

Near infra-red emission from a *mer*-Ru(II) complex: consequences of strong σ -donation from a neutral, flexible ligand with dual binding modes†

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A rare example of dual coordination modes by a novel tridentate ligand gives rise to unique *fac*- and *mer*-Ru(II/III) complexes. The *mer*-Ru(II)-complex displays the farthest red-shift of a triplet metal-to-ligand charge transfer (³MLCT) emission with a tridentate ligand for a mononuclear complex. This observation is a consequence of large bite angle and strong σ -donation by the ligand, the combined effect of which helps to separate the energy of the ³MLCT and ³MC states.

Ruthenium(II) polypyridyl complexes continue to grow in interest due to their remarkable photophysical properties, which are readily tuned by ligand modifications.¹ The interest in these compounds arises from their potential application as photosensitizers in solar energy conversion,² water-splitting catalysis,³ and electroluminescent dyes in organic light-emitting devices.⁴ Red-emitting Ru(II)-photosensitizers⁵ associated with long excited state lifetimes and Ru(III)-polypyridyl complexes⁶ are of particular interest as luminescence probes in cell-imaging systems and catalytic applications. In general, the tris(bidentate) [Ru(bpy)₃]²⁺-type (bpy = 2,2'-bipyridine) complexes exhibit more advantageous photophysical properties (*e.g.*, longer excited-state lifetimes and higher room-temperature emission quantum yields) than the bis(tridentate) [Ru(tpy)₂]²⁺-type (tpy = 2,2':6',2''-terpyridine) complexes (C1 in Fig. 1). This is a consequence of the lower ligand field splitting due to geometric constraints in the latter complex, resulting in thermal accessibility of the metal-centered (³MC) states, whose population leads to non-radiative deactivation.⁷ However, red-emitting complexes of bis(tridentate) ligand(s) are enticing for incorporation into larger assemblies⁸ and vectorial energy transfer in molecular electronics,⁹ as substitution on

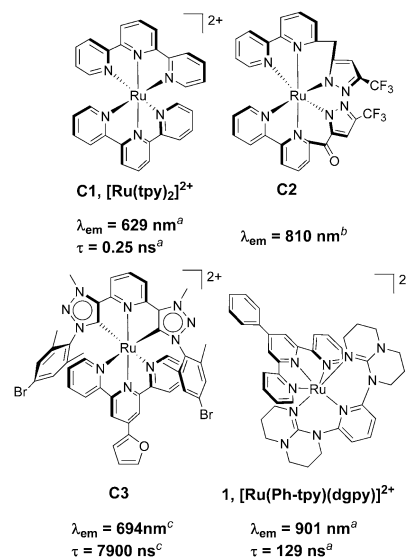


Fig. 1 Benchmark complexes (C1, C2 and C3) and one of the title Ru-complexes (1) (anions are not shown). ^a In deaerated acetonitrile, ^b as solid, ^c in EtOH/MeOH (80 : 20, v/v).

the 4-position leads to linear structures without the formation of enantiomers or diastereomers as found for the bidentate ligands.¹⁰

Many strategies have been used to prolong the excited-state lifetimes of complexes with tridentate ligands, with most focusing on the manipulation of the energies of non-emissive ³MC states relative to emissive ³MLCT states. Stabilization of the ³MLCT state can be achieved by substitution of the tpy ligands by the introduction of: (i) electron-withdrawing functionalities;¹¹ (ii) coplanar aromatic moieties,¹² which results in complexes with red-shifted and longer emission lifetimes compared to the parent compounds; (iii) an organic chromophore to establish an equilibrium between the ³MLCT and chromophore triplet ³LC states;¹³ (iv) tridentate neutral or anionic ligands that form six-membered chelate rings in a bis(tridentate)Ru(II)-complex that have reduced steric strain compared to that of five-membered chelate rings in [Ru(tpy)₂]²⁺, thereby increasing the ligand-field strength, which helps increase

