

Dalton Paper No. b304085b**B. J. Coe *et al.*****Supplementary Experimental Information****Materials and Procedures**

All reactions were performed under an Ar atmosphere and in Ar-purged solvents. All reactions and chromatographic purifications involving complex salts were performed in the dark. The compounds *cis*-[Ru^{III}(NH₃)₄Cl₂]Cl,¹ [MeQ⁺]I,² [PhQ⁺]Cl•2H₂O,³ [4-AcPhQ⁺]Cl•2H₂O³ and [2-PymQ⁺]Cl⁴ were synthesized by previously published methods. Products were dried overnight in a vacuum desiccator (CaCl₂) prior to characterization.

General physical measurements

Proton NMR spectra were recorded on a Varian Gemini 200 spectrometer and all shifts are referenced to SiMe₄. The fine splitting of pyridyl or phenyl ring AA'BB' patterns is ignored and the signals are reported as simple doublets, with *J* values referring to the two most intense peaks. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester and UV/VIS spectra were obtained by using a Hewlett Packard 8452A diode array spectrophotometer. Infrared spectroscopy was performed on non-diluted samples using an Excalibur BioRad FT-IR spectrometer equipped with a Golden Gate attenuated total reflectance accessory.

Cyclic voltammetric measurements were performed on a BAS CV50W voltammetric analyzer. A single-compartment cell was used with a Ag/3M NaCl/saturated AgCl reference electrode separated by a salt bridge from a platinum-disc working electrode and platinum-wire auxiliary electrode. Anhydrous acetonitrile (HPLC grade distilled under Ar from CaH₂ drying agent) was used as the solvent and tetra-*n*-butyl ammonium hexafluorophosphate, twice recrystallized from ethanol and dried *in vacuo*, was used as supporting electrolyte. Solutions containing *ca.* 10⁻³ mol dm⁻³ analyte (0.1 mol dm⁻³ electrolyte) were deaerated by purging with N₂. All *E*_{1/2} values were calculated from (*E*_{pa} + *E*_{pc})/2 at a scan rate of 200 mV s⁻¹.

Syntheses

***cis*-[Ru^{II}(NH₃)₄(MeQ⁺)₂][PF₆]₄ (1).** A solution of *cis*-[Ru^{III}(NH₃)₄Cl₂]Cl (55 mg, 0.200 mmol) in degassed water (5 mL) acidified with trifluoroacetic acid (3 drops) was reduced over zinc amalgam (5 lumps) for 15 min with Ar agitation. The solution was filtered under Ar into a flask containing [MeQ⁺]I (298 mg, 1.00 mmol) and the reaction was stirred in the dark under Ar for 5 h. Acetone (850 mL) was added and the crude halide salt product was collected by filtration, washed with acetone and dried. This material was metathesised using water/aqueous NH₄PF₆ to yield a dark blue solid. Purification was achieved by precipitation from acetone/aqueous NH₄PF₆: yield 109 mg (49%). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 9.12 (d, 4 H, *J* 6.9 Hz, 2C₅H₄N), 8.88 (d, 4 H, *J* 6.9 Hz, 2C₅H₄N), 8.66 (d, 4 H, *J* 7.0 Hz, 2C₅H₄N), 7.95 (d, 4 H, *J* 6.9 Hz, 2C₅H₄N), 4.61 (s, 6 H, 2Me), 3.39 (s, 6 H, 2NH₃), 2.99 (s, 6 H, 2NH₃). (Found: C, 23.69; H, 3.19; N, 9.63. Calc. for C₂₂H₃₄N₈RuP₄F₂₄•1.5H₂O: C, 23.62; H, 3.33; N, 10.02%).

***cis*-[Ru^{II}(NH₃)₄(PhQ⁺)₂][PF₆]₄ (2).** This was prepared in an identical fashion to **1** by using [PhQ⁺]Cl•2H₂O (305 mg, 1.00 mmol) in place of [MeQ⁺]I. Acetone (150 mL) was added to precipitate the crude chloride product. Purification was achieved by sequential precipitations from acetone/diethyl ether: yield 120 mg (49%). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 9.42 (d, 4 H, *J* 7.2 Hz, 2C₅H₄N), 8.95 (d, 4 H, *J* 6.9 Hz, 2C₅H₄N), 8.84 (d, 4 H, *J* 7.2 Hz, 2C₅H₄N), 8.05 (d, 4 H, *J* 7.0 Hz, 2C₅H₄N), 8.01–7.96 (m, 4 H, 2Ph), 7.85–7.79 (m, 6 H, 2Ph), 3.45 (s, 6 H, 2NH₃), 3.04 (s, 6 H, 2NH₃). (Found: C, 31.34; H, 3.24; N, 9.01. Calc. for C₃₂H₃₈N₈RuP₄F₂₄•0.5H₂O: C, 31.38; H, 3.21; N, 9.15%).

