Electrochemical, photophysical and photochemical properties of a hexanuclear ruthenium(II) bis(2,2'-bipyridyl) complex containing a tris(pyrazyltriazole)benzene ligand

Hans E.B. Lempers[a], Jaap G. Haasnoot[a,*], Jan Reedijk[a], Ronald Hage[b],
Frances M. Weldon[c], Johannes G. Vos[c,*]

[a]Leiden Institute of Chemistry, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, Netherlands
[b]Unilever Research Laboratory, Olivier van Noortlaan 120, 3133 AT Vlaardingen, Netherlands
[c]School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Abstract

The synthesis of a hexanuclear ruthenium(II) bis(2,2'-bipyridyl) complex with 1,3,5-tris(5-(pyrazine-2-yl)-1,2,4-triazol-3-yl)benzene (H_3tpzb) is reported. Three Ru(bpy)$_2$ groups are bound to the ligand in a bidentate mode (via N1 of the triazole and N2 of the pyrazine ring) and three Ru(bpy)$_2$Cl groups are bound in a monodentate fashion (via N4 of the pyrazine ring). The absorption spectrum of the deprotonated complex shows two intense MLCT bands in the visible region, one at 465 nm originated from the bidentate Ru(bpy)$_2$ moieties and the other one at 515 nm from the Ru(bpy)$_2$Cl groups. Protonation leads to a shift to 445 nm of the MLCT band for the bidentate sites and to 530 nm for the monodentate sites. The oxidation potential of the bidentate Ru(bpy)$_2$ groups is 220 mV higher than that of the monodentate bound Ru(bpy)$_2$Cl for the deprotonated complex. Protonation of the triazole rings leads to a further increase of the redox potential of only the Ru(bpy)$_2$ site. No differences in redox potentials for each of the three Ru(bpy)$_2$ groups and each of the three Ru(bpy)$_2$Cl groups were observed, suggesting at best a very weak interaction between these metal centres. The electrochemical properties have been correlated with the electronic energies. Photolysis experiments have revealed that the monodentate ruthenium groups are dissociated when the complex is irradiated. This process is much faster for the deprotonated complex than the protonated compound. The analysis of the reaction products indicate the formation of [{Ru(bpy)$_2$}$_3$(tpzb)]$^{3+}$ and [{Ru(bpy)$_2$}$_3$(H_3tpzb)]$^{6+}$, respectively.

1. Introduction

The electrochemical and photophysical properties of [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) and its analogues have been investigated in great detail during the last decades because of the application of these compounds in solar energy devices [1,2]. As a result an extensive chemistry has been developed around these compounds which is aimed at obtaining photostable coordination compounds with well-developed excited-state properties [3,4]. The synthetic control available for these compounds has subsequently led to their incorporation in polynuclear structures in search of well-defined supramolecular structures [5–23]. As the photochemical and

photophysical of the mononuclear complexes are fairly well understood [4], the effect of the presence of more metal ions on the photochemical and photophysical properties of multinuclear compounds can now be studied in detail.

Recently, we reported the synthesis and characterisation of a number of mononuclear, dinuclear and trinuclear ruthenium and osmium complexes with various triazole ligands [9–20]. With the 3,5-bis(pyridin-2-yl)-1,2,4-triazolate anion, both mononuclear and dinuclear Ru(bpy)$_2$ complexes have been isolated and studied [9–18]. Electrochemical and photophysical experiments showed that in the dinuclear compounds the interaction between the two metal centres is very efficient. It was furthermore found that the deprotonated mononuclear compound is photostable, whilst the pro-
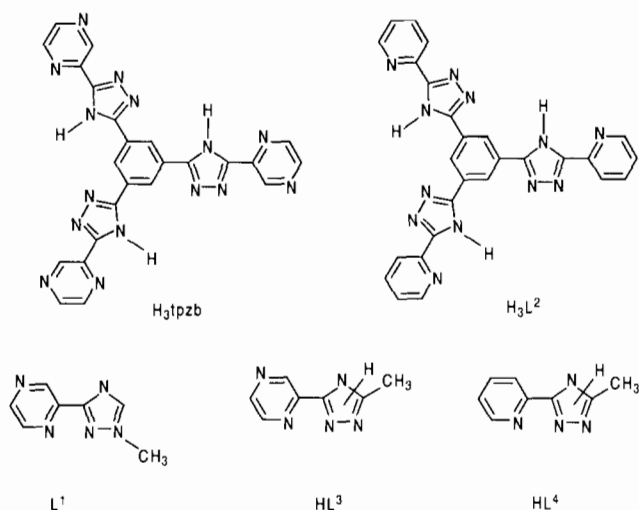
*Corresponding authors.

