The First Report of the Isolation and Characterisation of an Intermediate formed upon Photolysis of a Ruthenium(II) Diimine Compound, in which One of the Chelating Ligands is Bound in a Monodentate Fashion

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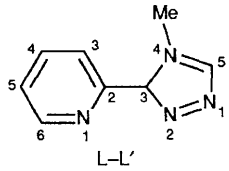
The isolation and characterisation of an intermediate produced upon photolysis of $[Ru(bipy)_2(L–L')](PF_6)_2$ in MeCN [bipy = 2,2′-bipyridyl and L–L′ = 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole], in which L–L′ is coordinated to the metal centre in a monodentate fashion, *via* the nitrogen of the triazole ring, is reported; this photochemically induced reaction can be reversed thermally.

At present much attention is paid to the study of ruthenium(II) diimine type complexes because of their possible application in solar energy conversion and in electrocatalytic systems.[1] One of the problems in the application of such compounds in solar energy systems is the small, but significant, photodecomposition of compounds such as $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl). It has been proposed that in these compounds photochemically initiated ligand substitution is going through an intermediate in which the ligand is bound in a monodentate fashion.[2] However, no direct evidence for the presence of such monodentate coordinated chelating ligands has as yet been reported.

In this communication we report for the first time the isolation and characterisation of such an intermediate. The intermediate is formed on photolysis of $[Ru(bipy)_2(L–L')](PF_6)_2$ **1** [L–L′ = 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole] in MeCN. It is shown that the photochemically induced ligand dissociation can be reversed thermally. This work is part of our systematic study of compounds containing asymmetric chelating ligands.[3]

UV–VIS spectra taken during the photolysis of **1**, clearly show the presence of more than one photoproduct. During the photolysis, the absorption maximum of the reaction mixture shifts from 450 to 425 nm. HPLC shows the initial formation of one product with the appearance of two new species upon further irradiation. By using the retention times observed and a diode array detector, the latter two species were identified as free L–L′ and $[Ru(bipy)_2(MeCN)_2]^{2+}$ (λ_{max} 425 nm). From the fact that no free ligand is formed during the formation of the first product and from the absorption maximum of 445 nm this species has been identified as $[Ru(bipy)_2(L–L')(MeCN)]^{2+}$ **2** in which the pyridyltriazole ligand is bound in a monodentate fashion.

To substantiate this assumption and to determine the coordination mode of the monodentate ligand a preparative photolysis was carried out at room temperature (30 mg of **1** in 300 cm^3 of MeCN). The product obtained was purified using semi-preparative HPLC and recrystallised from aqueous NH_4PF_6, overall yield 50%. As a small amount of **1** (up to 5%) is always formed during the recrystallisation of **2** no elemental analysis was performed. The product was identified further by ^1H NMR spectroscopy, as this technique has proved to be



