Accepted Manuscript

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 PII:
 S0277-5387(15)00225-9

 DOI:
 http://dx.doi.org/10.1016/j.poly.2015.04.028

 Reference:
 POLY 11292

To appear in: Polyhedron

Received Date:25 February 2015Accepted Date:23 April 2015



Please cite this article as: B.J. Coe, M.K. Peers, N.S. Scrutton, Syntheses and electronic and optical properties of complexes of the bis(2,2'-bipyrazyl)ruthenium unit, *Polyhedron* (2015), doi: http://dx.doi.org/10.1016/j.poly. 2015.04.028

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Syntheses and electronic and optical properties of complexes of the bis(2,2'-bipyrazyl)ruthenium unit

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ABSTRACT

Seven new complexes of the form cis-[Ru^{II}(bpz)₂(L-L)]ⁿ⁺ (bpz = 2,2'-bipyrazyl: n = 2; L-L = 4,4'-bis(tert-butyl)-2,2'-bipyridyl, 4,4'-diphenyl-2,2'-bipyridyl, 4,4'-dichloro-2,2'-bipyridyl, 4,4'-bis(trifluoromethyl)-2,2'-bipyridyl, 4.4'-4,4'-diamino-2,2'-bipyridyl, bis(methoxycarbonyl)-2,2'-bipyridyl: n = 4; L-L = N'', N'''-dimethyl-4,4':2',2'':4'',4'''quaterpyridinium) are prepared and isolated as their PF_6^- and CI^- salts. Improved methods for described synthesising 4,4'-bis(trifluoromethyl)-2,2'-bipyridyl bpz and are also. Characterisation involves various techniques including ¹H NMR spectroscopy and mass spectrometry. The new compounds are studied alongside the known species where n = 2 and L-L = 2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl or 2,2'-bipyrimidine. Their UV-vis spectra display intense intraligand $\pi \to \pi^*$ absorptions, and also metal-to-ligand charge-transfer (MLCT) bands with two resolved maxima in the visible region. Red-shifts in the MLCT bands occur as the electron-donating strength of L-L increases. Cyclic voltammograms show reversible Ru^{III/II} oxidation waves, and several ligand-based reductions that are also mostly reversible. The variations in the redox potentials correlate with changes in the MLCT energies. Time-dependent density functional theory calculations give relatively good correlations with the experimental UV-Vis spectra for selected complexes when using the M06 functional and basis sets Def2-QZVP (on Ru) and Def2-SVP (on all other atoms) in acetonitrile. The lowest energy visible absorption band is confirmed to be due to $Ru^{II} \rightarrow bpz$ MLCT, while further such transitions occur along with MLCT to L-L at higher energies.

Keywords: ruthenium complexes, 2,2'-bipyrazyl, UV–Vis spectroscopy, electrochemistry, density functional theory

1. Introduction

Ruthenium occupies a central position among the d-block transition metals. It shows an amazingly rich coordination and organometallic chemistry, forming complexes with every kind of ligand imaginable [1,2]. Comparatively high stability and relative ease of synthesis have allowed this area to flourish. Beyond primary scientific value, such compounds are practically useful in many important fields including catalysis [3–5] and biology/medicine [6– 8]. Impinging on both of these areas, and of special current interest are technologies that exploit photophysical/chemical properties [9–11]. These include photoredox catalysis [12– 14], cellular imaging [15–17], organic light-emitting diodes (OLEDs) [18–20], and dyesensitized solar cells (DSSCs) [21–23]. All of these topics involve complexes of chelating polypyridyl ligands, especially 2,2'-bipyridyl (bpy), with Ru in the divalent oxidation state. Such compounds have fascinating electronic absorption, emission and electron/energytransfer properties, based on low energy metal-to-ligand charge-transfer (MLCT) excited states. Tuning the properties of these states by changing ligand structures is a mature area [9– 11].

While the complex $[Ru^{II}(bpy)_3]^{2+}$ and related species with bpy-based ligands have been studied very extensively, analogous complexes of 2,2'-bipyrazyl (bpz) have received somewhat less attention. $[Ru^{II}(bpz)_3]^{2+}$ was first reported in 1980 [24], its apparently favourable photoredox properties when compared with $[Ru^{II}(bpy)_3]^{2+}$ indicating substantial promise. Subsequent studies include examples focusing on basic synthesis and physical characterisation [25–31], and also reports of relatively more complicated structures and/or a focus on applications. The latter incorporate polymetallic complexes [32,33], DNA photocleavage [34], DSSCs [35,36], electron-transfer probes for enzymes [37,38], catalysis [39], and dyads for proton-coupled electron transfer studies [40]. Here we report a new and improved procedure for synthesising bpz, and the preparation of a series of new complexes containing the $\{Ru^{II}(bpz)_2\}^{2+}$ moiety. Experimental measurements are accompanied by theoretical studies in order to develop a thorough knowledge and understanding of the new complexes.

2. Experimental

2.1. Materials, procedures and physical measurements

The compounds 4,4'-dinitro-2,2'-bipyridyl [41], 4,4'-dichloro-2,2'-bipyridyl [41], 4,4'-diamino-2,2'-bipyridyl [42], 4,4':2',2'':4'',4'''-quaterpyridyl (qpy) [43], N'',N'''-dimethyl-4,4':2',2'':4'',4'''-quaterpyridinium hexafluorophosphate ([Me₂qpy²⁺](PF₆)₂) [44], *cis*-Ru^{II}(bpz)₂Cl₂ [26] and [Ru^{II}(bpz)₃]Cl₂ [24] were prepared according to published methods. All other reagents and solvents were used as supplied from Fluorochem, Sigma-Aldrich, Alfa-Aesar or Fisher Scientific. Products were dried at room temperature overnight in a vacuum desiccator (CaSO₄) or by direct attachment to a high-vacuum line for several hours prior to characterisation.

¹H NMR spectra were recorded on a Bruker AV-400 spectrometer, with all shifts referenced to residual solvent signals and quoted with respect to TMS. The AA'BB' patterns of pyridyl or phenyl rings 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. ESI and GC mass spectrometry were recorded respectively on a Waters SQD2 or Agilent 5975C spectrometer. UV–Vis absorption spectra were obtained by using a Shimadzu UV-2401 PC spectrophotometer. Cyclic voltammetric measurements were performed by using an Ivium CompactStat. A single-compartment BASi VC-2 cell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a 2 mm disc Pt working electrode and Pt wire auxiliary electrode. The ferrocene/ferrocenium couple was used as an internal standard. Acetonitrile was used as supplied from Fisher Scientific (HPLC grade), and [NBuⁿ₄]PF₆ (Sigma Aldrich, electrochemical grade) was used as the supporting electrolyte. Solutions containing *ca*. 10⁻³ M analyte (0.1 M [NBuⁿ₄]PF₆) were deaerated by purging with dried N₂. *E*_{1/2} values were calculated from (*E*_{pa} + *E*_{pc})/2 at a scan rate of 100 mV s⁻¹.