Fig. 1. Schematic representation of the ligands described in the text.

tonated mononuclear and the dinuclear ruthenium complexes are photolabile [18]. With the bridging ligand tris(5-(pyridin-2-yl)-1,2,4-triazol-3-yl)benzene (H$_3$L^2; see Fig. 1) trinuclear ruthenium and osmium complexes were obtained. Interestingly in this case no interaction between the different metal sites was observed [19].

In this contribution we report a novel ligand system: 1,3,5-tris(pyrazin-2-yl-1,2,4-triazole)benzene (H$_3$tpzb; see Fig. 1). The structure of this ligand allows for the coordination of three bidentate 'Ru(bpy)$_2$ groups' as well as three monodentate 'Ru(bpy)$_2$Cl groups'. In this study the interaction between the 'short distance' ruthenium groups, i.e. the Ru(bpy)$_2$ and Ru(bpy)$_2$Cl moieties at the same pyrazyltriazole ligand, and the 'long distance' Ru groups, i.e. the three Ru(bpy)$_2$ groups with each other or the Ru(bpy)$_2$Cl groups with each other, is investigated. The effect of protonation of the triazole rings on the electrochemical, photophysical and photochemical properties of the hexanuclear compound is also studied. Finally, the photochemical preparation of a trinuclear complex from the hexanuclear compound is reported. The properties observed for these compounds are compared with those observed for other similar dinuclear structures based on various triazole [9–20] and pyrazine [21–23] bridging ligands.

2. Experimental

2.1. Materials

Hydrated ruthenium trichloride was obtained as a loan from Johnson Matthey and used without further purification. The starting material, cis-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O, was synthesised according to literature methods [24].
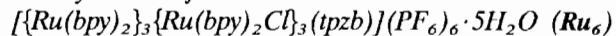
2.2. Synthesis of H$_3$tpzb

The bridging ligand 1,3,5-tris(5-(pyrazin-2-yl)-1,2,4-triazol-3-yl)benzene (H$_3$tpzb) was synthesised in four steps. A suspension of 30 g (0.24 mol) of 2-pyrazinamide and 150 ml of phosphorylchloride was stirred for 4 h at room temperature. After the mixture had been heated at reflux for 20 min, the excess of phosphorylchloride was evaporated under reduced pressure. The remaining red oil was neutralised with a saturated sodium bicarbonate solution. The 2-cyanopyrazine was extracted with diethyl ether and evaporated until dryness. Yield 14.4 g [25].

In a beaker 14.1 g (0.137 mol) of 2-cyanopyrazin was heated and after melting 6.9 g (0.137 mol) of hydrazine monohydrate were added. Ethanol was added until a clear solution was obtained. The mixture was allowed to react for 16 h, after which the pale yellow 2-pyrazylamidrazone was isolated by filtration. Yield 11.3 g.

A solution of 7.3 g (27 mmol) of 1,3,5-benzenetricarbonyl chloride in 20 ml of N,N-dimethylacetamide was added dropwise to a suspension of 11.3 g (82 mmol) of 2-pyrazylamidrazone and 8.7 g (82 mmol) of sodium carbonate in 80 ml of N,N-dimethylacetamide at 0 °C. The reaction mixture was stirred at room temperature for 3 h, after which it was poured into an ice/water mixture to precipitate a yellow solid. This material was isolated, washed with water and dried. Thermal cyclisation of the product was performed by heating the material at 200 °C for 1 h. The reaction was finished when no more water vapour escaped, yielding a grey–yellow product. Purification took place by boiling the product in ethylene glycol, in which impurities dissolved. After filtration a grey powder was isolated. Yield of H$_3$tpzb: 8.65 g (total yield 4%).