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the excited state lifetime¹⁴ and also red-shift the ³MLCT emission maxima¹⁵ (**C2** in Fig. 1); (v) ligands with strongly donating moieties such as carbene-type ligands,¹⁶ (**C3** in Fig. 1) or (hetero)aromatic N⁺C⁻N type anionic ligands that destabilize the ³MC states.¹⁷

Following a similar argument and within approaches (iv) and (v) we decided to substitute a {6,6}-derivative of guanidine in polypyridyl chelating ligands to increase its donor strength. The coordination chemistry of the {6,6}-derivative of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2- α]pyrimidine (H-hpp) is well documented¹⁸ as a good donor and such a substitution in the 2,6-positions of pyridine (py) should furnish six-membered chelates upon coordination to the metal centre, which in turn would increase the ligand-field strength by forming complexes with near-octahedral geometry.^{14,19} Herein we report a new symmetrical tridentate ligand (**L1** or dgpy; diguanidylpyridine) consisting of two hpp units and its homo- and hetero-leptic ruthenium complexes which constitute a rare set of complexes displaying dual coordination geometries (facial and meridional) with the same tridentate ligand (**L1**).²⁰ The consequences of introducing strong σ -donor hpp units on the electrochemical and photophysical behavior of the complexes are also discussed.

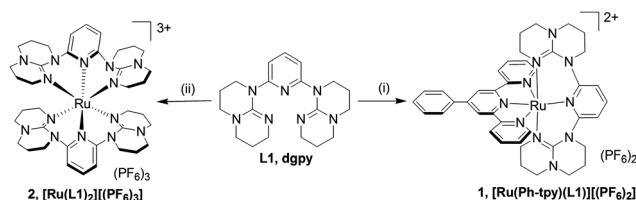
The N-heterocycle-guanidyl ligand **L1** (Scheme 1) was synthesized by reaction of H-hpp with 2,6-dibromopyridine in 1:2 molar ratio, taking advantage of Pd-catalyzed C–N bond forming reactions.²¹ The stoichiometric reaction of **L1** with Ru(Ph-tpy)Cl₃ (Ph-tpy = 4'-phenyl-2,2':6',2''-terpyridine) in refluxing *n*-butanol, in presence of few drops of 4-ethylmorpholine, provided complex **1**, [Ru(Ph-tpy)(**L1**)](PF₆)₂ in modest yield (Scheme 1). Complex **2** [Ru(**L1**)₂](PF₆)₃ was prepared by microwave-assisted reaction with direct mixing of [Ru(DMSO)₄Cl₂] and **L1** in 1:2 molar ratio, followed by anion metatheses in high yield. Although **2** could be prepared by a conventional reflux method, the microwave assisted reaction is less time consuming and improves the yield to obtain a single product, exclusively. The coordination of four donor hpp units in complex **2** stabilises the Ru-atom in its 3+ oxidation state irrespective of the presence of 4-ethylmorpholine in the reaction mixture.

For ligand **L1**, incorporation of a heterocycle at the amidine NH position of H-hpp renders the six annular methylene units nonequivalent by NMR spectroscopy and thereby **L1** exhibits six different methylene signals, each integrating for four protons whereas in free H-hpp only three types of methylene groups are found.²² The appearance of multiple peaks over 0–4 ppm region in ¹H NMR spectrum of **1** (Fig. S2 in ESI[†]) suggests that upon

coordination to the metal center, the exchange between the equatorial and axial protons in the saturated backbone of **L1** is slow compared to the NMR time scale. The presence of paramagnetic Ru^{III} centre in **2** considerably influences the chemical shifts of the protons (Fig. S3 in ESI[†]).²³ The unpaired electron of Ru^{III} accelerates the relaxation processes of neighbouring nuclei, masking the ¹H–¹H coupling interaction with a distance-dependency of 1/*r*³. Thus, all signals appear as broad singlets within –10 to +35 ppm range, with an overall integration corresponding to the sum of protons in **2**.