2.2. Syntheses

2.2.1. 2,2 '-Bipyrazyl, bpz

2-Iodopyrazine (5.00 g, 24.3 mmol), Pd^{II}(OAc)₂ (34 mg, 0.151 mmol), K₂CO₃ (3.4 g, 24.6 mmol) and poly(ethylene glycol) (Mw 4000, 24.0 g) were combined in an argon-purged flask. The mixture was gradually heated to 120 °C and the temperature maintained for 48 h with stirring. The mixture was cooled to *ca.* 80 °C and warm water (30 mL) was added to prevent solidification. On cooling to room temperature, further water (100 mL) was added and the suspension exhaustively extracted with ethyl acetate. The combined extracts were washed once with saturated aqueous Na₂S₂O₃ and then thrice with brine. The organic layer was dried over MgSO₄ and solvent removed under vacuum. The residue was triturated with *n*-pentane and the white crystalline solid filtered off, washed with *n*-pentane and dried. Yield: 1.35 g (70%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 9.60 (2H, d, *J* = 1.1 Hz), 8.68–8.66 (4H). GC-MS: *m/z* = 158 ([M]⁺). *Anal.* Calc. (%) for C₈H₆N₄: C, 60.8; H, 3.8; N, 35.4. Found: C, 60.4; H, 3.4; N, 35.8.

2.2.2. 4,4'-Bis(trifluoromethyl)-2,2'-bipyridyl

This compound was prepared in a manner similar to bpz by using 2-bromo-4-(trifluoromethyl)pyridine (2.25 g, 9.96 mmol) in place of 2-iodopyrazine, Pd^{II}(OAc)₂ (56 mg, 0.249 mmol), K₂CO₃ (1.38 g, 9.99 mmol) and poly(ethylene glycol) (10.0 g). After evaporation of the dried ethyl acetate extracts, the residue was purified by column chromatography on silica gel eluting with dichloromethane. A white crystalline solid was obtained. Yield: 811 mg (56%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.89 (2H, dt, J = 5.0, 0.7 Hz), 8.73 (2H, dt, J = 1.6, 0.8 Hz), 7.59 (2H, ddd, J = 5.0, 1.7, 0.7 Hz). GC-MS: m/z = 291.9 ([M]⁺). *Anal.* Calc. (%) for C₁₂H₆F₆N₂: C, 49.3; H, 2.1; N, 9.6. Found: C, 49.3; H, 2.1; N, 9.8.

2.2.3. $[Ru^{II}(bpz)_2(bpy)](PF_6)_2(1)$

cis-Ru^{II}(bpz)₂Cl₂ (100 mg, 0.205 mmol) and bpy (64 mg, 0.410 mmol) were combined in an argon-purged flask. An argon-sparged mixture of 2-methoxyethanol (7 mL) and water (3

mL) was added and the mixture heated at reflux for 24 h. After cooling to room temperature, the solvents were removed under vacuum and a small amount of water was added. The suspension was filtered, and an excess of solid NH₄PF₆ was added to the filtrate to precipitate the crude product. The solid was filtered off and purified by column chromatography on silica gel eluting with 0.1 M NH₄PF₆ in acetonitrile. The main orange fraction was evaporated to dryness and the product washed extensively with ice-cold water, then dried to give an orange solid. Yield: 95 mg (56%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.75 (4H, t, *J* = 1.2 Hz), 8.59 (4H, dd, *J* = 3.2, 2.2 Hz), 8.53 (2H, d, *J* = 8.0 Hz), 8.15 (2H, td, *J* = 7.9, 1.5 Hz), 7.85 (2H, dd, *J* = 3.2, 1.2 Hz), 7.78 (2H, dd, *J* = 3.2, 1.2 Hz), 7.69 (2H, ddd, *J* = 5.6, 1.4, 0.7 Hz), 7.46 (2H, ddd, *J* = 7.7, 5.7, 1.3 Hz). ES-MS: m/z = 718 ([M – PF₆]⁺), 287 ([M – 2PF₆]²⁺). Anal. Calc. (%) for C₂₆H₂₀F₁₂N₁₀P₂Ru•H₂O: C, 35.4; H, 2.5; N, 15.9. Found: C, 35.5; H, 2.1; N, 15.7.

2.2.4. $[Ru^{II}(bpz)_2(4,4'-Me_2bpy)](PF_6)_2(2)$

This compound was prepared and purified in a manner similar to **1** by using 4,4'dimethyl-2,2'-bipyridyl (76 mg, 0.413 mmol) in place of bpy to give a dark red solid. Yield: 91 mg (50%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.74 (4H, dd, J = 2.7, 1.2 Hz), 8.62 (4H, dd, J = 9.9, 3.2Hz), 8.38 (2H, dd, J = 1.0, 0.6 Hz), 7.84 (2H, dd, J = 3.2, 1.2 Hz), 7.77 (2H, dd, J = 3.3, 1.3Hz), 7.48 (2H, d, J = 5.9 Hz), 7.30–7.28 (2H), 2.55 (6H, s). ES-MS: m/z = 746 ([M – PF₆]⁺), 301 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₂₈H₂₄F₁₂N₁₀P₂Ru: C, 37.7; H, 2.7; N, 15.7. Found: C, 38.0; H, 2.7; N, 15.4.

2.2.5. $[Ru^{II}(bpz)_2(4,4'-{}^tBu_2bpy)](PF_6)_2(3)$

This compound was prepared and purified in a manner similar to **1** by using 4,4′bis(*tert*-butyl)-2,2′-bipyridyl (110 mg, 0.410 mmol) in place of bpy to give a dark red solid. Yield: 112 mg (55%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.75 (4H, dd, J = 3.6, 1.2 Hz), 8.62 (2H, d, J = 3.2 Hz), 8.58 (2H, d, J = 3.2 Hz), 8.49 (2H, d, J = 2.4 Hz), 7.84 (2H, dd, J = 3.2, 1.2 Hz), 7.77 (2H, dd, J = 3.2, 1.2 Hz), 7.54 (2H, d, J = 6.0 Hz), 7.42 (2H, dd, J = 6.1, 2.1 Hz), 1.41 (18H, s). ES-MS: m/z = 831 ([M - PF₆]⁺), 343 ([M - 2PF₆]²⁺). *Anal.* Calc. (%) for C₃₄H₃₆F₁₂N₁₀P₂Ru•H₂O: C, 41.1; H, 3.9; N, 14.1. Found; C, 41.4; H, 3.4; N, 13.9.