^{1}H NMR data ((CD)$_3$SO) (ppm): 9.45 (d; H3); 8.97 (s; Hbenzene); 8.82 (q; H5); 8.65 (d; H6). Mass spectroscopy: $\{M+H\}^+$: 514 [26].

2.3. Synthesis of [{Ru(bpy)$_2$}$_3$[Ru(bpy)$_2$Cl]$_3$(tpzb)](PF$_6$)$_6$·5H$_2$O (Ru$_6$)

This compound was synthesised by refluxing 50 mg (0.1 mmol) of H$_3$tpzb with 360 mg (0.7 mmol) of cis-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O in 50 ml ethanol/water (1/1 vol./vol.) for 48 h. The solution was filtered and the solvent was removed by rotary evaporation. The remaining solid was dissolved in water and precipitated by adding an excess of an aqueous NH$_4$PF$_6$ solution. The precipitate was dissolved in acetone and purified by column chromatography (neutral alumina; acetone as eluent). The compound was further purified by crystallisation from water/acetone. Yield 310 mg (78%). Anal. Found: C, 43.0; H, 3.1; N, 13.2; P, 4.3. Calc.: C, 42.6; H, 3.0; N, 13.5; P, 4.6%. Addition of acid leads to protonation

of the triazole rings, yielding [{Ru(bpy)$_2$}$_3${Ru(bpy)$_2$Cl}$_3$-(H$_3$tpzb)]$^{9+}$ in situ (abbreviated as **H$_3$Ru$_6$**).

2.4. Instrumentation and methods

^{1}H NMR spectra were recorded on a Bruker WM 300 spectrometer. UV–Vis measurements were obtained on 10^{-5}–10^{-4} molar solutions on a Perkin-Elmer 330 spectrophotometer using 1 cm quartz cells. The absorption spectra of the photolysis experiments were recorded on a Shimadzu UV-240 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer LS5 and on a Perkin-Elmer LS50 luminescence spectrometer with a variable slit width between 2.5 and 20 nm. The room temperature measurements were carried out in acetonitrile solutions, while the luminescence measurements at 77 K were carried out in methanol (approximately 10^{-5} M solutions). The spectra were not corrected for photomultiplier response. Small-scale photolysis experiments were carried out at room temperature in acetone using 1 cm cells and a 400 W medium-pressure mercury lamp with a glass cut-off filter. Preparative photochemical experiments were carried out using a medium-pressure 400 W mercury lamp fitted in an immersion well. The differential pulse polarography (DPP) experiments and the cyclic voltammograms (CV) were carried out on a EG&G Par C model 303 instrument with an EG&G 384 B polarographic analyser. The scan rate was 4 mV/s for the DPP experiments with a pulse height of 20 mV. For the cyclic voltammograms the scan rate was 100 mV/s. A saturated calomel electrode (SCE) was used as a reference electrode. The electrolyte used was acetonitrile, containing 0.1 M tetrabutylammonium perchlorate (TBAP).

Laser desorption mass spectrometry experiments were carried out as reported elsewhere [19,26].

