Inorganica Chimica Acta, *171* (1990) 223–228

Synthesis, Spectroscopic and Electrochemical Properties of Bis(2,2′-bipyridyl)(3,3′-dimethyl-5,5′-bis-1,2,4-triazole)ruthenium(II) Hexafluorophosphate

BENNE D. J. R. FENNEMA, RONALD HAGE, JAAP G. HAASNOOT*, JAN REEDIJK
Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)
and JOHANNES G. VOS
School of Chemical Sciences, Dublin City University, Dublin 9 (Ireland)

(Received October 27, 1989; revised December 27, 1989)

Abstract

A new coordination compound of the type [Ru(bpy)$_2$(H$_2$L)]$^{2+}$ has been prepared and characterised, where H$_2$L is 3,3′-dimethyl-5,5′-bis-1,2,4-triazole and bpy is 2,2′-bipyridine. The coordination mode of the chelating ligand H$_2$L has been determined using 1D NOE and 2D COSY ^{1}H NMR spectroscopy. The electronic and electrochemical properties of the complex have been studied by means of UV–Vis absorption and emission spectra as well as by cyclic voltammetry and differential pulse polarography. Deprotonation of the H$_2$L ligand in the complex results in lower oxidation potentials and in a red shift of the lowest energy dπ–π^* absorption band. This has been explained by a stronger σ-donor ability of the deprotonated ligand. The pK_a values of the ruthenium compound have been measured by UV–Vis titrations and two distinct deprotonation steps have been observed. The results obtained suggest that the bis(triazole) ligand is a rather weak π-acceptor ligand for the title compound and that only the bpy ligands are directly involved in the photophysical processes.

Introduction

The tris(2,2′-bipyridine)ruthenium(II) cation, [Ru(bpy)$_3$]$^{2+}$, has been studied widely as a possible electrocatalyst and photocatalyst for the conversion of solar energy [1, 2]. We are interested in ruthenium complexes containing asymmetric ligands and we have prepared complexes containing asymmetric bidentate ligands, such as pyridyltriazoles and pyrazyltriazoles [3–7]. In ruthenium compounds containing pyridyltriazole type ligands, the spectroscopic and electronic properties are controlled by the σ-donor capacity of the triazole ring and the π-accepting properties at the pyridine ring [5–7].

Evidence for the fact that π^* levels of the bpy ligands in those compounds are lower than those of the triazole ligand has been obtained by means of resonance Raman spectroscopy [7]. Detailed analysis of a number of such ruthenium complexes has revealed that only the bpy ligands are directly involved in the photophysical processes, while the triazole ligands are merely spectator ligands [8]. On the other hand, recent results obtained for the corresponding ruthenium compounds containing pyrazyltriazole ligands suggest a close proximity of the bpy and the pyrazyltriazole π^* levels [3].

In the present paper the synthesis, characterisation, electrochemical and electronic properties of a new cation [Ru(bpy)$_2$(H$_2$L)]$^{2+}$, where H$_2$L is 3,3′-dimethyl-5,5′-bis-1,2,4-triazole (Fig. 1) is reported. This ligand system is of interest as it can in principle coordinate through N$_1$ and N$_1$′, N$_1$ and N$_4$′ or N$_4$ and N$_4$′ to form mononuclear or dinuclear species. Furthermore the properties of the compound are expected to be pH-dependent due to (de)protonation of the triazole ring. The physical properties of the compound will be compared with those observed for other ruthenium complexes with triazole type ligands [5–7]. By comparing the data of the title compound with those of the earlier reported compounds [6–8], we hope to obtain more information about the influences of triazole ligands on the photophysical properties of ruthenium systems.

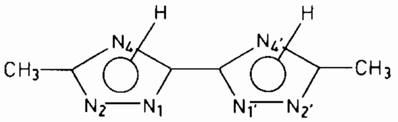

Fig. 1. Schematic structure and numbering scheme of 3,3′-dimethyl-5,5′-bis-1,2,4-triazole.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50 © Elsevier Sequoia/Printed in Switzerland

Experimental

Materials

$RuCl_3 \cdot xH_2O$ was obtained from Johnson Matthey and was used without further purification. Other chemicals were also used as received.