2.2.6. $[Ru^{II}(bpz)_2(4,4'-Ph_2bpy)](PF_6)_2(4)$

This compound was prepared and purified in a manner similar to **1** by using 4,4'diphenyl-2,2'-bipyridyl (126 mg, 0.409 mmol) in place of bpy to give an orange solid. Yield: 141 mg (65%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.77 (4H, t, *J* = 1.4 Hz), 8.93 (2H, t, *J* = 1.2 Hz), 8.62 (4H, dd, *J* = 4.3, 3.3 Hz), 7.95–7.93 (4H), 7.90 (4H, ddd, *J* = 5.6, 3.3, 1.2 Hz), 7.72 (4H, d, *J* = 1.2 Hz), 7.64–7.60 (6H). ES-MS: *m*/*z* = 870 ([M – PF₆]⁺), 363 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₃₈H₂₈F₁₂N₁₀P₂Ru•2H₂O: C, 43.4; H, 3.1; N, 13.3. Found: C, 43.2; H, 2.6; N, 13.3.

2.2.7. $[Ru^{II}(bpz)_2(4,4'-Cl_2bpy)](PF_6)_2(5)$

This compound was prepared and purified in a manner similar to **1** by using 4,4'dichloro-2,2'-bipyridyl (92 mg, 0.409 mmol) in place of bpy to give an orange solid. Yield: 97 mg (51%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.75 (4H, dd, J = 4.8, 1.1 Hz), 8.63 (4H, t, J = 2.3 Hz), 8.59 (2H, d, J = 3.2 Hz), 7.83 (4H, ddd, J = 7.0, 3.2, 1.2 Hz), 7.61 (2H, d, J = 6.1 Hz), 7.54 (2H, dd, J = 6.2, 2.2 Hz). ES-MS: m/z = 787 ([M – PF₆]⁺), 321 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₂₆H₁₈Cl₂F₁₂N₁₀P₂Ru: C, 33.5; H, 1.9; N, 15.0. Found: C, 33.4; H, 1.8; N, 14.6.

2.2.8. $[Ru^{II}(bpz)_2(4,4'-(NH_2)_2bpy)](PF_6)_2(6)$

This compound was prepared and purified in a manner similar to **1** by using 4,4'diamino-2,2'-bipyridyl (76 mg, 0.408 mmol) in place of bpy to give a dark red-brown solid. Yield: 103 mg (54%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.71 (2H, d, *J* = 1.3 Hz), 9.69 (2H, d, *J* = 1.3 Hz), 8.62 (2H, d, *J* = 3.3 Hz), 8.50 (2H, d, *J* = 3.3 Hz), 7.96 (2H, dd, *J* = 3.3, 1.3 Hz), 7.80 (2H, dd, *J* = 3.3, 1.3 Hz), 7.40 (2H, d, *J* = 2.5 Hz), 6.92 (2H, d, *J* = 6.5 Hz), 6.53 (2H, dd, *J* = 6.5, 2.5 Hz), 5.72 (4H, s). ES-MS: m/z = 748 ([M – PF₆]⁺), 302 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₂₆H₂₂F₁₂N₁₂P₂Ru•2H₂O: C, 33.6; H, 2.8; N, 18.1. Found: C, 33.7; H, 2.5; N, 18.0.

2.2.9. $[Ru^{II}(bpz)_2(bpym)](PF_6)_2(7)$

This compound was prepared and purified in a manner similar to **1** by using 2,2'bipyrimidine (65 mg, 0.411 mmol) in place of bpy to give a bright orange solid. Yield: 77 mg

(43%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.76 (4H, dd, J = 3.3, 1.2 Hz), 9.18 (2H, dd, J = 4.8, 2.0 Hz), 8.65 (2H, d, J = 3.2 Hz), 8.60 (2H, d, J = 3.2 Hz), 8.02 (2H, dd, J = 5.8, 2.0 Hz), 7.96 (2H, dd, J = 3.2, 1.1 Hz), 7.84 (2H, dd, J = 3.2, 1.1 Hz), 7.60 (2H, dd, J = 5.7, 4.9 Hz). ES-MS: m/z =720 ([M – PF₆]⁺), 288 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₂₄H₁₈F₁₂N₁₂P₂Ru•H₂O: C, 32.6; H, 2.3; N, 19.0. Found: C, 32.8; H, 2.2; N, 18.9.

2.2.10. $[Ru^{II}(bpz)_2(Me_2qpy^{2+})](PF_6)_4(8)$

This compound was prepared in a manner similar to **1** by using $[Me_2qpy^{2+}](PF_6)_2$ (194 mg, 0.308 mmol) in place of bpy. Purification was effected by using Sephadex-CM C-25 with an eluent of water/acetone (5:3) and a progressively increasing concentration of NaCl (0.025–0.125 M). The product was eluted as a red band; partially evaporating the solvents under vaccum and adding an excess of solid NH₄PF₆ gave a precipitate which was filtered off, washed with water and dried to give a bright orange solid. Yield: 126 mg (45%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.80 (4H, s), 9.15 (2H, d, J = 1.7 Hz), 8.83 (4H, d, J = 6.7 Hz), 8.65 (4H, dd, J = 3.2, 2.4 Hz), 8.49 (4H, d, J = 7.0 Hz), 7.98 (2H, d, J = 6.0 Hz), 7.90–7.85 (6H), 4.39 (6H, s). ES-MS: m/z = 1192 ([M – PF₆]⁺), 524 ([M – 2PF₆]²⁺), 302 ([M – 3PF₆]³⁺), 189 ([M – 4PF₆]⁴⁺). *Anal.* Calc. (%) for C₃₈H₃₂F₂₄N₁₂P₄Ru•H₂O: C, 33.7; H, 2.5; N, 12.4. Found: C, 33.7; H, 2.4; N, 12.2.