3. Results and discussion

3.1. Synthesis of the ruthenium complex

The synthesis of the hexanuclear ruthenium(II) complex proved to be straightforward based on the known chemistry of pyrazyltriazole and tris(pyridyltriazole)-benzene ligands [9–20]. Refluxing an excess of [Ru(bpy)$_2$Cl$_2$]·2H$_2$O with the H$_3$tpzb ligand yielded the hexanuclear compound in high yield. This compound contains three bidentate Ru(bpy)$_2$ moieties and three monodentate Ru(bpy)$_2$Cl groups. From our experience with other similar triazole ligands it is likely that the coordination mode of the bidentate coordination unit is via N1 of the triazole ring, rather than N4, and the pyrazine ring. Such a coordination mode would minimise steric hindrance in the molecule [9–20]. It is noted

that many geometrical isomers may exist, depending on the relative alignment of the bpy ligands [10]. We did not attempt to separate these isomers as it has already been shown that the electronic and electrochemical properties of the geometrical isomers are very similar [27]. In the compound isolated the three triazole rings are deprotonated. This compound can easily be protonated, yielding a species that exhibits different electronic and electrochemical properties (vide infra). Refluxing smaller quantities of Ru(bpy)$_2$Cl$_2$ with the ligand, yielded mixtures of mono-, di-, tri-, tetra- and pentanuclear species [28]. Unfortunately, we were not able to obtain these complexes in a pure form.

3.2. Redox properties

The redox potentials of **Ru$_6$** and **H$_3$Ru$_6$** are listed in Table 1. The deprotonated compound exhibits a first reduction potential at -1.14 V versus SCE which is considerably less negative than in the analogous mononuclear complex with pyrazyltriazole, RuL^4 (see Table 1). Also the analogous tris(pyridyltriazole)benzene complex shows a much more negative first bpy-based reduction. The much less negative reduction reported here is in agreement with the presence of an extra electron-withdrawing metal centre on the pyrazine ring [21–23]. The ligand-based reductions of these compounds are not very well defined. This is most likely due to adsorption processes and/or deprotonation of the ligands. Nevertheless the first reduction potential observed for **Ru$_6$** strongly suggests that the first reduction potential is based on the bridging ligand [4,9–20]. The further reductions observed for **Ru$_6$** are assigned to bpy-based reductions.

The first oxidation wave is assigned to a Ru(bpy)$_2$Cl oxidation, as the presence of the chloride ion reduces the charge on the metal ion. The second oxidation wave is therefore located on the bidentate coordination unit. The metal-based oxidation potentials have some interesting features. First of all, the Ru(bpy)$_2$Cl based oxidation wave is not effected very much by protonation of the triazole ring. Furthermore, if one compares the redox potential observed for the Ru(bpy)$_2$Cl units in the hexanuclear complex (0.94 V) with that reported for [Ru(bpy)$_2$(pyrazine)Cl]$^+$ (0.88 V) [21], it is clear that the value of this redox potential is also not changed very much by the formation of the dinuclear compound. The same observation has been made for other pyrazine-based dinuclear systems [21–23]. Clearly, the distance between the Ru(bpy)$_2$Cl centre and the triazole ring is too large to result in an appreciable interaction and therefore no substantial shift of the redox potential upon formation of a dinuclear compound, or alternatively, protonation has been observed. The fact that the first metal-based redox potential is only slightly affected by protonation of the triazole ring confirms

Table 1
Electrochemical data of the ruthenium complexes discussed in the text. Relevant compounds reported before have also been included. The measurements were carried out in acetonitrile containing 0.1 M TBAP. The values were obtained by using differential pulse polarography. Potentials are listed in volt vs. SCE

Compound	Oxidation potential		Reduction potential (V)	Reference
	Ru(bpy)$_2$Cl	Ru(bpy)$_2$		
Ru$_6$	0.94	1.16	−1.14 −1.50 −1.71	this work
H$_3$Ru$_6$	0.97	1.35	adsorption	this work
Ru$_3$		1.05	adsorption	this work
RuL^1		1.32	−1.27 −1.54 −1.81	[20]
Ru$_2$L^1	0.92	1.41	−0.97 −1.51 −1.57 −1.76	[20]
Ru$_3$L^2		0.86	−1.47 −1.66 −1.82	[19]
Ru$_3$H$_3$L^2		1.18	not observed	[19]
RuHL^3		1.20	−1.48 −1.74 −2.27	[10]
RuL^3		0.80	−1.55 −1.88	[10]
RuHL^4		1.29	−1.22 −1.52 −1.77	[10]
RuL^4		0.92	−1.44 −1.66 −1.80	[10]