***cis*-[Ru^{II}(NH₃)₄(4-AcPhQ⁺)₂][PF₆]₄ (3).** This was prepared and purified in an identical fashion to **1** by using [4-AcPhQ⁺]Cl•2H₂O (347 mg, 1 mmol) in place of [MeQ⁺]I. Acetone (100 mL) was added to precipitate the crude chloride product: yield 121 mg (46%). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$ 9.47 (d, 4 H, *J* 6.9 Hz, 2C₅H₄N), 8.95 (d, 4 H, *J* 6.8 Hz, 2C₅H₄N), 8.87 (d, 4 H, *J* 6.8 Hz, 2C₅H₄N), 8.36 (d, 4 H, *J* 8.8 Hz, 2C₆H₄), 8.15 (d, 4 H, *J* 8.8 Hz, 2C₆H₄), 8.05 (d, 4 H, *J* 6.8 Hz, 2C₅H₄N), 3.46 (s, 6 H, 2NH₃), 3.05 (s, 6 H, 2NH₃), 2.72 (s, 6 H, 2Me). $\nu(\text{C}=\text{O})$ 1686 cm⁻¹. (Found: C, 32.92; H, 2.87; N, 8.26. Calc. for C₃₆H₄₂N₈O₂RuP₄F₂₄•H₂O: C, 32.81; H, 3.37; N, 8.50%).

cis-[Ru^{II}(NH₃)₄(2-PymQ⁺)₂][PF₆]₄ (**4**). This was prepared and purified in an identical fashion to **3** by using [2-PymQ⁺]Cl (271 mg, 1 mmol) in place of [4-AcPhQ⁺]Cl•2H₂O. Further purification was achieved by precipitation from acetone/aqueous NH₄PF₆: yield 64 mg (26%). δ_{H} (CD₃COCD₃) 10.26 (d, 4 H, *J* 7.3 Hz, 2C₅H₄N), 9.27 (d, 4 H, *J* 4.8 Hz, 2C₄H₃N₂), 9.01–8.92 (m, 8 H, 4C₅H₄N), 8.11 (d, 4 H, *J* 7.0 Hz, 2C₅H₄N), 8.04 (t, 2 H, *J* 4.9 Hz, 2C₄H₃N₂), 3.53 (s, 6 H, 2NH₃), 3.09 (s, 6 H, 2NH₃). (Found: C, 27.13; H, 2.64; N, 13.13. Calc. for C₂₈H₃₄N₁₂RuP₄F₂₄•H₂O: C, 27.17; H, 2.93; N, 13.58%).

Stark spectroscopy

The Stark apparatus, experimental methods and data analysis procedure were exactly as previously reported,⁵ with the only modification being that a Xe arc lamp was used as the light source in the place of a W filament bulb. To fit the Stark data, the absorption spectrum was modelled with combinations of Gaussian curves that reproduce the data and separate the peaks. After taking the first and second derivatives of the model, the Liptay equation was used to yield the dipole moment change ($\Delta\mu_{12}$) associated with each of the optical transitions considered in the fit. For all of the complexes two or three Gaussian functions were necessary to fit the absorption spectrum. In each case, two of the Gaussians contributed the majority of the Stark signal, so the data yielded by the insignificant peaks have been neglected.

The Liptay equation is:⁶

$$\Delta\varepsilon(\nu)/\nu = \left[A_x \varepsilon(\nu)/\nu + \frac{B_x}{15h} \frac{\partial(\varepsilon(\nu)/\nu)}{\partial\nu} + \frac{C_x}{30h^2} \frac{\partial^2(\varepsilon(\nu)/\nu)}{\partial\nu^2} \right] \mathbf{F}_{\text{int}}^2$$

where ν is the frequency of the light in Hz and the internal electric field is related to the applied external field by $\mathbf{F}_{\text{int}} = f_{\text{int}}\mathbf{F}_{\text{ext}}$. Butyronitrile was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.⁵

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