2.2.11. $[Ru^{II}(bpz)_2(4,4'-(CF_3)_2bpy)](PF_6)_2(9)$

A solution of *cis*-Ru^{II}(bpz)₂Cl₂ (100 mg, 0.205 mmol) and AgNO₃ (77 mg, 0.453 mol) in water (25 mL) was heated at reflux for 48 h. After cooling to room temperature, the mixture was filtered through Celite to remove AgCl, and the filtrate was evaporated to dryness. The residue was dissolved in DMF (15 mL) and the solution purged with argon for 15 min. 4,4'-bis(trifluoromethyl)-2,2'-bipyridyl (121 mg, 0.414 mmol) was added and the mixture heated at 100 °C for 24 h under argon. After cooling to room temperature, the solution was evaporated under vacuum to a small volume and diethyl ether (150 mL) added. The precipitate was filtered off and dissolved in a minimum of cold water to which solid NH₄PF₆ was added. The solid was filtered off and purified by column chromatography as for

1 to give an orange solid. Yield: 73 mg (35%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 9.77 (4H, d, J = 1.2 Hz), 8.96 (2H, t, J = 3.2 Hz), 8.63 (4H, d, J = 3.2 Hz), 7.97 (2H, d, J = 5.9 Hz), 7.84 (2H, dd, J = 3.2, 1.2 Hz), 7.80 (2H, dd, J = 3.2, 1.2 Hz), 7.75 (2H, dd, J = 6.0, 1.4 Hz). $\delta_{\rm F}$ (400 MHz, CD₃CN) –63.89 (6H, s), –71.36 (12H, d, J = 707 Hz). ES-MS: m/z = 854 ([M – PF₆]⁺), 355 ([M – 2PF₆]²⁺). *Anal.* Calc. (%) for C₂₈H₁₈F₁₈N₁₀P₂Ru•H₂O: C, 33.1; H, 2.0; N, 13.8. Found: C, 32.7; H, 1.5; N, 13.7.

2.2.12. $[Ru^{II}(bpz)_2(4,4'-(CO_2Me)_2bpy)](PF_6)_2(10)$

This compound was prepared and purified in a manner similar to **9** by using 4,4'bis(methoxycarbonyl)-2,2'-bipyridyl (112 mg, 0.411 mmol) in place of 4,4'bis(trifluoromethyl)-2,2'-bipyridyl to give an orange solid. Yield: 98 mg (48%). $\delta_{\rm H}$ (400 MHz, CD₃CN) 10.02 (4H, t, *J* = 1.5 Hz), 9.25 (2H, d, *J* = 1.1 Hz), 8.72 (2H, d, *J* = 3.2 Hz), 8.69 (2H, d, *J* = 3.2 Hz), 8.07 (2H, dd, *J* = 5.8, 0.5 Hz), 8.05–8.02 (4H), 7.94 (2H, dd, *J* = 3.2, 1.2 Hz), 3.35 (6H, s). ES-MS: *m*/*z* = 835 ([M – PF₆]⁺), 345 ([M – 2PF₆]²⁺). Anal. Calc (%) for C₃₀H₂₄F₁₂N₁₀O₄P₂Ru•H₂O: C, 36.1; H, 2.6; N, 14.0. Found: C, 36.0; H, 2.3; N, 13.9.

2.3. Theoretical calculations

Geometry optimisation (in the gas phase only) and subsequent time-dependant density functional theory (TD-DFT) calculations were carried out by using the Gaussian 09 suite of programs [45]. A range of calculations was performed with the functionals BP86 [46,47], B3LYP [48], PBE1PBE [49] and M06 [50] with the basis set Def2-QZVP [51] on Ru and Def2-SVP [51] on all other atoms. The M06 functional allowed the most accurate modeling of the experimental data when including a CPCM [52,53] solvent model of acetonitrile during TD-DFT calculations. Using this approach, the first 100 excited singlet states were calculated and simulated UV–Vis spectra in the range of 200–800 nm were convoluted with Gaussian curves of FWHM of 3000 cm⁻¹ by using GaussSum [54].

3. Results and discussion



Fig. 1. Chemical structures of the Ru^{II} complex salts investigated.

3.1. Syntheses

The bpz proligand was synthesised from 2-iodopyrazine, by adapting the Pd-catalysed homocoupling method of Wang et al. [55]. Previous syntheses from 2-pyrazinecarboxylate with Cu [25,56] or from 2-chloropyrazine with Ni [57] or Pd [58] catalysts give isolated yields well below the 70% achieved here. The compound 4,4'-bis(trifluoromethyl)-2,2'-bipyridyl was prepared also via the Wang method from 2-bromo-4-trifluoromethylpyridine, again giving higher isolated yields when compared with published methods using 2-chloro-4-trifluoromethylpyridine with Ni catalysis [59–61].

The complex salts **1**, **2** and **7** (Fig. 1) have been studied previously on a number of occasions. The original preparation of **1** [27] involved the precursor $Ru^{IV}Cl_4(bpy)$; while subsequent related reports have mentioned using instead *cis*- $Ru^{II}(bpz)_2Cl_2$ [62–64], details are lacking. The latter complex is significantly less reactive towards chloride ligand substitutions when compared with *cis*- $Ru^{II}(bpy)_2Cl_2$, so the use of a relatively high-boiling solvent mixture is required to give reasonable yields of *ca*. 45–65%. **1**–**7** were purified by using column chromatography on silica gel, while Sephadex-CM C-25 was used for **8** in order to remove uncoordinated Me₂qpy²⁺. For **9**, using Ag(I) to abstract the chloride ligands is necessary to give satisfactory results, probably due to the decreased basicity of the incoming bpy-based ligand. The same method was applied for **10**, because that used for **1** leads to coordination but also trans-esterification by 2-methoxyethanol of the 4,4'-bis(methoxycarbonyl)-2,2'-bipyridyl

ligand. The identities and purities of all the compounds prepared are confirmed by diagnostic 1 H NMR spectra, together with mass spectra and CHN elemental analyses. Most of the complex salts retain *ca*. 1–2 equivalents of water, as is typically observed for such compounds. Portions of representative 1 H NMR spectra for the complex salts **1**, **3** and **9** are shown in the Supplementary Information (Fig. S1).



Fig. 2. UV–Vis absorption spectra of the complex salts **1** (green), **3** (blue), **6** (red) and **9** (gold) in acetonitrile at 293 K; (a) full spectra; (b) expansion of the low energy region.

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3.2. Electronic spectroscopy

UV–Vis absorption spectra were recorded for **1–10** in acetonitrile, and the results are listed in Table 1. Representative spectra of **1**, **3**, **6** and **9** are shown in Fig. 2.