L^1 = 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole.
H$_3$L^2 = 1,3,5-(tris(5-(pyridin-2′-yl)-1,2,4-triazol-3-yl)benzene.
HL^3 = 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole.
HL^4 = 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole.

the nature of the redox process as being based on the ruthenium–chloro site. An interesting comparison can also be made with the 2-pyrazinecarboxylate dimer reported by Goldsby and Meyer [23]. In this compound the coordination sites are also asymmetric and the second site contains a negative charge on the bridge as well. In this compound the redox potential of the Ru–chloro site is only 40 mV higher than that observed for the symmetrical pyrazine dimer which does not contain a negatively charged carboxylate group. So clearly there is very little interaction in this type of pyrazine-based dimer between the metal centres. The differential pulse polarograms of the hexanuclear **Ru$_6$** and **H$_3$Ru$_6$** complexes each show two sharp oxidation peaks, indicating there is at best a very weak long range interaction between the three Ru(bpy)$_2$ and Ru(bpy)$_2$Cl moieties coordinated to the bridging (H$_3$)tpzb ligands [8,19]. The relative position of the redox potentials observed for the bidentate Ru(bpy)$_2$ dinuclear site and the RuCl site suggests that interaction over the pyrazine bridge is also weak.

There is, however, one interesting feature. The value observed for the second oxidation potential for the deprotonated complex (**Ru$_6$**) is surprisingly high. This value is 300 mV higher than that of the analogous trinuclear Ru(bpy)$_2$ complex with tris(pyridyltriazole)-benzene [19] and 240 mV higher than observed in a mononuclear pyrazine analogue RuL^4 (see Table 1). Furthermore, the difference between the redox potential observed for the protonated and deprotonated complex is rather small (190 mV), when compared to the one observed for the mononuclear analogue Ru(H)L^4 where it is 370 mV. Since interaction via the pyrazine ring is weak, the increased redox potential cannot be ex-

plained by strong delocalisation or by electrostatic effects. In similar pyrazine dimers the shift observed for the second redox site is generally less than 150 mV [22,23]. This suggests one could expect a maximum value of about 1.07 V for the second oxidation potential. The reduction potential measured for **Ru$_6$** suggested that the lowest π^* level is tpzb based. It is known that in general a strong π-accepting ligand yields a decrease in electron density on the metal centres and therefore a raise in oxidation potential is expected [4]. Therefore, it is likely that the relatively low π^* for the tpzb compound, yields an unexpected increase in redox potential. This conclusion is supported by the electronic spectra (vide infra). This shift in redox potential of the bidentate ruthenium moiety upon protonation of the triazole ring has been explained previously by the weaker σ-donor properties of the protonated triazole ring [8,19].

Spectroelectrochemical investigations were also carried out. However, using both electrochemical and chemical oxidation methods no evidence was obtained for the presence of an intervalence band in the near-IR region. An investigation of the visible part of the spectrum did show the expected spectroscopic changes. Also the appearance of the LMCT band at about 900 nm confirms that the complexes are indeed oxidised. This unexpected phenomenon is at present under further investigation.