Synthesis of 3,3′-Dimethyl-5,5′-bis-1,2,4-triazole (H_2L)

Through a mixture of 31.25 g $H_2NNH_2 \cdot H_2O$ (0.5 mol) and 50 ml $EtOH/H_2O$ (1:1) a gentle flow of $(CN)_2$ (Matheson) was passed for 30–45 min under continuous stirring, while the reaction mixture was kept between −35 and −45 °C. The flow was stopped when white needles started to precipitate, after which the mixture was kept at −20 °C for another 30 min. After filtration and drying *in vacuo* at ambient temperature the yield for oxalic-acid-bis(amidrazone) was 50% (29.7 g) [9].

In the next step 3.5 g (0.03 mol) of oxalic-acid-bis(amidrazone) was added in portions, under stirring, to a mixture of 50 ml $HOAc/Ac_2O$ (1:1) at −20 °C. A white precipitate was formed and after 30–45 min the suspension was allowed to warm to room temperature. After filtration the product was washed with water, ethanol and finally diethyl ether. After drying *in vacuo* at room temperature, the yield was 75% (4.6 g).

The final step in the synthesis was the formation of the triazole rings by heating the white solid obtained on a hot plate until no more water was evaporating (15–20 min). After recrystallisation from methanol, a yellowish solid was obtained in a 45% yield (overall yield 17%).

Characterisation was carried out by means of LC-MS and ^1H NMR.

LC-MS: $m/q = 165$ ($M + 1$ peak)

^1H NMR: $\delta = 2.36$ ppm (s, CH_3) in $(CD_3)_2SO$.

Synthesis of $[Ru(bpy)_2(H_2L)](PF_6)_2 \cdot H_2O$

$[Ru(bpy)_2Cl_2]$ was synthesised according to the method described by Sullivan *et al.* [10]. One equivalent of $[Ru(bpy)_2Cl_2]$ (0.52 g, 1 mmol) was heated at reflux with H_2L (0.25 g, 1.5 mmol) in $EtOH/H_2O$ (5:1, 120 ml) for two days. The dark red solution was evaporated to dryness and the brown solid obtained was dissolved in a minimal amount of water. Purification was performed by column-chromatography (stationary phase Sephadex C-25, eluent 0.06 M NaCl). The fraction was concentrated under reduced pressure to 10–20 ml and $[Ru(bpy)_2(H_2L)](PF_6)_2 \cdot H_2O$ was precipitated by adding a filtered saturated solution of two equivalents of NH_4PF_6. The red solid was filtered. Recrystallisation from acetone/ethanol yielded a microcrystalline product. No crystals suitable for a X-ray structure determination were obtained. Yield 40% (320 mg).

Anal. Calc. for $[Ru(bpy)_2(H_2L)](PF_6)_2 \cdot H_2O$: C, 35.26; H, 2.96; N, 15.82; P, 7.00. Found: C, 35.22; H, 3.01; N, 15.18; P, 6.67%. All efforts to obtain a dinuclear species $[(Ru(bpy)_2)_2(H_2L)]^{4+}$, with H_2L as the bridging ligand by using procedures described earlier in the literature [5, 6] failed.

Equipment and Physical Measurements

UV–Vis spectra were recorded on a Perkin-Elmer 330 spectrophotometer or a Shimadzu UV-240 spectrophotometer using matched 1 cm quartz cells in a Britton Robinson buffer (0.04 mol/l in acetic acid, phosphoric acid and boric acid). Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrophotometer equipped with a Hamamatsu red sensitive detector using an emission slit width of 2.5 and 10 nm (at 77 K and room temperature respectively) in methanol or in a Britton Robinson buffer. No correction for photomultiplier response was made.