Each complex salt shows two broad, overlapping bands in the visible region, assigned to transitions of MLCT character. The λ_{max} value for the well-defined lowest energy band shows a clear trend of increasing as the co-ligand (L–L) becomes more electron-donating, in the order 4,4'-(NH₂)₂bpy > 4,4'-Me₂bpy = 4,4'-^tBu₂bpy > 4,4'-Ph₂bpy \geq bpy > 4,4'-Cl₂bpy \geq Me₂qpy²⁺ \geq bpym \geq 4,4'-(CO₂Me)₂bpy \geq 4,4'-(CF₃)₂bpy > bpz. Within the bpy-containing series, the energy of this band decreases by *ca*. 0.3 eV on replacing the most strongly electron-withdrawing -CF₃ with the most donating -NH₂ groups. The higher energy band shows a similar shifting pattern, but its position is less clearly defined and the decrease between the two extremes is less pronounced at *ca*. 0.16 eV. Anion metathesis allowed isolation of the Cl⁻ salts (see the Supplementary Information for details), and their spectra were measured in water (Supplementary Information, Table S1). In most cases, very slight blue-shifts are observed on moving from acetonitrile to water, but the overall trend in λ_{max} values remains essentially unchanged.

Assignment of the separate low energy MLCT transitions to specific ligands is nontrivial. Resonance Raman spectroscopic measurements on heteroleptic complexes such as $[Ru^{II}(bpz)_2(bpy)]^{2+}$ indicate that the transitions to bpz occur at lower energies than those to bpy or substituted bpy ligands [63, 65, 66]. This conclusion agrees with the expected relative stabilisation of the π^* -orbitals of bpz. The red shift of the lowest energy visible band maximum observed here on increasing the electron-donating ability of L–L is consistent with destabilisation of the Ru-based HOMO, while the bpz-based LUMO remains essentially unchanged. The position of the higher energy band depends on changes in both the HOMO and L–L-based LUMO. However, given that both of the homoleptic complexes $[Ru^{II}(bpz)_3]^{2+}$ and $[Ru^{II}(bpy)_3]^{2+}$ also show two overlapping MLCT bands in this region, this analysis is probably somewhat over-simplified. The band assignments are best addressed by using TD-DFT calculations (see below).

Additional absorptions in the region *ca*. 320–400 nm are probably also due to MLCT transitions primarily, while the more intense bands to higher energies in the UV region are attributable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions.

3.3. Electrochemistry

1–10 were studied by using cyclic voltammetry in acetonitrile, and the results are included in Table 1. Representative voltammograms for 1, 3, 6 and 9 are shown in Fig. 3. All potentials are quoted with respect to the Ag–AgCl reference electrode.



Fig. 3. Representative cyclic voltammograms of the complex salts **1** (green), **3** (blue), **6** (red) and **9** (gold) at 293 K in acetonitrile (Pt disc working electrode, scan rate = 100 mV s^{-1}). The single-headed arrow indicates the direction of the initial scans.

In each case, a reversible Ru^{III/II} wave is observed with $E_{1/2}$ in the range 1.43–1.92 V. All of these values are lower than that found for $[Ru^{II}(bpz)_3]^{2+}$ under the same conditions, showing that the Ru centre is more electron-rich when even 4,4'-(CF₃)₂bpy replaces bpz. $E_{1/2}$ decreases as L–L becomes more electron-donating, with the order following essentially the same sequence as noted for λ_{max} of the lowest energy MLCT band, i.e. excluding L–L = bpz, $E_{1/2}$ is highest when L–L is 4,4'-(CF₃)₂bpy (in **9**) and lowest with 4,4'-(NH₂)₂bpy (in **6**). The total difference between these extremes is *ca*. 0.5 V.

Each of 1–10 also shows at least three reversible, ligand-based reduction processes, excepting **6** for which the third process is irreversible. **8** is a special case and discussed separately below. In every other case, the first two reductions can be assigned to the bpz ligands, and their $E_{1/2}$ values increase slightly as L–L becomes less electron-donating and the bpz ligands become progressively easier to reduce. The extreme values for the first two reductions are -0.76/-1.06 V for **6** and -0.69/-0.88 V for **9**, and slightly higher again for [Ru^{II}(bpz)₃][PF₆]₂. Hence, the second wave is more sensitive to the nature of L–L. The third reduction wave is assigned to L–L, its $E_{1/2}$ or E_{pc} value increasing as this coligand becomes more electron deficient.

For **8**, the reductive region shows overlapping waves that were resolved by using differential pulse voltammetry. The closely related compound $[Ru^{II}(bpy)_2(Me_2qpy^{2+})][PF_6]_4$ shows the first two reductions as overlapped waves with $E_{1/2}$ values of -0.62 and -0.73 V, then further waves at -1.19, -1.42 and -1.59 V [43]. The waves at -0.58 and -0.69 V in **8** are therefore attributable to reduction of the pyridinum units in Me₂qpy²⁺, while the next one at -0.82 V and the irreversible process at $E_{pc} = -1.04$ V likely correspond with the bpz-based reductions.

Table 1

UV–Vis absorption and electrochemical data for the complex salts [${ m Ru}^{ m I}$	$(bpz)_2(L-L)][PF_6]_n$ in
acetonitrile. ^a	