3.3. Absorption spectra

The absorption spectra of [{Ru(bpy)$_2$}$_3${Ru(bpy)$_2$Cl}$_3$-(H$_3$tpzb)]$^{9+}$ and [{Ru(bpy)$_2$}$_3${Ru(bpy)$_2$Cl}$_3$(tpzb)]$^{6+}$ are shown in Fig. 2. Both species exhibit two intense
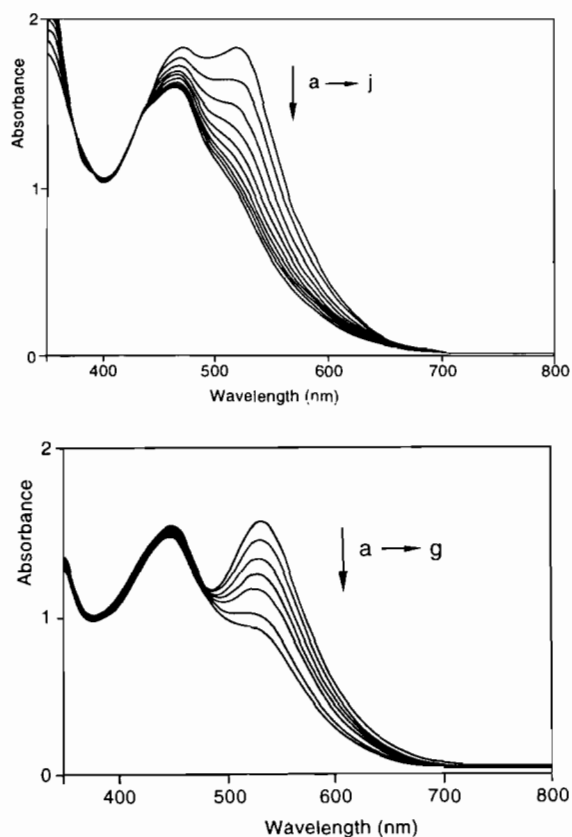
Fig. 2. Changes of the absorption spectra on irradiation of **Ru₆** (top) and **H₃Ru₆** (bottom) in acetone. For the **Ru₆** compound every 15 s a spectrum was taken (a→j: from $t=0$ to 150 s). For **H₃Ru₆**: a ($t=0$); b ($t=15$ min); c ($t=30$ min); d ($t=45$ min); e ($t=60$ min); f ($t=90$ min); g ($t=120$ min).

absorption bands in the visible region. By comparison with other similar mononuclear and dinuclear compounds (see Table 2) the higher energy band around 450 nm has been assigned to a metal-to-ligand charge transfer (MLCT) transition located on the Ru(bpy)₂ moiety bound to the pyrazyltriazole ligand in a bidentate manner [20,34]. The low-energy absorption band has been assigned to an MLCT band located on the Ru(bpy)₂Cl moiety [20]. In other dinuclear complexes which also contain the RuCl–pyrazine moiety an absorption band at similar energy is observed [21]. The electrochemical data strongly suggest that the lowest unoccupied molecular orbital (LUMO) is located on the bridging (H₃)tpzb ligand. The highest occupied molecular orbital (HOMO) is related to the oxidation potential of the metal centres [4]. As the oxidation potential of the Ru(bpy)₂Cl moiety is much lower than that of the Ru(bpy)₂ group, the energy gap between the HOMO and LUMO is smaller for the monodentate Ru(bpy)₂Cl group than for the bidentate Ru(bpy)₂ mode.

Protonation of the triazole rings leads to a blue shift of the high-energy MLCT band. This effect has been noted before (see also Table 2) and has been explained by a stabilisation of the HOMO level upon protonation

due to the weaker σ-donor properties of the protonated triazole rings [10]. A major difference with the tpzb-containing complexes and other mononuclear ruthenium–pyrazyltriazole complexes is that in the latter case a change of the LUMO from the auxiliary bpy ligands to the pyrazyltriazole ligand has been observed upon protonation [34]. For the tpzb system, the LUMO is always located on the bridging ligand system and therefore the shift in absorption energy is dominated by the change in HOMO levels rather than the switch-over of the LUMO levels.

Interestingly, the absorption energy of the Ru(bpy)₂Cl group moves to a *lower* energy level when the triazole ring becomes protonated. As discussed before, the oxidation potential of the Ru(bpy)₂Cl site is hardly affected by protonation of the triazole rings. As a result the energy of the HOMO level will not be affected to a large extent. On the other hand the protonation leads to a stabilization of the lowest π^* level [35] with the result that the energy gap between the LUMO and HOMO level becomes smaller and consequently a lowering of the MLCT band is observed.