The ^1H COSY and NOE spectra were obtained on a Bruker 300 MHz spectrometer in $(CD_3)_2CO$. For the COSY spectrum 256 FIDs of 8 scans each, consisting of 1K data points, were accumulated. After digital filtering (sine-bell squared), the FID was zerofilled to 512 W in the F_1 dimension. Acquisition parameters were $F_1 = \pm 500$ Hz, $F_2 = 1000$ Hz, and $t_{1/2} = 0.001$ s; the recycle delay was 1.5 s. For the NOE measurements the technique described by Neuhaus was applied [11]. The ^1H NMR spectrum of the ligand was obtained on a Jeol FX-200 200 MHz spectrometer in $(CD_3)_2SO$. All peaks positions are relative to TMS.

High performance liquid chromatography (HPLC) was carried out using a Waters 990 Photodiode array HPLC system in conjunction with a NEC APC III computer, a Waters pump model 6000 A, a 20 μl injector loop and a μ Partisil SCX radial PAK cartridge. The detection wavelength used was 280 nm. The mobile phase used was CH_3CN/H_2O (80/20, vol./vol.) containing 0.08 M $LiClO_4$ with a flow rate of 2.0 ml/min.

Differential pulse polarographic measurements between −2.0 and +2.0 V were carried out in a 0.1 M solution of tetrabutylammonium perchlorate in CH_3CN, by using an EG & G Par C 303 combined with an EG & G 384 B polarographic analyser. The scan rate was 4 mV/s with a pulse height of 20 mV; for the cyclic voltammograms a scan rate of 100 mV/s was used. The reference electrode was a saturated potassium chloride calomel electrode (SCE) in combination with a glassy carbon working electrode and a platinum wire as counter electrode. Before each measurement the CH_3CN solutions were purged with argon for 30 s.

The electrochemical data of the species $[Ru(bpy)_2(HL)]^{1+}$ and $[Ru(bpy)_2(L)]^0$ were obtained by adding small amounts of a concentrated solution of

TABLE 1. ^1H NMR data for $[Ru(H_2L)(bpy)_2](PF_6)_2$ and $[Ru(bpy)_2(L)]$ in $(CD_3)_2CO$ (δ in ppm)

Compound	CH_3 [a]	CH_3 [b]	H_3 [c]	H_6 [c]	H_4 [c]	H_5 [c]
$[Ru(H_2L)(bpy)_2]^{2+}$	2.47 (+0.11)	1.82 (−0.54)	8.71−8.79 (4H)	8.09−8.19 (4H)	7.45−7.64 (4H)	7.92−8.44 (4H)
$[Ru(bpy)_2(L)]^0$	2.15 (−0.21)	1.37 (−0.99)	8.53−8.64 (4H)	7.91−7.98 (4H)	7.32−7.46 (4H)	7.84−8.07 (4H)

The shift of the methyl signals relative to the free ligand is given in parentheses. [a] Methyl signal of the N_1 bound triazole ring. [b] Methyl signal of the N_4' bound triazole ring. [c] bpy resonances.

KOH in EtOH before measurement. The presence of the correct species was checked using UV–Vis measurements.

Mass spectroscopy (LC-MS) was performed on a Finnigan MAR SQ-70 triple quadrupole mass spectrometer equipped with a thermospray interface in the discharge-on mode with methanol as solvent. By this method the mass of the protonated molecule is found. Due to the fact that LC–MS uses a soft ionisation technique almost no fragmentation occurs.

Results and Discussion

NMR Spectroscopy

The proton NMR spectrum of the title compound shows apart from the bpy resonances two non-equivalent methyl signals with equal intensities (Table 1). This could originate either from a mixture of two isomers, present in an equal ratio, or one compound containing an asymmetrically coordinated H_2L ligand. As will be discussed in the next section, the fact that only one oxidation peak is present for this compound, suggests that only one isomer is present. This is further confirmed by HPLC showing the presence of only one species with a retention time of 15.1 min. The coordination mode of H_2L resulting in non-equivalent methyl signals is via N_1 and N_4'.