Compound $(I - I)$	$\lambda_{\rm max}$, nm	$E_{\rm max}$	Assignment	$E_{1/2}$, V vs, A	ag–AgCl
Compound (E E)	$(\varepsilon 10^3 \text{ M}^{-1} \text{ cm}^{-1})^{\text{b}}$	(eV)	rissignment	$(\Delta E_{\rm n}, {\rm mV})^{\rm c}$	
	(0,10 11 011)			Ru ^{III/II}	Ligand-based
$[Ru^{II}(bpz)_3][PF_6]_2$	239 (19.6)	5.18	$\pi \rightarrow \pi^*$	2.01 (90)	-0.66 (70)
L (1 /51L 012	292 (53.3)	4.25	$\pi \rightarrow \pi^*$		-0.83 (70)
	338sh (15.7)	3.67	$d \rightarrow \pi^*$		-1.10 (90)
	414sh (10.5)	3.00	$d \rightarrow \pi^*$		-1.74 (90)
	441 (13.0)	2.81	$d \rightarrow \pi^*$		
1 (bpy)	241 (22.3)	5.15	$\pi \rightarrow \pi^*$	1.79 (80)	-0.73 (80)
	254sh (20.0)	4.88	$\pi \rightarrow \pi^*$		-0.96 (70)
	295 (49.3)	4.20	$\pi \rightarrow \pi^*$		-1.50 (70)
	342sh (11.5)	3.63	$d \rightarrow \pi^*$		
	378 (5.7)	3.28	$d \rightarrow \pi^*$		
	420 (9.2)	2.95	$d \rightarrow \pi^*$		
	464 (11.7)	2.68	$d \rightarrow \pi^*$		
$2(4.4'-Me_{a}bnv)$	241 (21.2)	5.15	$\pi \rightarrow \pi^*$	1.72 (80)	-0.75 (70)
= (.,	296 (45.6)	4.19	$\pi \rightarrow \pi^*$		-0.99 (60)
	374sh (11.0)	3.32	$d \rightarrow \pi^*$		-1.58(70)
	422 (8.4)	2.84	$d \rightarrow \pi^*$		
	470 (11.0)	2.64	$d \rightarrow \pi^*$		
$(4.4' - ^{t}Bu_{2}bnv)$	208 (39.3)	5.96	$\pi \rightarrow \pi^*$	1.72 (100)	-0.75 (70)
(I,I Du ₂ opj)	240 (22.7)	5.17	$\pi \rightarrow \pi^*$		-0.98 (60)
	296 (51.2)	4.19	$\pi \rightarrow \pi^*$		-1.58(70)
	345 sh (11.8)	3.59	$d \rightarrow \pi^*$		1.00((0))
	374 sh(7.4)	3.32	$d \rightarrow \pi^*$		
	422 (9.5)	2.94	$d \rightarrow \pi^*$		
	470 (12.1)	2.64	$d \rightarrow \pi^*$		
1 (4 4'-Ph_bny)	243 (37 2)	5 10	$\pi \rightarrow \pi^*$	1 74 (90)	-0.73(70)
(1,1 III20PJ)	262 (39.3)	4.73	$\pi \rightarrow \pi^*$	1.7 1 (20)	-0.96(70)
	298 (80 2)	4 16	$\pi \rightarrow \pi^*$		-143(70)
	388 (9 5)	3 20	$n \rightarrow n$ $d \rightarrow \pi^*$		-1.83(70)
	425(15.4)	2.92	$d \rightarrow \pi^*$		1.05 (70)
	465 (13.8)	2.52	$d \rightarrow \pi^*$		
$(A A' Cl_{b} hny)$	215(42.8)	5 77	$u \rightarrow \pi$ $\pi \rightarrow \pi^*$	1.82(100)	-0.73 (80)
5 (4,4 -Cl ₂ 0py)	213 (42.0) 289 (54.2)	4 29	$\pi \rightarrow \pi^*$	1.02 (100)	-0.95(30)
	340sh (13-3)	3.65	$n \rightarrow n^{*}$		-1.27(70)
	430 sh (10.5)	2.88	$d \rightarrow \pi^*$		1.27 (70)
	455 (11.3)	2.00	$d \rightarrow \pi^*$		
$S(AA'(\mathbf{NH}))$ here)	260 (48.1)	2.72 1 77	$u \rightarrow \pi^*$	1 / 3 (80)	-0.76 (60)
$(+,+-(1411_2)_20py)$	200(+0.1) 303 (40 1)	4 00	$n \rightarrow n^{*}$	1.75 (00)	-1.06 (70)
	350(77.1)	3 /5	$n \rightarrow n^{*}$		-1 89 ^d
	436(7.8)	2. 4 5 2.84	$d \rightarrow \pi^*$		1.07
	400 (1.0) 400 (11 0)	2.04	$d \rightarrow \pi^*$		
(bnym)	777 (11.7) 711 (11.7)	∠.40 5.09	$u \rightarrow \pi^*$	1.01.(00)	_0.71 (70)
(opym)	277 (71.7) 262 (30.6)	172	$\pi \to \pi^*$	1.91 (90)	-0.71(70) -0.92(60)
	202 (30.0)	4.75 A 10	$\pi \to \pi^*$		-0.92(00) -1.17(70)
	250 (+2.1) 340ch (15.1)	3.65	$\pi \to \pi^*$		-1.17(70) -1.80(100)
	$\sqrt{13} \ln (13.1)$	3.00	$u \rightarrow \pi^*$		-1.00 (100)
	413811 (9.3)	2.00	$u \rightarrow \pi^{*}$		
$P(M_{2}, q_{2})$	431(12.0)	2.73	$d \rightarrow \pi^*$	1 95 (00)	0 59 (70) ^e
(me ₂ qpy)	233 (34.3)	4.90	$\pi \rightarrow \pi^*$	1.85 (90)	$-0.58(70)^{\circ}$
	298 (30.0)	4.10	$\pi \rightarrow \pi^*$		-0.09 (70)
	$423 \sin(1/.1)$	2.92	$d \rightarrow \pi^*$		-0.82(00)
	455 (21.5)	2.14	$d \rightarrow \pi^*$	1.00 (100)	-1.04
$(4,4 - (CF_3)_2 bpy)$	241 (20.9) 255 -h (10, 4)	5.15	$\pi \rightarrow \pi^*$	1.92 (120)	-0.09 (70)
	2008 (18.4)	4.80	$\pi ightarrow \pi^*$		-0.88 (00)
	293 (00.1)	4.23	$\pi \rightarrow \pi^*$		-1.13 (70)

10 (4,4'-(CO ₂ Me) ₂ bpy)	344sh (11.6) 417sh (10.6) 447 (13.3) 220 (29.9) 298 (65.1) 343sh (15.6) 418sh (13.9) 449 (17.0)	3.60 2.97 2.77 5.64 4.16 3.62 2.97 2.76	$d \rightarrow \pi^{*}$ $d \rightarrow \pi^{*}$ $d \rightarrow \pi^{*}$ $\pi \rightarrow \pi^{*}$ $d \rightarrow \pi^{*}$ $d \rightarrow \pi^{*}$ $d \rightarrow \pi^{*}$	1.89 (90)	-0.69 (70) -0.89 (60) -1.15 (70) -1.65 (70)	
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^a n = 2 for all except **8**, where n = 4.

^b Solutions *ca.* $10^{-5} - 10^{-4}$ M.

^c Solutions *ca*. 10^{-3} M in analyte and 0.1 M in [NBu^{*n*}₄]PF₆ with a 2 mm disc Pt working electrode with

a scan rate of 100 mV s⁻¹. Fc/Fc⁺ internal reference, $E_{1/2} = 0.44$ V, $\Delta E_p = 70-90$ mV.

^d $E_{\rm pc}$ value for an irreversible process.

^e Strongly overlapping waves resolved by using differential pulse voltammetry (potential increment = 2 mV; amplitude = 50 mV; pulse width = 0.01 s).

3.4. Computations

In order to rationalise their electronic structures and optical properties, DFT and TD-DFT calculations have been performed on $[Ru^{II}(bpz)_3]^{2+}$ and the complexes in salts **1**, **3**, **6**, **8** and **9** (denoted **1'**, etc.) by using Gaussian 09 [45]. $[Ru^{II}(bpz)_3]^{2+}$ has been subjected to such calculations previously, with the B3LYP [67–69] or B3PW91 [70] functionals. Having experimented with various methods, we found that the M06 functional gives the best prediction of UV–Vis absorption spectra in acetonitrile. Also, the Ru–N distances derived from this level of theory for $[Ru^{II}(bpz)_3]^{2+}$ (2.072–2.074 Å) are shorter than those predicted using other methods and closer to the average X-ray crystallographic value of 2.05 Å [71]. Selected calculated geometric parameters are in the Supplementary Information (Table S8).

