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Photochemical and thermal ligand exchange in a ruthenium(II) complex based on a scorpionate terpyridine ligand

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A ruthenium(II) complex containing a 1,10-phenanthroline unit and a terpyridine fragment covalently linked to a benzonitrile group has been synthesised; coordination and decoordination of the benzonitrile group can be induced thermally and photochemically respectively, in an acetone–water mixture.

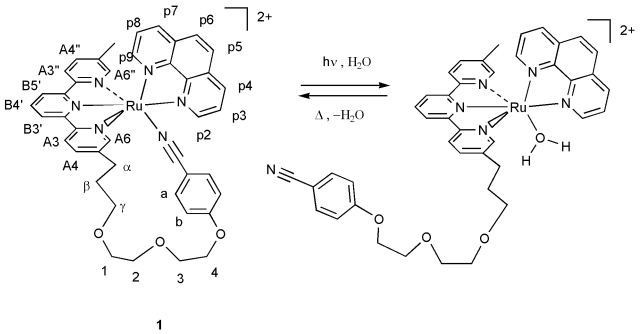
Macrocyclic ligands bearing a functionalised tail,[1] for example a coordination site, belong to the scorpionand[2] family of ligands which are currently utilised in a variety of molecular probes and sensors. Also of interest in the area of optical sensors and switches[3] are ruthenium(II) complexes of N-heterocyclic chelating ligands which undergo reversible light-driven reactions such as photoisomerisation[4] or photosubstitution.[5] In the present work, we propose a system which combines the general properties of scorpionate ligands with the ability of ruthenium(II) complexes to undergo ligand exchange under light irradiation. Among the numerous ruthenium(II) complexes described in the literature, several lead to interesting photolabilisation reactions which are both efficient and selective.[6] For example, $[Ru(tpy)(dmbp)(L)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine, dmbp = 6,6′-dimethyl-2,2′-bipyridine, L = pyridine or CH_3CN) undergoes a reversible interchange of the sixth ligand L under visible light irradiation.[7]

$$[Ru(ttpy)(dmbp)(CH_3CN)]^{2+} \xrightarrow{h\nu,\ py} [Ru(ttpy)(dmbp)(py)]^{2+} + CH_3CN \quad (1)$$

$$[Ru(ttpy)(dmbp)(py)]^{2+} \xrightarrow{h\nu,\ CH_3CN} [Ru(ttpy)(dmbp)(CH_3CN)]^{2+} + py \quad (2)$$

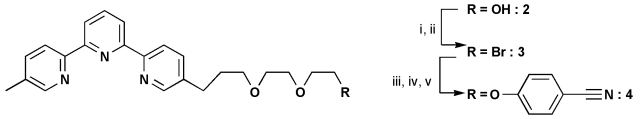
In order to investigate such systems further, we have prepared and characterized a series of ruthenium(II) complexes of the type $[Ru(tpy)(phen)(L)]^{2+}$ (phen = 1,10-phenanthroline) in which L is a monodentate ligand such as pyridine, 2-isoquinoline, 4-dimethylaminepyridine, 4-(4′-methylpyridinium)pyridine, phenothiazine, DMSO, CH_3CN, 4-methoxybenzonitrile and H_2O.[8]

Our investigations of these complexes show that the nitrile ligand in $[Ru(tpy)(phen)(CH_3CN)]^{2+}$ can be selectively photoexpelled and replaced by H_2O under visible light irradiation[9] in an acetone–water mixture (85:15, v/v). This process has been monitored by UV-visible and ^1H NMR spectroscopy. Both techniques demonstrate that the photochemical reaction is highly selective and quantitative. The reverse reaction, *i.e.* the thermal recoordination of an acetonitrile molecule, also takes place quantitatively at room temperature. The rate of exchange of H_2O by CH_3CN is substantially accelerated by a high concentration of CH_3CN as previously established in a kinetic study.[10] We have also observed that a similar photochemical reaction occurs for the substitution of CH_3CN by pyridine. We have therefore prepared the ruthenium complex $[\mathbf{1}]^{2+}$ in which a benzonitrile group is tethered to the terpyridine subunit (Scheme 1). In this complex, the benzonitrile coordinating group can be photoexpelled and thermally recoordinated. The effect of tethering the benzonitrile group is to facilitate the recoordination of the nitrile functionality, since the effective concentration of the nitrile in the scorpionate complex is expected to be higher than if it were free in the bulk of the solution.



Scheme 1 Photolabilisation and thermal recoordination of complex $[\mathbf{1}]^{2+}$.