3.4. Emission spectra

The luminescence bands of **Ru₆** and **H₃Ru₆** at room temperature and 77 K are listed in Table 2. The emission intensity for **H₃Ru₆** is much weaker than that for its deprotonated analogue. Comparison with the emission bands of the trinuclear L² complex [19], reveals that the emission energy for **Ru₆** is at a much lower energy. This does not correlate with the fact that the absorption bands observed for the bidentate Ru(bpy)₂ groups attached to L² and tpzb have similar energies. The emission energy observed for **Ru₆** is very similar to those observed for the pyrazine-bridged ruthenium dinuclear complexes (L¹) as shown in Table 2. No change in the emission spectrum of **Ru₆** has been observed upon changing the excitation wavelength between 400 and 500 nm, suggesting efficient energy-transfer processes. We therefore conclude that the emission band observed originates from the monodentate Ru(bpy)₂Cl groups and that energy-transfer processes take place from the high-energy ³MLCT states (originated from the bidentate Ru(bpy)₂ groups) to the low-energy ³MLCT states (monodentate Ru(bpy)₂Cl sites). In Fig. 3, the various processes (absorption, emission and energy transfer) are schematically presented. This interpretation is in agreement with the observation that the emission energy, like the absorption obtained for the Ru(bpy)₂Cl moiety, does not change upon protonation of the triazole ring.

3.5. Photochemistry

As mentioned before, many of the ruthenium(II) complexes studied show photoinstability. We have shown

Table 2
Electronic data for the complexes

Compound	Absorption max. λ_{max} (nm)	$(\epsilon \ (10^4 \ M^{-1} \ cm^{-1}))^a$	Emission max. (nm)		Reference
			300 K[b]	77 K[c]	
Ru_6	465 (6.72)	515 (6.72)	775	685	this work
H_3Ru_6	445 (6.35)	530 (6.50)	769	695	this work
Ru_3	460		677	650	this work
H_3Ru_3	445		675	645	this work
RuL^1	437 (1.46)		633	577	[20]
Ru_2L^1	440 (1.70)	530 (1.90)	not observed	705	[20]
Ru_3L^2	475 (2.71)		683	632	[19]
$Ru_3H_3L^2$	441 (3.23)		620	604	[19]
$RuHL^3$	438 (1.07)		612	587	[10]
RuL^3	467 (0.85)		660	610	[10]
$RuHL^4$	441 (1.27)		665	620	[10]
RuL^4	458 (1.21)		670	627	[10]

[a]Measured in ethanol.
[b]Measured in acetonitrile.
[c]Measured in methanol.
L^1 = 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole.
H_3L^2 = 1,3,5-(tris(5-pyridin-2'-yl)-1,2,4-triazol-3-yl)benzene.
HL^3 = 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole.
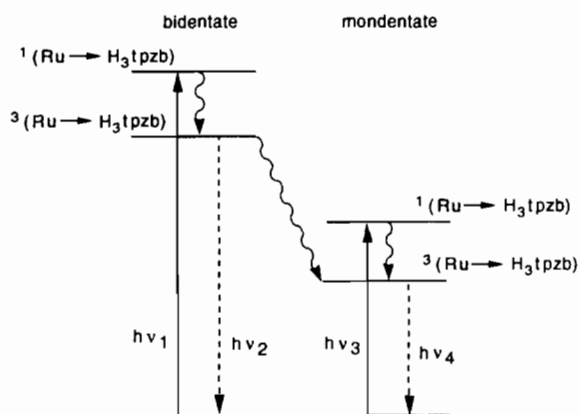HL^4 = 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole.