Selected TD-DFT-calculated electronic transitions are presented in Table 2, and simulated UV–Vis spectra are shown together with the experimental ones in Fig. 4. The corresponding results for $[Ru^{II}(bpz)_3]^{2+}$ (can be found in the Supplementary Information (Table S9 and Fig. S2). Selected MOs for **1'** and **8'** are shown in Figs. 5 and 6, while further contour surface diagrams for these and the other complexes can be found in the Supplementary Information (Figs. S3–S8). The tetracationic complex **8'** shows behaviour significantly different from that of the dicationic complexes, so merits separate discussion.

Table 2

Selected data obtained from TD-DFT calculations on the complexes $[Ru^{II}(bpz)_2(L-L)]^{n+}$ (M06/Def2-QZVP/Def2-SVP) in acetonitrile (CPCM).^a

Complex	λ	ΔE	$f_{\rm os}{}^{\rm b}$	Major contributions (%)
(L–L)	(nm)	(eV)		
1' (bpy)	455	2.73	0.14	HOMO-2 \rightarrow LUMO (69)
				HOMO-1 \rightarrow LUMO+1 (25)
	425	2.92	0.08	HOMO-2 \rightarrow LUMO+1 (71)
				HOMO-1 \rightarrow LUMO (10)
				HOMO-1 \rightarrow LUMO+2 (10)
	383	3.24	0.07	HOMO-1 \rightarrow LUMO+2 (78)
				HOMO \rightarrow LUMO+5 (14)
	352	3.52	0.04	HOMO-1 \rightarrow LUMO+5 (10)
				HOMO \rightarrow LUMO+4 (87)
	337	3.68	0.06	HOMO-2 \rightarrow LUMO+3 (74)
				HOMO-1 \rightarrow LUMO+5 (11)
$3'(4,4'-^{t}Bu_{2}bpy)$	459	2.70	0.14	HOMO-2 \rightarrow LUMO (72)
				HOMO-1 \rightarrow LUMO+1 (24)
	428	2.90	0.08	HOMO-2 \rightarrow LUMO+1 (73)
				HOMO-1 \rightarrow LUMO (10)
	375	3.31	0.10	HOMO-1 \rightarrow LUMO+2 (77)
				HOMO \rightarrow LUMO+5 (19)
	356	3.48	0.03	HOMO-1 \rightarrow LUMO+5 (12)
				HOMO \rightarrow LUMO+4 (85)
	344	3.60	0.05	HOMO-1 \rightarrow LUMO+5 (72)
				HOMO \rightarrow LUMO+4 (10)
6' (4,4'-(NH ₂) ₂ bpy)	484	2.56	0.13	HOMO-2 \rightarrow LUMO (79)
	$<$ \neg			HOMO-1 \rightarrow LUMO+1 (13)
	444	2.79	0.06	HOMO-2 \rightarrow LUMO+1 (75)
	381	3.25	0.04	HOMO-1 \rightarrow LUMO+2 (65)
				HOMO \rightarrow LUMO+4 (26)
	366	3.39	0.10	HOMO-1 \rightarrow LUMO+4 (35)
				HOMO \rightarrow LUMO+5 (56)
	364	3.41	0.06	HOMO-1 \rightarrow LUMO+3 (34)
				HOMO-1 \rightarrow LUMO+5 (39)
1				HOMO \rightarrow LUMO+4 (10)
$8'(Me_2qpy^{2+})$	475	2.61	0.07	HOMO-1 \rightarrow LUMO (43)
- 11 /				HOMO-1 \rightarrow LUMO+1 (53)
	449	2.76	0.19	HOMO-2 \rightarrow LUMO+3 (23)
				HOMO-1 \rightarrow LUMO (42)
				HOMO-1 \rightarrow LUMO+1 (24)
	440	2.82	0.13	HOMO-2 \rightarrow LUMO+1 (68)
				HOMO-1 \rightarrow LUMO+3 (23)
	418	2.97	0.10	HOMO-2 \rightarrow LUMO+3 (27)
				HOMO \rightarrow LUMO+2 (53)
	393	3.16	0.13	HOMO-1 \rightarrow LUMO+2 (86)

				HOMO-1 \rightarrow LUMO+3 (11)
	380	3.27	0.07	HOMO-2 \rightarrow LUMO+2 (62)
				HOMO-2 \rightarrow LUMO+3 (21)
	319	3.89	0.28	HOMO-5 \rightarrow LUMO (47)
				HOMO-4 \rightarrow LUMO (14)
				$HOMO-2 \rightarrow LUMO+5 (16)$
9' (4,4'-(CF ₃) ₂ bpy)	444	2.79	0.12	$HOMO-2 \rightarrow LUMO(75)$
				HOMO-1 \rightarrow LUMO+1 (20)
	426	2.91	0.14	$HOMO-2 \rightarrow LUMO+1 (50)$
				HOMO-1 \rightarrow LUMO+2 (38)
	345	3.59	0.03	HOMO \rightarrow LUMO+4 (71)
				HOMO \rightarrow LUMO+9 (19)
	339	3.66	0.03	HOMO-1 \rightarrow LUMO+3 (78)
				HOMO \rightarrow LUMO+5 (12)
	332	3.74	0.02	HOMO-1 \rightarrow LUMO+4 (14)
				HOMO \rightarrow LUMO+6 (58)
	331	3.74	0.02	HOMO-1 \rightarrow LUMO+5 (56)
				HOMO \rightarrow LUMO+4 (10)
				HOMO \rightarrow LUMO+7 (14)

^a n = 2 for all except **8'**, where n = 4. Only the main transitions within each absorption band above 300 nm are included.

^b Oscillator strength.

The calculated spectra match the experimental ones relatively well (Fig. 4), but do not predict the two maxima observed in the visible region. The major orbital contributions for the lowest energy transition of significant intensity are the same for each of the dicationic complexes 1', 3', 6' and 9'; largely HOMO-2 \rightarrow LUMO with some HOMO-1 \rightarrow LUMO+1. Both HOMO-2 and HOMO-1 are primarily metal-based (Fig. 5); the former is derived from the d_{xy} and d_{xz} orbitals, while the latter has mostly d_x²-y² character with a variable d_{yz} contribution. However, HOMO-1 also features a significant contribution from L-L in the amino derivative 6'. The LUMO and LUMO+1 comprise predominantly equal contributions from the π^* -orbitals of the two bpz ligands. Thus, the lowest energy transitions have largely Ru^{II} \rightarrow bpz MLCT character, as expected (see above). Also, their calculated energies reproduce closely the trend observed in the measured E_{max} values for the lowest energy band for 1, 3, 6 and 9.