Ligand **4** has been synthesised in four steps from 5′,5″-dimethyl-2,2′:6′,2″-terpyridine[11] (dmtpy). The reaction of dmtpy at −78 °C with one equivalent of LDA generated the corresponding mono-anion, which was then reacted with the THP-protected 1-bromodiethylene glycol (THP = tetrahydropyran-2-yl) to give **2**. Mesylation followed by bromination in acetone gave the precursor **3**, which in a classical Williamson reaction (NaH/DMF) gave ligand **4** (Scheme 2).



Scheme 2 Synthesis of ligand **4**. *Reagents and conditions*: (i) LDA, dmtpy, $Br(CH_2CH_2O)_2THP$, thf; (ii) HCl(aq); (iii) NEt_3, MsCl, DCM; (iv) LiBr, acetone; (v) NaH, 4-hydroxybenzonitrile, dmf.

The reaction of $[Ru(phen)(DMSO)_4Cl_2]$[12] with **4** in EtOH–H_2O (9:1) at reflux afforded the chloro derivative [Ru(**4**)(phen)Cl]Cl. Complex $[\mathbf{1}][PF_6]_2$ was obtained by reaction of this precursor with an exces of $AgBF_4$ in refluxing acetone and PF_6^- anion metathesis (65% yield). Mass (FAB-MS) and ^1H NMR spectroscopy in a series of solvents including CH_3CN, acetone, CH_2Cl_2 and pyridine confirm the scorpionate-type structure of the complex in the dark.[13] Single crystals were grown by slow diffusion of benzene in an acetone solution of **1** and an X-ray structure was obtained.[14] The ORTEP diagram is shown in Fig. 1.

The Ru–N bond lengths range from 1.956(7) to 2.098(8) Å and are similar to those observed in related complexes.[15] In particular, the Ru–N6 (benzonitrile) distance (2.033 Å) is very close to that previously reported for $[Ru(bipy)_2(C_6H_5CN)_2]^{2+}$[16] (2.032 Å) or in other $[Ru(phen)_2(NN)]^{2+}$ complexes

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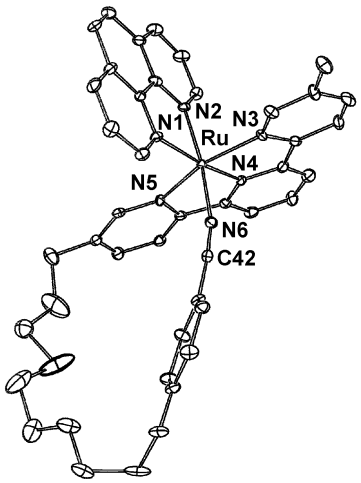

Fig. 1 ORTEP view of the ruthenium complex $[\mathbf{1}]^{2+}$ Ellipsoids are scaled to enclose 30% of the electronic density.

(2.022–2.047 Å)[17] (NN = bichelating ligand with two nitrile coordination sites). However, the Ru–N6–C42 angle (166.6°) indicates some constraint in the 20-membered macrocyclic ring formed by the benzonitrile arm and the metal centre.

The photolabilisation of the benzonitrile arm has initially been examined in pyridine solution. Fig. 2 shows the evolution of the ^{1}H NMR spectrum of $[\mathbf{1}][PF_6]_2$ in pyridine-d_5 during the reaction (proton H_{P2} of the phenanthroline unit is a very convenient probe). The photolabilisation is complete within 25 min.

Both ^{1}H NMR and UV-vis measurements show that the reaction is clean and quantitative. Due to the strong coordination ability of pyridine it was not possible to restore the starting compound either thermally or photochemically. By contrast, a reversible system was obtained in acetone–H_2O. At a low concentration of $[\mathbf{1}]^{2+}$ in acetone–water (85:15 v/v) the monitoring of the photochemical reaction by electronic absorption spectroscopy and TLC clearly indicates the complete disappearance of $[\mathbf{1}]^{2+}$ (λ_{max} = 454 nm) and the simultaneous appearance of the aqua-form (λ_{max} = 490 nm). By ^{1}H NMR, in a more concentrated solution (10^{-3} M), a stationary equilibrium is reached. In fact, a constant percentage (16%) of the starting compound remained after irradiation which is probably a result of the steady-state equilibrium which occurs because there is no spectral window allowing to photoexcite $[\mathbf{1}]^{2+}$ exclusively. The nature of the reaction product has also been unambigously confirmed by ES-MS spectroscopy (peak at *m*/*z* 939.2 for the aqua form; calculated for M − PF_6 939.0). The thermal recoordination of the nitrile arm takes places slowly at room temperature (82% of recovery in one day) or faster by heating the mixture at reflux for 1 h. At this concentration no by-product resulting from intermolecular complexation has been detected