Single crystals of **1** and **2**, suitable for X-ray structure diffraction, were obtained by slow vapour diffusion of diethyl-ether into concentrated acetone solutions of the title compounds. The ruthenium centre in complex **1** has the expected distorted octahedral geometry where both the tridentate ligands coordinate meridionally (Fig. 2-left). The bite angle subtended by the two *trans* N-atoms from the hpp units and the Ru-atom (N4–Ru1–N10 = 173.8(1)°) is substantially increased from that exhibited by the Ph-tpy ligand (N1–Ru1–N3 = 159.2(1)°), and is closer to ideal octahedral geometry around Ru^{II} in complex **1**, compared to that in [Ru(Ph-tpy)₂](PF₆)₂. The coordinatively saturated Ru(III) in **2** (Fig. 2-right) has a distorted octahedral geometry, in which the tridentate ligand **L1** coordinates in a facial geometry, which is facilitated due to the flexible aliphatic backbone of **L1**. To the best of our knowledge this is one of the rare reports where a tridentate ligand adopts both *fac*- and *mer*-coordination geometries around ruthenium.²⁰ The angular separation between the centroid of py ring containing atom N1 and the centroid of py ring containing atom N8 around ruthenium is 88.2°, suggesting the two central py rings are in 'cis-eclipsed' conformation. The average Ru–N bond distance [2.065(3) Å] in **2**, is found to be in close proximity to that is found in tripodal [Ru{(2-Py)₃CH₂]₂²⁺ or [Ru{(2-Py)₃N]₂²⁺ [2.066(3) Å] (Py = substituted py) as observed by Keene *et al.*²⁴ The average (86.41(10)°) of all the facial N–Ru–N bite angles, in **2**, is close to ideal facial octahedral angle of 90°. The conformation of the saturated ring does not appear to have any noticeable influence on the structure, as opposed to other coordination complexes incorporating (CH₂)-bridged donor atoms.²⁵

The electrochemical behavior of complexes **1** and **2** has been examined by cyclic voltammetry. Each redox process was found



Scheme 1 Syntheses of complexes **1** and **2**. (i) [Ru(Ph-tpy)Cl₃] (1 eq.) in *n*-butanol at reflux followed by the addition of KPF₆, 37%; (ii) [Ru(DMSO)₄Cl₂] (0.5 eq.) in ethylene glycol by microwave heating at 200 °C followed by the addition of KPF₆, 80%.

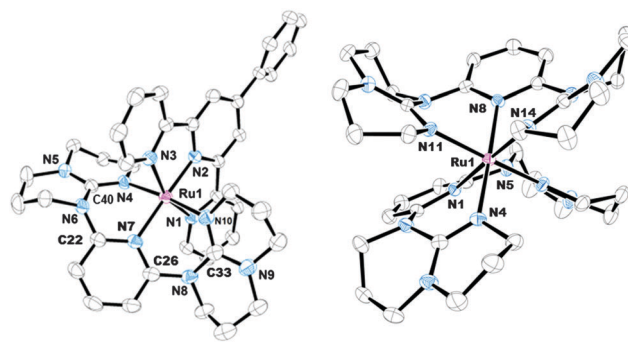


Fig. 2 ORTEP views of **1** (left) and **2** (right). Hydrogen atoms, anions, and solvent molecules have been omitted for clarity. Ellipsoids correspond to a 50% probability level.

