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Cyclometalated Ru^{II} Complexes with Improved Octahedral Geometry: Synthesis and Photophysical Properties

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Cyclometalated bis-tridentate ruthenium(II) complexes incorporating 2,6-diquinolin-8-ylpyridine ligands and exhibiting broad visible absorptions are described. A [Ru(N^N^N)(N^C^N)]$^+$ complex based only on ligands with expanded bite angles has a metal-to-ligand charge-transfer excited-state lifetime of 16 ns, which is attributed to a strong ligand field and therefore reduced deactivation via metal-centered states.

Ruthenium(II) polypyridyl complexes continue to be of high interest owing to their remarkable photophysical properties, which are readily tuned by ligand modifications.[1] Much of this work has involved tris-bidentate Ru^{II} complexes, which usually display a lowest excited state of metal-to-ligand charge-transfer (MLCT) character with lifetimes of around ~1 μs. Structurally, however, these complexes are less attractive because they are chiral (Δ and Λ isomers) and geometrical isomers may form when they are incorporated in larger multiunit assemblies.[2] The related achiral bis-tridentate complex [Ru(tpy)$_2$]$^{2+}$ (tpy = 2,2′:6′,2″-terpyridine), in contrast, allows by virtue of its C_2 axis the facile preparation of linear multicomponent assemblies.[3] However, the complex exhibits a short MLCT excited-state lifetime (0.25 ns),[4] which has restricted its use. This is due to the efficient thermal population of metal-centered (MC) states, leading to rapid nonradiative decay, which has been attributed to the unfavorable bite angles of the tridentate ligands and therefore a weak ligand field.[5]

Several strategies to increase the excited-state lifetimes have been reported,[6] where a few approaches specifically aim at destabilizing the MC states. These include the use of 2,6-diquinolin-8-ylpyridine (dqp) ligands, which give improved octahedral geometries (Figure 1),[7] or the use of strong-field cyclometalating ligands.[8] The former approach has resulted in bis-tridentate Ru^{II} complexes that exhibit microsecond ^{3}MLCT excited-state lifetimes,[7] while the latter strategy has led to the recent development of a new class of sensitizers that show broad absorptions over much of the visible region for dye-sensitized solar cells.[9] The anionic carbon significantly changes the electronic properties of the ligand, leading to both red-shifted absorptions and an increase of the excited-state lifetime by 1 order of magnitude compared to [Ru(tpy)$_2$]$^{2+}$.[8b] The excited-state decay in these N$_5$C complexes has been attributed to a balance between activated decay via ^{3}MC states and nonradiative decay governed by the energy gap law.[8d] Given the established effect on the ^{3}MC states of the dqp ligands due to more octahedral coordination,[7] we were interested in the effect of an N^C^N donor set on the photophysical properties using these ligands (Figure 1), the first results of which are presented herein.

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(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277. (b) Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117–214.

(2) Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121–159.

(3) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993–1019.

(4) Winkler, J. R.; Netzel, T.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381–2392.

(5) Calvert, J. M.; Caspar, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6620–6627.

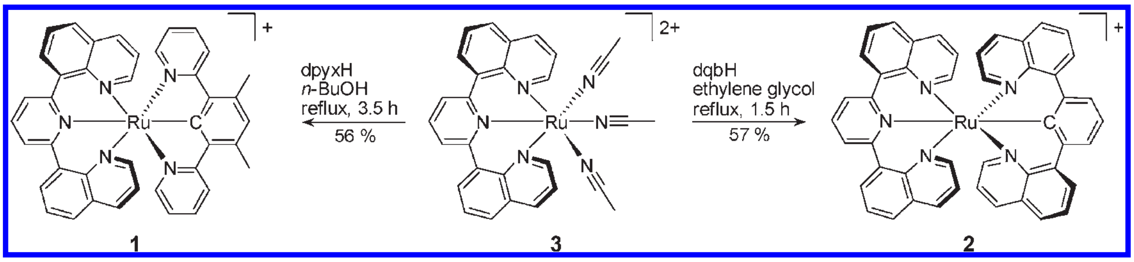
(6) Medlycott, E. A.; Hanan, G. S. *Coord. Chem. Rev.* **2006**, *250*, 1763–1782.