In order to assign the two methyl resonances, NOE (Nuclear Overhauser Effect) experiments were also carried out. Irradiation of the singlet signal at 2.47 ppm did not enhance any bpy resonance. On the other hand, after irradiation of the methyl signal at 1.82 ppm, a clear increase in intensity for two H_6 protons was observed. The methyl group of the N_1 bound triazole ring is not expected to have a significant interaction with a bpy ligand, because of the large distance between the two groups. The methyl group of the N_4' coordinated triazole ring, however, is located in the vicinity of a bpy ligand. As observed by Steel *et al.* [12], the methyl group adjacent to the coordinating nitrogen atom of 3,5-dimethyl-1-(2-pyridyl)-pyrazole is shifted significantly upfield.

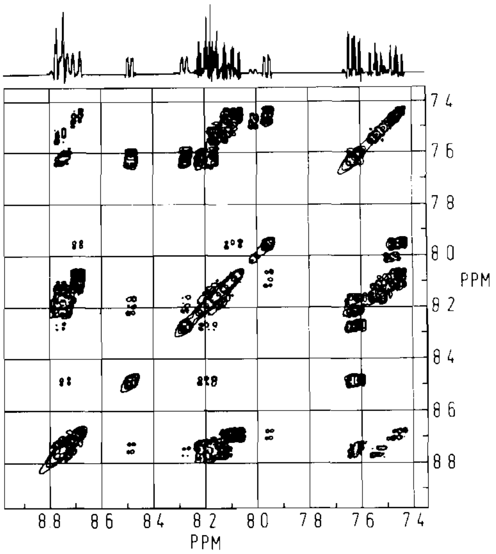

Fig. 2. ^1H COSY spectrum of $[Ru(bpy)_2(H_2L)]^{2+}$ cation at room temperature in $(CD_3)_2CO$.

This shift is caused by the ring current of that pyridine ring, resulting in a downfield shift of the signal. It is therefore concluded that the methyl resonance of the N_4' bound ring, is found at 1.82 ppm, while the methyl signal of the N_1 coordinated triazole ring, is located at 2.47 ppm. A similar behaviour has been observed for the deprotonated complex (Table 1). The consequence of this coordination mode is also that the two bpy ligands are also magnetically non-equivalent. This is consistent with the observed 4 sets each of 4 protons (Fig. 2). The chemical shift ranges of the bpy protons are given in Table 1.

Electrochemistry

The results obtained from differential pulse polarography are presented in Table 2. The cyclic voltammetric measurements indicate that all redox processes are quasi-reversible as shown by the peak-to-peak separations of 90–200 mV [14]. The data indicate that the oxidation potential is lowered upon deprotonation of the triazole ligand. This suggests that the deprotonated ligand has better σ-donor properties than bpy. For $(HL)^{1-}$ and $(L)^{2-}$ the increased σ-donor capacities can be explained by a higher electron density on the ligand system. A similar behaviour has been observed for ruthenium(II) complexes with pyridyltriazole ligands (see also Table 2). Deprotonation of this type of ligands tends to destabilise the metal d orbitals [15], which results

TABLE 2. Electrochemical and electronic properties of $[Ru(bpy)_2(H_xL)](PF_6)_2$ and related compounds

Entry	Compound[a]	Oxidation (V)[b]	Reductions (V)[b]			d–π* (nm) (ε)[c]	Emission (nm)		Reference
							77 K	RT	
1	$[Ru(bpy)_2(H_2L)]^{2+}$	1.16	−1.40	−1.50		450 (0.8)	586	620	
2	$[Ru(bpy)_2(HL)]^{+}$	0.78	−1.50	−1.88		472 (0.8)	592	660	
3	$[Ru(bpy)_2(L)]^{0}$	0.49	−1.59	−1.87		494 (0.8)	660	690	
4	$[Ru(bpy)_3]^{2+}$	1.27	−1.31	−1.50	−1.77	451 (1.4)	582	608	13
5	$[Ru(bpy)_2(HL1)]^{2+}$	1.20	−1.55	−1.81		444 (1.0)	587	600	6
6	$[Ru(bpy)_2L1)]^{1+}$	0.79	−1.50	−1.72		476 (0.9)	610	660	6
7	$[Ru(bpy)_2(L2)]^{2+}$	1.20	−1.42	−1.64		452 (1.0)	585	600	6

