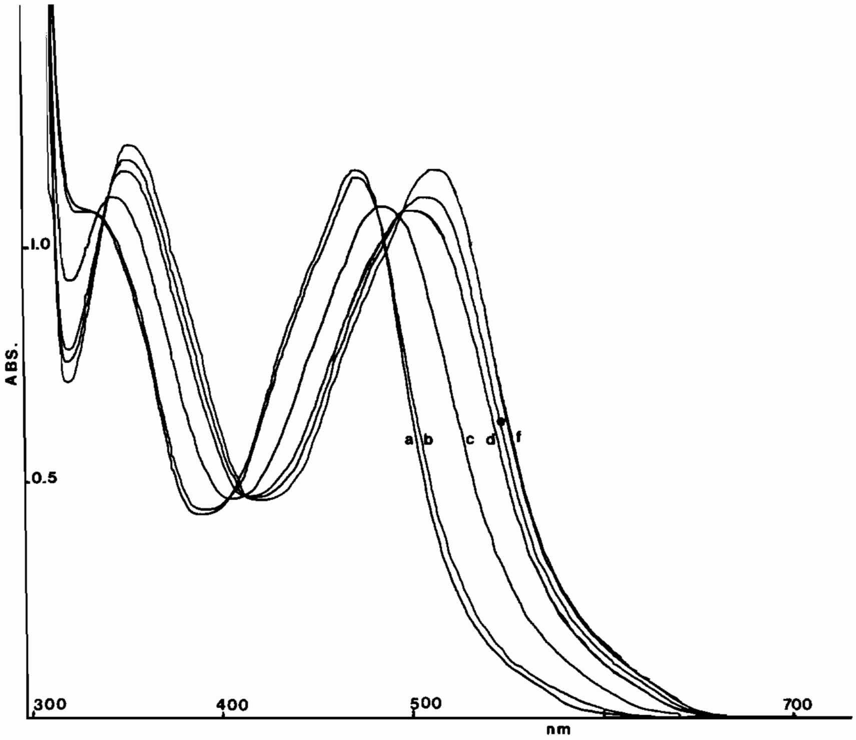


Fig. 5. Absorption spectrum of $[(bpy)_2Ru(Htrz)_2]^{2+}$ in 50% aqueous ethanol at different pH. (Conc. 1.2×10^{-4} *M*/l) a) pH = 3.5; b) pH = 5.3; c) pH = 6.9; d) pH = 8.0; e) pH = 8.5; f) pH = 9.5.

$[(bpy)_2Ru(Htrz)_2]^{2+}$ is observed in ethanol. $(bpy)_2Ru(trz)_2$ has a λ_{max} of 512 nm in ethanol but addition of water to an ethanol solution shifts the maximum to 480 nm, indicating a partial protonation of the trz-groups. NMR experiments showed that in CD_3CN no detectable deprotonation of coordinated Htrz is taking place. Figure 5 shows the pH dependency of the electronic spectrum of the Htrz complex in 50% ethanol/water. Two different protonation steps are observed:

$$[(bpy)_2Ru(Htrz)_2]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}$$

$$[(bpy)_2Ru(trz)(Htrz)]^{+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} (bpy)_2Ru(trz)_2 \qquad (3)$$

$$pK_a1 \sim 6.5 \qquad pKa_2 \sim 8.0$$

Furthermore a shift of the λ_{max} from 470 to 462 at pH < 2 suggests that at low pH a second protonation of Htrz is taking place:

$$[(bpy)_2Ru(Htrz)_2]^{2+} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}}$$

$$[(bpy)_2Ru(H_2trz)(Htrz)]^{3+} \qquad (4)$$

pKa (base)

This later reaction was confirmed by ^1H NMR spectra of the Phtrz derivative in CD_3CN (see Fig. 4).

An estimation of the pK values was made using UV/VIS spectroscopy. An accurate determination of the pKa values is difficult, as a number of equilibria are involved. For pKa_1 and pKa_2, values of 6.5 ± 0.4 and 8.0 ± 0.4 respectively, were obtained using a 0.1 *M* phosphate buffer. No attempts were made to measure the pKa (base) of the complex. For the free ligand at pKa (base) of 2.27 and a pKa (acid) of 10.26 have been reported [15]. The results obtained for the coordinated ligand therefore seem acceptable.

Conclusions

The results of this investigation show that under the used reaction conditions monodentate coordination of 1,2,4-triazoles in bis(bpy) complexes of Ru(II) occurs. This is especially surprising in the case of the triazolato complex. The spectroscopic data indicate that the π-bonding properties of 1,2,4-triazole are relatively weak. This possibly explains the monodentate behaviour of these ligands in the bis(bpy)Ru complexes, as the highest occupied metal orbitals have a strong π-character and MLCT processes are important. The observed weak metal-to-ligand π-backbonding is in agreement with results obtained for a series of Group VI metal pentacarbonyl complexes with 4R-1,2,4-triazoles [6d,e]. This suggests that in polynuclear transition metal compounds, the magnetic exchange through bridging 1,2,4-triazoles is mainly determined by the overlap of the metal-ligand σ-bonds and not by the π-system of the ligand as was suggested before [6a].

We are currently investigating these compounds with regard to their photochemical properties. Further studies will also be carried out to elucidate the exact structure of the Htrz complexes.

Acknowledgements

The authors are indebted to Professor J. Reedijk and Dr. J. M. Kelly for their interest in this study. We thank Professor T. J. Meyer and Drs. W. R. Murphy and J. Schreurs for the electrochemical data and Mr. G. Lawless for the NMR spectra. The investigations were supported by the Netherlands Organisation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO). JGV thanks the National Board for Science and Technology for a fellowship. Johnson-Matthey is thanked for a generous loan of ruthenium trichloride.

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