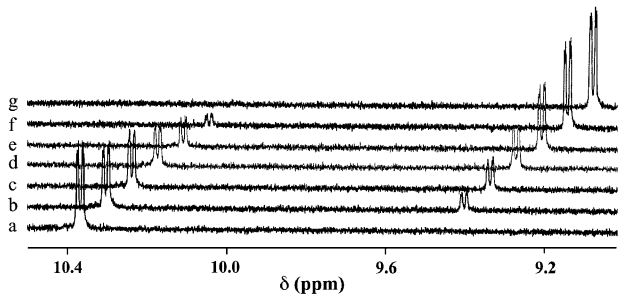

Fig. 2 ^{1}H NMR spectra (400 MHz) of $[\mathbf{1}][PF_6]_2$ in pyridine-d_5 (9.0–10.5 ppm range) under light irradiation: a, t = 0; b, 1; c, 2; d, 3.5; e, 6.5; f, 12.5; g, 25 min. H_{p2} appears as a doublet at 10.36 ppm in $[\mathbf{1}]^{2+}$ whereas it is strongly shifted upfield in $[Ru(tpy)(phen)(py)]^{2+}$, as a result of substitution of the nitrile ligand by pyridine (δ 9.40).

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13 ^{1}H NMR (400 MHz, acetone-d_6): δ 10.28 (dd, H_{P2}, *J* 5.2 and 1.2 Hz), 9.07 (dd, H_{P4}, *J* 8.3 and 1.2 Hz), 8.88 (dd, $H_{B3'}$,*J* 8.1 and 0.8 Hz), 8.87 (dd, $H_{B5'}$, *J* 8.1 and 0.8 Hz), 8.68 (dd, H_{A3}, *J* 7.6, 0.5 Hz), 8.64 (d, $H_{A3''}$, *J* 8.2 Hz), 8.60 (dd, H_{P7}, *J* 8.3 and 1.2 Hz), 8.52 (t, $H_{B4'}$, *J* 8.1 Hz), 8.50 (dd, H_{P3}, *J* 8.3, 5.2 Hz), 8.48 (d, H_{P5}, *J* 8.9 Hz), 8.30 (d, H_{P6}, 8.9 Hz), 8.04 (br d, H_{A6}, *J* 2.4 Hz), 8.01 (dd, H_{A4}, *J* 8.1 and 1.9 Hz), 7.97 (dd, H_{P9}, *J* 5.3 and 1.2 Hz), 7.90 (ddd, $H_{A4''}$, *J* 8.3, 2, 0.8 Hz), 7.81 (m, $H_{A6''}$), 7.67 (dd, H_{P8}, *J* 8.3 and 5.3 Hz), 7.49 (d, $2H_a$, *J* 9 Hz), 7.19 (d, $2H_b$, *J* 9 Hz), 4.44–4.42 (m, $2H_4$), 3.69 (t, $2H_3$, *J* 4.2 Hz), 3.46–3.37 (m, $2H_2$), 3.23 (t, $2H_1$, *J* 3.6 Hz), 3.17–2.96 (m, 2Hγ), 2.50–2.30 (m, 2Hα), 2.07 (s, $3H_{CH_3}$), 1.71–1.57 (m, $2H_\beta$). FAB-MS: found (calc.): *m*/*z* 921.1 (921.0) (M − PF_6)$^+$; 776.1 (776.0) (M − $2PF_6$)$^+$.
14 *Crystal data* for $[\mathbf{1}][PF_6]_2{\cdot}C_6H_6$: $C_{42}H_{38}N_6O_3Ru{\cdot}2PF_6{\cdot}C_6H_6$, orange crystal, 0.14 × 0.08 × 0.02 mm, M = 1143.92, triclinic, space group $P\bar{1}$, a = 9.5547(3), b = 15.5888(5), c = 18.1759(7) Å, α = 70.074(5), β = 81.099(5), γ = 80.222(5)°, U = 2494.4(1) Å^3, T = 173 K, Z = 2, D_c = 1.52 g cm^{-3}, μ = 0.471 mm^{-1}, F_{000} = 1160, λ = 0.71073 Å, radiation: Mo-Kα graphite monochromated, diffractometer: KappaCCD, Φ scans, *hkl* limits :–10 to 12/–20 to 19/–23 to 22, θ limits: 2.5–27.14°, number of data measured: 14511, number of data with $I > 3\sigma(I)$: 5115, weighting scheme: $4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$, number of variables: 603, $R(F)$: 0.061, $wR(F)$: 0.076, GOF: 1.463, largest peak in final difference map: 1.447 e Å^{-3}. The disordered C31 atom of the macrocyclic ring was modeled over two positions with 60/40% occupancies. Hydrogen atoms were placed in calculated positions and constrained with isotropic thermal parameters with the execption of H atoms on C31. Package use: OpenMolen, Interactive Structure Solution, B. V. Nonius, Delft, The Nederlands, 1997. CCDC 197241. See http://www.rsc.org/suppdata/cc/b2/b210607h/ for crystallographic data in CIF or other electronic format.
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