L–L′

$[Ru(bipy)_2(L–L')](PF_6)_2$

1

$[Ru(bipy)_2(L–L')(MeCN)](PF_6)_2$

2

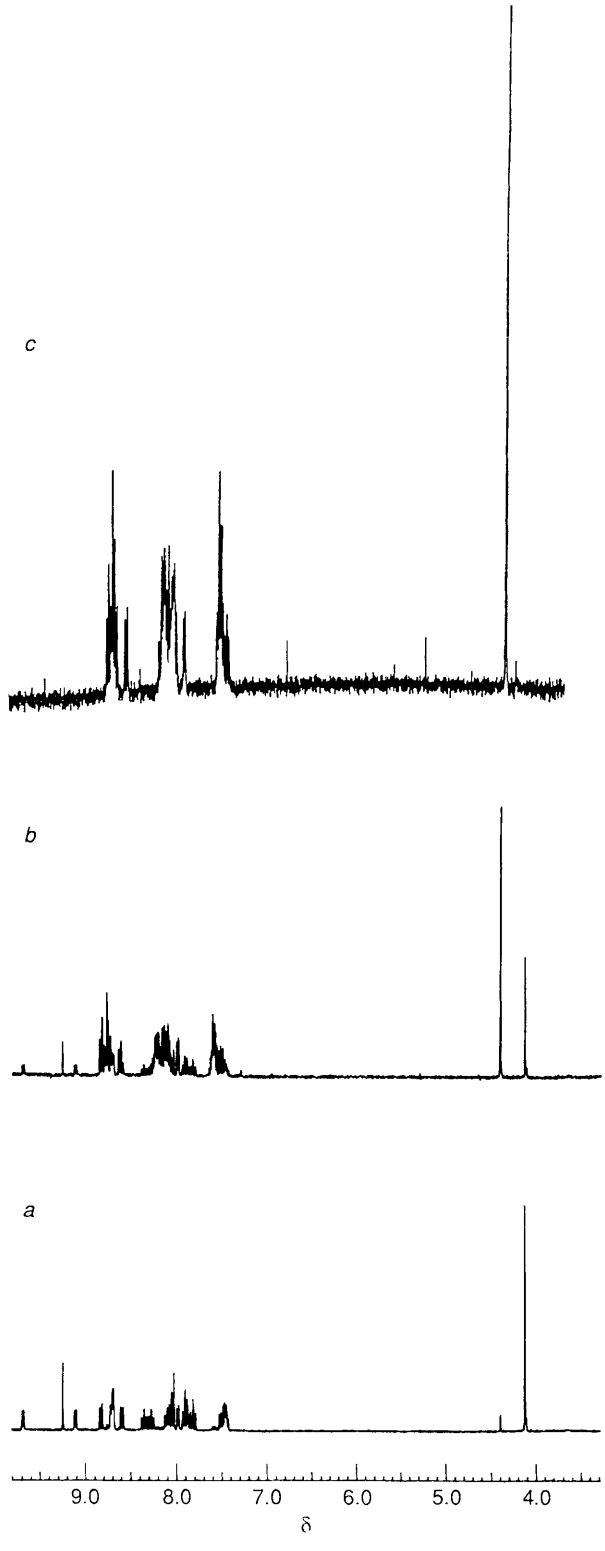


Fig. 1 ^{1}H NMR spectra in CD_3CN showing the thermal conversion of **2** to **1**; (*a*) **2**; (*b*), **2** after 2 h at 80 °C; (*c*) **2** after 5 h at 80 °C (spectrum of **1**)

powerful in determining the coordination mode of such ligands[3,4] (see Fig. 1*a*). An MeCN resonance at δ 2.55 clearly indicates that this molecule is coordinated to the ruthenium(II) centre, as free acetonitrile is found at δ 1.95.[5] In particular the position of the H^3 (δ 7.80, at rather high field owing to the absence of steric hindrance from other protons), H^6 (δ 8.70 at rather low field as this proton does not interact with bipy rings), and methyl resonances (δ 4.12) of the pyridyltriazole ligand suggest that the ligand is coordinated to the metal centre *via* the triazole ring.

The most convincing evidence for the proposed structure is the fact that upon heating to 80 °C **2** reverts to **1** quantitatively. The resonances observed for **2** (see Fig. 1*a*) disappear and are replaced by signals that can be attributed to **1** (see Fig. 1*b* and *c*;[3] also the resonance of coordinated MeCN is lost upon heating.

In conclusion, we have confirmed the mechanism for the photoinduced ligand exchange in these compounds as proposed by Durham *et al.* [eqn. (1)],[2] in which monodentate intermediates are formed upon photolysis of ruthenium polypyridyl compounds, and thermal ring closure regenerates the starting compound. We have also for the first time characterised such an intermediate using spectroscopic techniques.

$$[Ru(bipy)_2(L\text{–}L')]^{2+} + MeCN \underset{}{\overset{h\nu}{\rightleftharpoons}} [Ru(bipy)_2(L\text{–}L')(MeCN)]^{2+} \quad (1)$$

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References

1 A. Juris, V. Balzani, F. Barigelletti, S. Campana, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.

2 B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4803.

3 R. Hage, R. Prins, J. G. Haasnoot, J. Reedijk and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, 1987, 1389; R. Hage, A. H. J. Dijkhuis, J. G. Haasnoot, R. Prins, J. Reedijk, B. E. Buchanan and J. G. Vos, *Inorg. Chem.*, 1988, **27**, 2185; F. Barigelletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chem.*, 1989, **28**, 4344; R. Hage, J. G. Haasnoot, D. J. Stufkens, T. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, 1989, **28**, 1413; 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.*, 1990, 2425; R. Hage, J. H. van Diemen, G. Ehrlich, J. G. Haasnoot, D. J. Stufkens, T. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, 1990, **29**, 988.

4 P. J. Steel and E. C. Constable, *J. Chem. Soc., Dalton Trans.*, 1990, 1389; E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443; E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1669; C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1990, 621.

5 R. J. Crutchly and A. B. P. Lever, *Inorg. Chem.*, 1982, **21**, 2276; P. J. Steel, F. Lahousse, D. Lerner and C. Marzin, *Inorg. Chem.*, 1983, **22**, 1488.