to be mono-electronic by differential pulse voltammetry and values are reported *vs.* SCE. At positive potentials, complex **1** shows a quasi-reversible Ru(III/II) couple at 0.50 V, as suggested by DFT calculations (Table S3 in ESI†). This value is nearly 800 mV less positive than that observed for the same Ru(III/II) couple in [Ru(tpy)₂]²⁺ which appears at 1.31 V *vs.* SCE.²⁶ The higher energy calculated for the highest occupied molecular orbital (HOMO) of **1** ($E_{\text{HOMO}} = -5.37$ eV) compared to that of [Ru(tpy)₂]²⁺ ($E_{\text{HOMO}} = -6.18$ eV) using same function and basis sets are in good agreement with the lower anodic potentials measured for **1** (Tables S4 and S5 and Fig. S7 in ESI†) in comparison to [Ru(bpy)₃]²⁺ and they clearly suggest a strong σ -donation from the saturated ligand backbone to the metal-based orbitals. The low positive oxidation potential indicates that **L1** is a much stronger donor than tpy. The Ru(III/II) couple in **1** is more similar to the value obtained for the cyclometallated complex [Ru(tpy)(1,3-di(2-pyridyl)benzene)]⁺ (E_{ox1} *vs.* SCE = 0.51 V) and its derivatives.²⁷ At negative potentials, complex **1** displays two quasi-reversible ligand-based reduction peaks at -1.47 V and -2.01 V. As suggested by DFT calculation of **1**, the lowest unoccupied molecular orbital (LUMO) predominantly resides on Ph-tpy ligand, thereby the first reduction peak is believed to be tpy-based. The more electron-rich metal center in **1**, compared to that in [Ru(tpy)₂]²⁺ (E_{red1} *vs.* SCE = -1.23 V), increases back-donation to both ligands and accordingly shifts the ligand-based reduction to more negative potentials, albeit to a lesser extent than that observed for the oxidation couple.²⁸ The destabilization of the LUMO of **1** ($E_{\text{LUMO}} = -2.46$ eV) explains the shift of 240 mV to more negative values measured for the first reduction potential of **1** compared to that of [Ru(tpy)₂]²⁺ ($E_{\text{LUMO}} = -2.60$ eV). The above results clearly indicate that, although neutral, the donor capacity of **L1** is very comparable to cyclometallating ligands. In complex **2**, no metal-based oxidation was observed. Indeed the quasi-reversible one-electron oxidation centered at ~1.2 V is based on ligand, as suggested by DFT calculation, as the SOMO (SOMO = singly occupied molecular orbital) is predominantly residing on the hpp units. A one-electron, quasi-reversible metal-based reduction at a sufficiently low negative potential, -0.29 V is suggested by DFT calculation, as the SUMO (SUMO = singly unoccupied molecular orbital) has significant contribution from the metal centre. The reduction is metal-based especially considering that no reduction process is observed in the cyclic voltammogram of the free ligand at low negative potentials.

The UV-vis spectrum of **1** in acetonitrile solution displays singlet metal-to-ligand charge transfer (¹MLCT) bands in the 350–630 nm region. The UV region is dominated by the $\pi \rightarrow \pi^*$ transitions in the ligand moieties centered around 220–320 nm (Fig. S9 and Tables S6 and S7 in ESI†). The most noticeable feature in the visible region is that the lowest energy ¹MLCT maxima is red-shifted (~150 nm) with respect to that of [Ru(tpy)₂]²⁺. As discussed above, ligand **L1** being a stronger donor than tpy, it is expected to interact with the t_2 [d(Ru)] orbitals of ruthenium more strongly than tpy. This interaction reduces the energy-gap between the metal-based HOMO and tpy-based LUMO and hence the observed red-shift in $d\pi \rightarrow \pi^*$ ¹MLCT transition. Moreover, complex **1** shows two additional bands at ~540 nm

and 380 nm, which are $d\pi(\text{Ru}) \rightarrow \pi^*(\text{ph-tpy})$ ¹MLCT transitions as suggested by TD-DFT calculation of **1**. It may be noted that such a band near 345 nm is usually observed for RuN₄(diimine)²⁺ chromophores.²⁸ The highest energy transition in complex **2** at 234 nm is LC, and the transition at 326 nm is predominantly singlet ligand-to-metal charge transfer (¹LMCT), borrowing energy from higher energy LC transitions, as predicted by TD-DFT calculation of **2** (Fig. S9 and Tables S6 and S10 in ESI†). The other two transitions at 433 and 564(sh) nm may be assigned predominantly to ¹LMCT transitions (Table S10 in ESI†).