Fig. 3. Schematic energy-level diagram for H_3Ru_6. The excited states are indicated by the electronic transitions needed to obtain them starting from the ground states.

before that $Ru(bpy)_2$ complexes containing deprotonated triazole ligands yield complexes that do not decompose upon irradiation [10,13]. This has been explained by the strong donating properties of the triazolate ring, yielding a large ligand-field splitting. As a consequence population of metal-centred excited states, that cause photo-decomposition, is not feasible. As already mentioned above we were not successful in preparing compounds of the type Ru_3, where only bidentate coordination ruthenium groupings are present. Based on our expectation that the bidentate coordination $Ru(bpy)_2$ unit would be photostable it was decided to try and prepare the trinuclear Ru_3 compound

by photochemical means, since the photo-instability of the $Ru(bpy)_2Cl$ groupings is well documented [36]. No detailed photochemical experiments have been carried out on dinuclear pyrazine compounds, although the decomposition of such a species upon photolysis in acetonitrile has been noted [21].

Fig. 2 shows the absorption spectra taken during the photolysis of H_3Ru_6 and Ru_6 in acetone. The deprotonated complex is very photo-instable; in 2 min nearly all of the complex has decomposed. An isosbestic point at 430 nm was observed, suggesting a clean photochemical reaction. The H_3Ru_6 compound shows a much slower decomposition, as a reaction time of approximately 2 h is needed to fully decompose the compound (isosbesic point at 478 nm). Fig. 4 shows the changes in the emission spectrum of Ru_6 upon irradiation.

The increased photostability upon protonation of the triazole ring is surprising since it is contrary to the results obtained for other pyrazyl- and pyridyltriazole complexes [9–20]. As the luminescence measurements have revealed similar emission energies and thus ^3MLCT energies for both the protonated and deprotonated species, the difference in photostability is likely to be caused by different ^3MC levels. This very unusual feature is at present under further investigation.

After preparative photolysis (see Section 2 for details) crystallisation from water/acetone yields products that exhibit absorption and emission maxima as shown in Table 2 (Ru_3 and H_3Ru_3, respectively). It is interesting to note that the absorption and emission bands do not shift to a large extent upon protonation/deprotonation
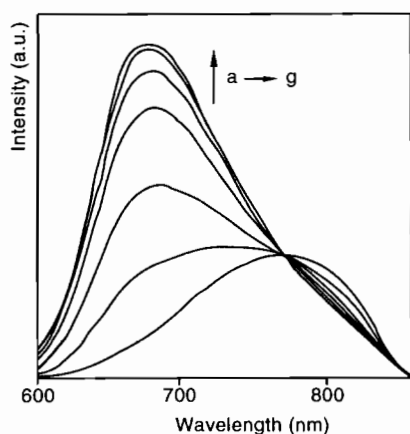
Fig. 4. Changes of the emission spectra (r.t.) upon irradiation of **Ru$_6$** in acetone (430 nm). Every 25 s a spectrum was taken (a→g: $t=0$ to 150 s).

of the triazole rings. Such behaviour has already been observed for the analogous mononuclear Ru(bpy)$_2$ complexes containing L^4 ligand (Table 2). Based on these results it is very likely that, upon irradiation, the three Ru(bpy)$_2$Cl groups are dissociated from the pyrazine ring, yielding the trinuclear tpzb complex. This is the case for both the protonated and the deprotonated complexes. Further indications for such a structure have been obtained by measuring the oxidation potential for **Ru$_3$** (Table 1). The oxidation potential is very similar to those found for other bidentate pyrazyltriazole Ru(bpy)$_2$ complexes [10–34].

4. Conclusions

The hexanuclear ruthenium compounds with tpzb and H$_3$tpzb exhibit very interesting and unusual properties. Although the electrochemical measurements point to at best a very weak interaction between the metal centres, the luminescence experiments revealed an efficient energy-transfer process from the bidentate Ru(bpy)$_2$ groups to the monodentate Ru(bpy)$_2$Cl moieties. Also the photolysis experiments suggest very efficient energy processes, as only the monodentate groups are dissociated upon irradiation. A very interesting observation is the different photostability for the protonated and deprotonated species. Although the emission experiments have clearly revealed that the ^{3}MLCT states for both the protonated and the deprotonated species are roughly equal in energy, the stability for the protonated species seems to be approximately 60 times higher. Currently we are carrying out temperature-dependent lifetime measurements to gain information about the ^{3}MLCT–^{3}MC gap for both species.

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