Fig. 4. Experimental (green) and TD-DFT calculated (blue dashed) UV–Vis absorption spectra of (a) 1', (b) 6', (c) 8' and (d) 9' in acetonitrile. The experimental data is for the PF_6^- salts and plotted against the ε -axes, with the calculated spectra scaled to allow for comparison of the main absorption bands. Individual calculated vertical transitions (red) are plotted against the f_{os} -axes

For complex 1', the next lowest energy transition of significant intensity (at 425 nm) also has mainly $Ru^{II} \rightarrow bpz$ MLCT character, but some involvement of LUMO+2 corresponds with MLCT towards the bpy ligand (Fig. 5). LUMO+2 is also predominantly located on L–L for 3' and 9', while for 6' it is spread approximately evenly across all three ligands. The only other dicationic complex for which LUMO+2 is involved significantly in the second lowest energy transition is 9', due to the stabilising effect of the electron-withdrawing -CF₃ substituents.



Fig. 5. M06/Def2-QZVP/Def2-SVP-derived contour surface diagrams of the HOMO and MOs involved in the transitions of **1'** at 455 and 425 nm (isosurface value 0.03 au).

A number of significantly intense transitions are predicted in the region 300–400 nm for **1'**, **3'**, **6'** and **9'**. These involve various combinations of metal-based donor orbitals with LUMO+2 or higher energy acceptor orbitals. The LUMO+3, LUMO+4 and LUMO+5 are almost exclusively spread over the bpz ligands in **1'** and **3'**, but in the case of **6'** and **9'**, LUMO+3 is located substantially on L–L, and LUMO+5 also features some contribution from this ligand in **6'**. Therefore, these relatively high energy transitions have a mixture of Ru^{II} \rightarrow bpz and Ru^{II} \rightarrow L–L MLCT character.

The intense band at *ca*. 300 nm is in most cases due to bpz-based $\pi \to \pi^*$ transitions primarily, involving orbitals like HOMO-4 and HOMO-5 in 1' and 3', which have very similar energies. In the case of 9', $\pi \to \pi^*$ transitions located on L–L have energies similar to the bpz-based ones, due to the relative electron deficiency of the 4,4'-(CF₃)₂bpy ligand.

For the tetracationic complex **8'**, the lowest energy transition (at 475 nm) corresponds with mostly HOMO-1 \rightarrow LUMO+1 and HOMO-1 \rightarrow LUMO. As for the dicationic complexes, HOMO-1 is still Ru-based, and LUMO+1 is spread over both bpz ligands, but the LUMO is in this case located largely on the Me₂qpy²⁺ ligand (Fig. 6). Three further main transitions are predicted above 400 nm, involving HOMO, HOMO-1 and HOMO-2 with LUMO, LUMO+1, LUMO+2 and LUMO+3. The donor orbitals are all Ru-based, while LUMO+2 is Me₂qpy²⁺-based and LUMO+3 involves again the bpz ligands. Therefore, the visible absorption band of this complex is attributable to a combination of Ru^{II} \rightarrow bpz and Ru^{II} \rightarrow Me₂qpy²⁺ MLCT. The same general conclusion can be drawn regarding the main transitions predicted for **8'** in the 300–400 nm region.



Fig. 6. M06/Def2-QZVP/Def2-SVP-derived contour surface diagrams of the two lowest energy Me_2qpy^{2+} -based MOs in **8'** (isosurface value 0.03 au).

The low energy shoulder on the first UV band for **8'** is due to a transition at 319 nm, mostly HOMO-5 \rightarrow LUMO which corresponds with $\pi \rightarrow \pi^*$ within the Me₂qpy²⁺ ligand. As for the other complexes, a number of primarily ligand-based transitions are also predicted at higher energies.

The calculated relative orbital energies are depicted in the Supplementary Information (Fig. S9). For the dicationic complexes, the predicted HOMO-LUMO gap follows the same trend as observed for E_{max} of the lowest energy MLCT band, while the relative size of this energy gap seems somewhat underestimated for 8'. This apparent anomaly is explained by the fact that the lowest energy transition for the latter complex has mixed Ru^{II} \rightarrow bpz and Ru^{II} \rightarrow Me₂qpy²⁺ character. The trends in the energies for 1', 3', 6', 8' and 9' are largely in agreement with the cyclic voltammetric data. For example, the predicted HOMO energy increases by 0.5 eV on moving from 9' to 6', while the corresponding decrease in $E_{1/2}[\text{Ru}^{\text{III/II}}]$ is 0.49 V (Table 1). Also, the predicted location of the LUMO and LUMO+1 on the bpz ligands is consistent with the assignment of the first two reduction waves for 1, 3, 6 and 9. In contrast, in 8' the LUMO is Me₂qpy²⁺-based and initial reduction involves this ligand rather than bpz.

4. Conclusions

Complexes of cis-{Ru^{II}(bpz)₂}²⁺ with a bpy-based coligand L–L have been synthesised and characterised as their PF₆⁻ and Cl⁻ salts by using ¹H NMR spectroscopy and other techniques. The UV–Vis spectra of these complex salts show intense intraligand $\pi \rightarrow \pi^*$ absorptions and low energy MLCT bands with two maxima. The lowest energy MLCT band red-shifts as the electron-donating strength of L–L increases, with an energy difference of *ca*. 0.3 eV between the complex salts containing 4,4'-(CF₃)₂bpy and 4,4'-(NH₂)₂bpy. Cyclic voltammetry with the PF₆⁻ salts reveals reversible Ru^{III/II} oxidation waves and multiple, mostly reversible ligand-based reductions. The trend shown by the MLCT energies correlates with the measured reduction potentials. TD-DFT calculations at the M06/Def2-QZVP/Def2-SVP level of theory with an acetonitrile solvent continuum give relatively good agreement with the experimental UV–Vis spectra. The assignment of the lowest energy visible absorption band as being due to Ru^{II} \rightarrow bpz MLCT is confirmed, while further such transitions occur together with Ru^{II} \rightarrow L–L MLCT at higher energies.

Acknowledgments

We thank the BBSRC for support in the form of a PhD studentship (MKP). NSS is supported by an EPSRC Established Career Fellowship (grant EP/J020192/1) and was funded by a Royal Society Wolfson Merit Award. We are grateful to Dr Octavia A. Blackburn for advice concerning TD-DFT calculations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015...

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