[a] H_2L = 3,3′-dimethyl-5,5′-bis-1,2,4-triazole, HL1 = 3-methyl-5-pyridin-2-yl-1,2,4-triazole, L2 = 1-methyl-3-pyridin-2-yl-1,2,4-triazole. [b] Obtained using differential pulse polarography; oxidation and reduction potentials are listed vs. SCE. [c] ε is given in $10^4\ mol^{-1}\ l\ cm^{-1}$.

in a lower oxidation potential. For all species, bpy-based reduction waves were observed between −1.4 and −1.6 V versus SCE and no H_2L based reduction waves were observed upto −2.0 V. Due to the poor solubility of H_2L in CH_3CN no electrochemical measurements were possible for the free ligand. Previous work on pyridyltriazole ligands [6] has shown however, that these ligands are more difficult to reduce than bpy and it is therefore likely that this also will be the case for the H_2L ligand.

Upon deprotonation the first reduction wave shifts to a more negative value, probably because the positive charge of the complex is lowered.

Electronic Spectra and Ground State Acid–Base Properties

The maxima obtained for the lowest energy MLCT bands are given in Table 2. The cation $[Ru(bpy)_2(H_2L)]^{2+}$ exhibits a pH dependence of the lower energy metal to ligand charge transfer (MLCT) band (see Table 2 and Figs. 3 and 4). The isosbestic points observed in Fig. 3 (376 and 458 nm) and Fig. 4 (394 and 482 nm) clearly suggests that two distinct equilibria are present in this system. The observed behaviour can be explained by the presence of two protonation equilibria

$$[Ru(bpy)_2(H_2L)]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Ru(bpy)_2(HL^-)]^{1+}$$

$$pK_{a_1} = 4.8 \pm 0.1$$

$$[Ru(bpy)_2(HL^-)]^{1+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [Ru(bpy)_2(L^{2-})]^{0}$$

$$pK_{a_2} = 7.9 \pm 0.1$$

The red shift of the MLCT band with increasing pH is consistent with a destabilisation of the metal d orbitals, because of the increased σ-donor capacities of the triazole ring. As the π* levels of the bpy ligands

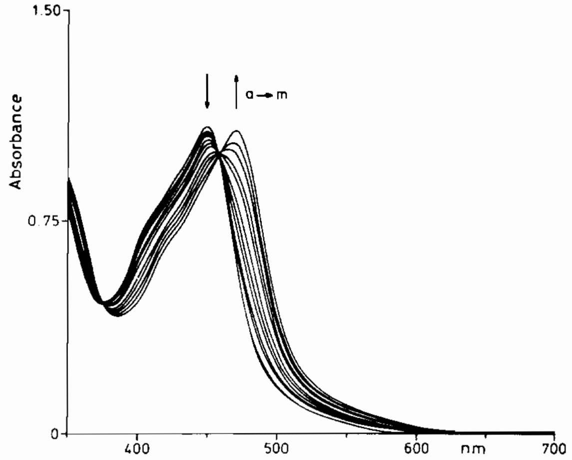

Fig. 3. UV–Vis absorption spectra of the $[Ru(bpy)_2(H_xL)]^{x+}$ cation (x = 2, 1) in aqueous Britton Robinson buffer at pH between 1 and 6. a → m: pH = 1.62; 3.20; 3.79; 4.00; 4.38; 4.44; 4.66; 4.88; 5.07; 5.31; 5.55; 6.03.