(7) (a) Abrahamsson, M.; Jäger, M.; Österman, T.; Eriksson, L.; Persson, P.; Becker, H.-C.; Johansson, O.; Hammarström, L. *J. Am. Chem. Soc.* **2006**, *128*, 12616–12617. (b) Jäger, M.; Eriksson, L.; Bergquist, J.; Johansson, O. *J. Org. Chem.* **2007**, *72*, 10227–10230. (c) Abrahamsson, M.; Jäger, M.; Kumar, R. J.; Österman, T.; Persson, P.; Becker, H.-C.; Johansson, O.; Hammarström, L. *J. Am. Chem. Soc.* **2008**, *130*, 15533–15542. (d) Jäger, M.; Kumar, R. J.; Görls, H.; Bergquist, J.; Johansson, O. *Inorg. Chem.* **2009**, *48*, 3228–3238.

(8) (a) Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *186*, 91–93. (b) Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543–2547. (c) Constable, E. C.; Cargill Thompson, A. M. W.; Cherryman, J.; Liddiment, T. *Inorg. Chim. Acta* **1995**, *235*, 165–171. (d) Barigelletti, F.; Ventura, B.; Collin, J.-P.; Kayhanian, R.; Gaviña, P.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **2000**, 113–119. (e) Wadman, S. H.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Hartl, F.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2009**, *48*, 1887–1900.

(9) Wadman, S. H.; Kroon, J. M.; Bakker, K.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Chem. Commun.* **2007**, 1907–1909.

Scheme 1



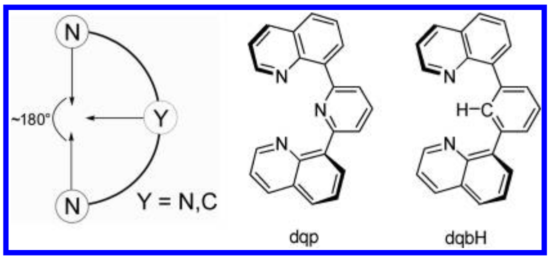


Figure 1. Tridentate ligands with N^N^N (dqp) and N^C^N (dqbH) donor sets.

The heteroleptic complexes **1** and **2** (Scheme 1) consist of one dqp ligand and a cyclometalating ligand, 1,3-dipyrid-2-yl-4,6-dimethylbenzene (dpyxH) and 1,3-diquinolin-8-ylbenzene (dqbH), respectively. The ligand dpyxH was prepared as reported previously,[10] while dqbH was conveniently synthesized via Suzuki–Miyaura coupling of quinolin-8-ylboronic acid and 1,3-dibromobenzene using the previously reported protocol.[7b]

The synthesis of the cyclometalated Ru^{II} complexes was based on the initial coordination of dqp to $RuCl_3 \cdot xH_2O$ and the subsequent isolation of well-characterized *mer*-$[Ru(dqp)(MeCN)_3]^{2+}$ (**3**).[7d] Reacting **3** with dpyxH in refluxing *n*-BuOH for 3.5 h gave complex **1** in 56% isolated yield as a dark-green solid (Scheme 1). In contrast, complex **2** required much longer reaction times under the same conditions. Following the reaction over time (liquid chromatography–mass spectrometry) showed the slow formation of **2**, and even after 2 days of reflux, only low yields (19%) were obtained. Instead, complex **2** was conveniently prepared in ethylene glycol at 196 °C using microwave heating (1.5 h) to give the desired complex as a dark-purple solid in 57% isolated yield. The difference in the relative rates of formation of **1** and **2** in refluxing *n*-BuOH, the same conditions as those successfully used for the related N_6 bis-dqp complexes,[7d] can be attributed to the lack of a central pyridyl unit in dqbH. In contrast to tpy, where the initial coordination is likely to occur at a peripheral pyridyl unit,[11] we previously reported that dqp initially coordinates to Ru^{II} via the central pyridine. A similar argument for dpyxH versus dqbH may explain the difference in reactivity.

The structures of complexes **1** and **2** were confirmed by ^{1}H NMR, mass spectrometry, elemental analysis, and X-ray diffraction. The ^{1}H NMR data show the expected upfield shifts due to anionic ligands (see the Supporting Information). While the dqp ligand in complex **1** is forced to adopt meridional coordination by the dpyx ligand, the tridentate ligands in complex **2** may adopt meridional or facial coordination in analogy to what has been observed for $[Ru(dqp)_2]^{2+}$.[7d] However, the high symmetry of the ^{1}H NMR spectrum for **2** with only two sets of quinoline protons, and the lack of any downfield shifts characteristic for a *trans,fac* arrangement,[7d] suggests the exclusive formation of the meridional complex. This is further supported by the X-ray structure of **2**.