The emission spectra of complexes **1** and **2** were measured in deaerated acetonitrile solution at 298 K upon excitation at their lowest energy absorption maxima. The emission maxima for complex **1** appear at 901 nm (Table S11 and Fig. S12 in ESI†), with an associated excited-state lifetime and quantum yield (Φ) of 129 ns and 0.001, respectively, using a NIR-emitting dye, cyanine IR-125, as quantum yield standard ($\lambda_{\text{max,em}} = 818$ nm in EtOH, $\Phi = 0.23$ in DMSO) and applying the optically diluted method for quantum yield determination.²⁹ To the best of our knowledge this is the first example of such a low energy ³MLCT emission from a bis(tridentate) Ru^{II}N₆ complex.^{7,15,16} As expected the emission wavelength is red-shifted upon introduction of **L1** in place of a terpyridine ligand in [Ru(tpy)₂]²⁺ ($\lambda_{\text{max,em}} = 629$ nm) and [Ru(Ph-tpy)₂]²⁺ ($\lambda_{\text{max,em}} = 715$ nm). It has been shown that substitution of a 2,6-bis(8'-quinolinyl)pyridine (bqp) ligand with a tpy ligand, which exhibits lower bite angle upon coordination than bqp, diminishes the lifetime of the *mer*-[Ru(bqp)(tpy)]²⁺ complex to only 7.4 ns compared to 3 μ s in *mer*-[Ru(bqp)₂]²⁺.^{14a,30} Although substituted by Ph-tpy, the strong σ -donation and larger bite angle of **L1** upon coordination, comparable to that of bqp (177.6(7)°), render the ³MC states higher in energy and thus increasing the lifetime and quantum yield by ~500 and ~1000 times, respectively, in **1** compared to that of [Ru(tpy)₂]²⁺. Compound **2** does not emit in the experimental conditions used here (RT fluid solution). This is in fact not surprising since the lowest-energy level of **2** is of LMCT nature, and such states are known to usually deactivate by radiationless decay processes.

In conclusion, we have synthesized a novel *N*_{amine}-substituted guanidyl-pyridine tridentate ligand (**L1**) that can coordinate meridionally to a ruthenium center forming two six-membered chelate rings, thus exhibiting large bite angles. Due to the flexible aliphatic backbone in **L1**, it can also coordinate facially to furnish the homoleptic Ru-complex (**2**). From the Ru(III/II) potential of the new heteroleptic complex (**1**), it is found that the neutral ligand **L1** displays σ -donating ability comparable to that of anionic N⁻C⁻N type tridentate ligands.²⁷ As a result of strong σ donation from **L1** complexes **1** and **2** have much lower energy ¹MLCT and ¹LMCT absorptions, respectively, in the visible region in comparison to ¹MLCT maxima of [Ru(tpy)₂]²⁺. The 298 K solution emission ³MLCT maxima of complex **1** is red-shifted by greater than 100 nm with respect to those for Ru-bis(terpyridine) systems, furthermore with much longer excited state lifetime. Although the phenomenon of *fac*- and *mer*-isomerisation has already been established in the literature with Co(III),³¹ complexes **1** and **2** constitute one of the rare set of examples in which the same tridentate ligand exhibit dual coordination modes around

ruthenium.²⁰ In addition, the *mer*-Ru^{II}-complex exhibits the farthest red-shift in the ³MLCT emission. At 129 ns, its excited state lifetime is coupled with a quantum yield, which is 1000 times greater than its Ru-bis(terpyridine) parent and makes it perfect for NIR applications. The structural, electrochemical and photophysical properties of these complexes may allow them to serve as promising light-harvesting components in artificial photosynthetic systems.

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