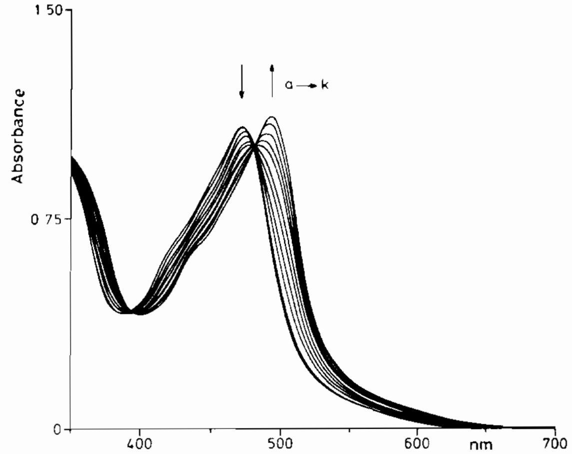

Fig. 4. UV–Vis absorption spectra of the $[Ru(bpy)_2(H_xL)]^{x+}$ cation (x = 1, 0) in aqueous Britton Robinson buffer at pH between 6 and 10. a → k: pH = 6.41; 6.76; 7.23; 7.47; 7.74; 8.00; 8.22; 8.39; 8.65; 9.04; 10.37.

are not altered significantly when the triazole ligand is deprotonated, this leads to a smaller energy difference between the filled d orbitals and the empty π^* orbitals of the bpy ligands.

A similar effect has been observed for $[Ru(bpy)_2(HL1)]^{2+}$, with HL1 = 3-methyl-5-(pyridin)-2-yl-1,2,4-triazole, suggesting that the electronic properties of the bistriazole ligand are rather similar to those of the pyridyltriazole ligands in this type of ruthenium compounds [6].

Emission Spectra and Excited State Acid–Base Chemistry

The emission data obtained at 77 K and room temperature are given in Table 2. Based on the results of the electrochemical measurements and resonance Raman spectroscopy of pyridyltriazole complexes, [7, 8] it is expected that the weak emissions observed are bpy based. The intensity of the emission at room temperature is pH dependent. Below pH = 4 and at high pH, only rather weak emission is observed and the maximum emission intensity is reached at pH = 6. Also the emission maximum is pH dependent with the value of 620 nm at pH = 0, a value of 660 nm at pH = 6, while at pH = 10.13, a value of 690 nm is obtained. This shows that all species have clearly different emission properties. The intensity maximum at pH = 6 suggest that $[Ru(bpy)_2(HL)]^{1+}$ is the strongest emitting species. Both ground state equilibria (see previous section) yield a maximum concentration of $[Ru(bpy)_2(HL)]^{1+}$ around pH = 6 (see Fig. 5).

Excited state pK_a values, $pK_a{}^*$, can be estimated using the Förster cycle [16]

$$pK_a{}^* = pK_a + (0.625/T)(\nu_b - \nu_a)$$

where T is the absolute temperature (300 K), ν_b and ν_a are the energies (in cm^{-1}) of the emission maxima for the base and acid forms respectively. Using the emission maxima obtained at 300 K as a measure of the 0–0 energy, $pK_a{}^*$ values of 2.8 ± 0.2 and 6.1 ± 0.2 were obtained. These values suggest that in the excited state $[Ru(bpy)_2(H_xL)]^{x+}$ with $x = 2$ or 1 are stronger Brønsted acids when excited. This is similar to the behaviour observed for $[Ru(bpy)_2(LL')]^{2+}$ with LL′ = various substituted pyridyltriazoles [4, 17]. The lowering of $pK_a{}^*$ with respect to the ground state pK_a, confirms that H_2L is merely a spectator ligand and is not directly involved in the emission processes [4, 17]. The red shift of the emission maxima (Table 2) upon deprotonation of the compound is again consistent with the stronger σ-donation properties of the deprotonated triazole ring.

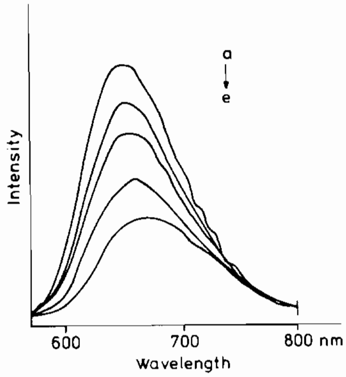

Fig. 5. Emission spectra of $[Ru(bpy)_2(H_xL)]^{x+}$ cation (x = 2, 1 or 0) at the pH values: a → e: pH = 6.02; 6.20; 6.69; 7.28; 7.84.