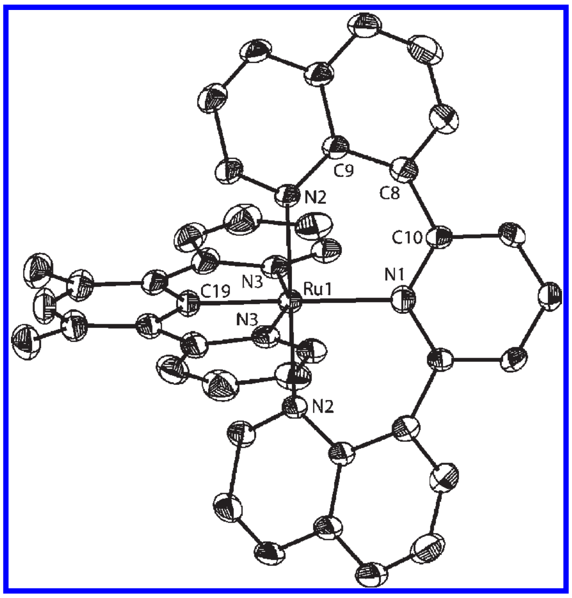


Figure 2. ORTEP view (40% probability ellipsoids) of **1**. Selected bond lengths (Å) and angles (deg): Ru1–N1, 2.150(6); Ru1–N2, 2.088(4); Ru1–N3, 2.085(5); Ru1–C19, 1.948(7); C19–Ru1–N1, 180.0; N2–Ru1–$N2^{\#}$, 179.6(2); N3–Ru1–$N3^{\#}$, 159.0(3); C9–C8–C10–N1, 36.5(6).

X-ray crystal analysis of **1** and **2** confirmed meridional coordination of the tridentate ligands (Figures 2 and 3). Complex **1** shows the expected nonideal bite angle of the cyclometalated dpyx ligand [159.0(3)°] with coplanar arrangement of the benzene and pyridyl units (Figure 2). The Ru1–N3 and Ru1–C19 bond lengths are within the expected range for such ligands.[8e] In contrast, the dqp ligand adopts a helical conformation with a close to ideal bite angle [179.6(2)°], similar to that observed for other Ru^{II} complexes containing the dqp ligand (N–Ru–N bite angles ~ 178–180° and dihedral angles ~ 35–40°).[7] However, the Ru1–N1 bond length in **1** is considerably longer [2.150(6) Å] than what has previously been observed as a result of the *trans* influence of the anionic donor.

In complex **2**, both tridentate ligands show almost ideal bite angles (Figure 3). As has been noted previously for $[Ru(dqp)_2]^{2+}$,[7] both ligands adopt the same helical arrangements (λ,λ or δ,δ), resulting in an almost coplanar arrangement of

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[10] Wilkinson, A. J.; Puschmann, H.; Howard, J. A. K.; Foster, C. E.; Williams, J. A. G. *Inorg. Chem.* **2006**, *45*, 8685–8699.

[11] (a) Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chim. Acta* **1994**, *223*, 177–179. (b) Jahng, Y.; Thummel, R. P.; Bott, S. G. *Inorg. Chem.* **1997**, *36*, 3133–3138.

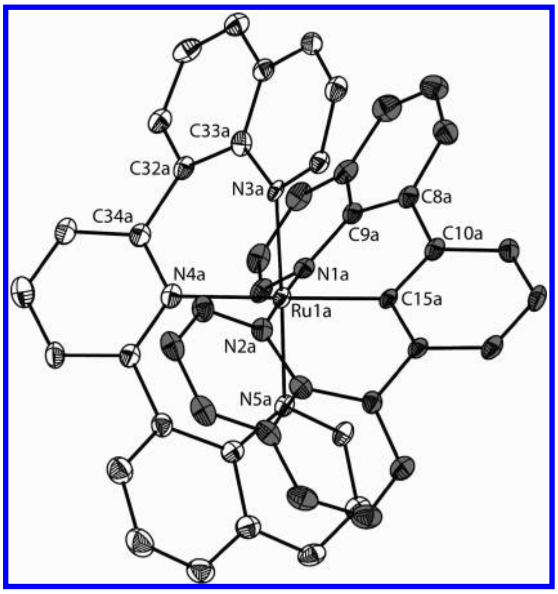

Figure 3. ORTEP view (40% probability ellipsoids) of **2**. Selected bond lengths (Å) and angles (deg): Ru1a−N1a, 2.058(5); Ru1a−N2a, 2.083(5); Ru1a−C15a, 2.015(6); Ru1a−N3a, 2.056(5); Ru1a−N4a, 2.087(5); Ru1a−N5a, 2.068(5); C15a−Ru1a−N4a, 179.3(2); N1a−Ru1a−N2a, 178.5(2); N3a−Ru1a−N5a, 178.2(19); C33a−C32a−C34a−N4a, −38.7(9); C9a−C8a−C10a−C15a, −34.19(8).