Conclusions

The spectroscopic, electrochemical, and HPLC data suggest that in the title compound the bistriazole ligand coordinates in an asymmetrical fashion. This is somewhat surprising, as coordination of N_4' will lead to increasing steric hindrance between the adjacent methyl group and the bpy ligands. The reason for this behaviour is at present not clear, but it is possible that, because of the better σ-donor properties of the N_1 atom [4, 17], a N_1,N_1' coordination would lead to unfavourable destabilisation of the metal orbitals. The ligand H_2L has better σ-donor capacities compared to bpy and the spectroscopic and electronic properties of the $[Ru(bpy)_2(H_2L)]^{2+}$ are pH dependent. The UV–Vis data show the presence of two clearly separated deprotonation steps. The two pK_a values obtained are similar to those found for the compound $[Ru(bpy)_2(Htrz)_2]^{2+}$ (6.2 and 8.5, Htrz = 1,2,4-triazole) [18]. The first deprotonation step is also close to the one observed for $[Ru(bpy)_2(HL1)]^{2+}$ of about 4.4 (HL1 = 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole) [6]. Probably because of the increased rigidity of the bis(triazole) ligand, the emission intensity of those bis(triazole) compounds reported here is higher than observed for $[Ru(bpy)_2(Htrz)_2]^{2+}$. Overall the physical properties of the title compound, more resemble the analogous pyridyltriazole compounds than those of $[Ru(bpy)_2(Htrz)_2]^{2+}$.

Acknowledgements

Johnson Matthey Ltd. (Reading, U.K.) are thanked for their generous loan of ruthenium trichloride. We are much obliged to C. Erkelens and A. W. M. Lefeber for measuring some of the ^1H NMR spectra and the COSY spectrum. We also want to express our gratitude to R. A. M. van der Hoeven for the MS spectrum. The authors are greatly indebted to J. W. van Hal for many successful ideas on the synthesis of the ligand and to E. Ryan (D.C.U.) for assistance with the emission experiments.

References

1 K. Kalyanasundaram, *Coord. Chem. Rev.*, *46* (1982) 159.

2 T. J. Meyer, *Pure Appl. Chem.*, *58* (1986) 1193.

3 H. A. Nieuwenhuis, J. G. Haasnoot, R. Hage, J. Reedijk, T. L. Snoeck, D. J. Stufkens and J. G. Vos, *Inorg. Chem.*, submitted for publication.

4 B. E. Buchanan, *Ph.D. Thesis,* Dublin City University, 1989.

5 R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chim. Acta, 118* (1986) 73.

6 R. Hage, R. Prins, J. G. Haasnoot, J. Reedijk and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, 1389 (1987).

7 R. Hage, J. G. Haasnoot, D. J. Stufkens, J. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, *28* (1989) 1413.

8 F. Barigalletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, to *Inorg. Chem.*, *28* (1989) 4344.

9 G. Dedichen, *Chem. Zentr. I,* (1937) 86.

10 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, *17* (1978) 3334.

11 D. Neuhaus, *J. Magn. Reson.*, *53* (1983) 109.

12 P. J. Steel, F. Lahousse, D. Lerner and C. Marzin, *Inorg. Chem.*, *22* (1983) 1488.

13 D. P. Rillema, G. Allen, T. J. Meyer and D. Conrad, *Inorg. Chem.*, *22* (1983) 1617.

14 H. B. Ross, M. Boldaji, D. P. Rillema, C. B. Blanton and R. P. White, *Inorg. Chem.*, *28* (1989) 1013.

15 M. Haga, *Inorg. Chim. Acta, 77* (1983) L39.

16 J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, *12* (1976) 131.

17 B. E. Buchanan, J. G. Vos, M. Kaneko, W. J. M. van der Putten, J. M. Kelly, R. Hage, R. A. G. de Graaff, R. Prins, J. G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

18 C. Long and J. G. Vos, *Inorg. Chim. Acta, 89* (1984) 125.