quinoline pairs. The dihedral angles and the bond lengths for the tridentate ligands are similar to those found for the dqp ligand in complex **1**, with an elongated Ru−N pyridyl distance [2.087(5) Å] due to the *trans* influence of the anionic carbon.

The redox properties were studied by cyclic voltammetry, which showed reversible metal-based oxidations ($Ru^{III/II}$) at −0.05 and −0.08 V (vs Fc) for **1** and **2**, respectively. These are cathodically shifted by approximately 0.8 V as a result of the carbanion donor compared to their N_6 analogues[7] but are also about 150−200 mV less positive than those for common tpy-based monocyclometalated complexes.[8,12] This is in line with the finding that Ru^{II}dqp-based N_6 complexes in general show a cathodic shift of the $Ru^{III/II}$ redox couple compared to the $[Ru(tpy)_2]^{2+}$ complexes. The first reduction, assigned to the reduction of the noncyclometalating dqp ligands in **1** and **2**, instead occurs at potentials (−1.89 and −2.00 V, respectively) similar to those of common tpy-based monocyclometalated complexes.[8e]

The absorption spectra show intense ligand-centered (LC) transitions in the UV region and broad MLCT transitions in the visible region, the latter extending beyond ~750 nm, which is more bathochromically shifted than is usually observed for these types of Ru^{II} complexes (Figure 4). This agrees well with the finding that the difference in the potential for the metal oxidation and first ligand reduction, $\Delta E_{1/2}$, is somewhat smaller for dqp-based complexes than for normal ruthenium(II) polypyridyl complexes. Notably, complex **1** exhibits two distinct absorption maxima, tentatively attributed to MLCT transitions involving the cyclometalated (high-energy) and noncyclometalated ligands, while **2** features a single broad band that extends from 400 to ~750 nm.

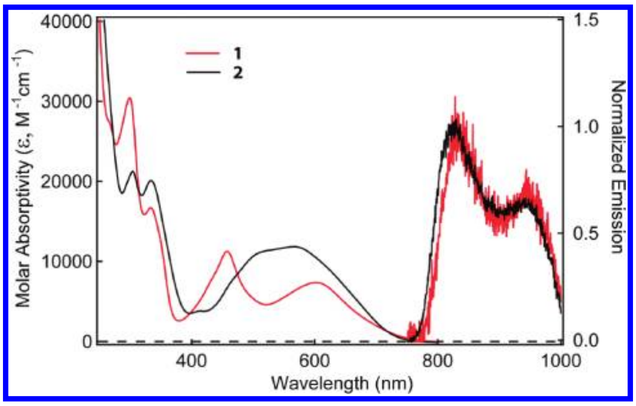

Figure 4. Steady-state absorption at room temperature (MeCN) and emission spectra at 77 K (4:1 EtOH/MeOH) of **1** (red) and **2** (black).

Both complexes are practically nonluminescent at room temperature,[13] and the excited-state lifetimes were therefore determined by transient absorption spectroscopy, which showed monoexponential ground-state recoveries with $\tau = 1.8$ and 16 ns for **1** and **2**, respectively (see the Supporting Information). Both complexes display structured emission at 77 K with spectral shapes typical for ruthenium(II) polypyridyl complexes (Figure 4).[1] The luminescence maxima are similar, 830 and 824 nm for **1** and **2**, respectively. The similar behavior for **1** and **2** can be attributed to the lowest excited states involved, both originating from a dqp-based ^{3}MLCT state.

The ^{3}MLCT lifetime of **1** is somewhat shorter than that for the analogous tpy-based $[Ru(Me\text{-}tpy)(dpb)]^{2+}$ (dpb = 1,3-pyrid-2-ylbenzene) complex (4.0 ns),[14] which is probably due to its lower ^{3}MLCT energy and increased nonradiative decay according to the energy gap law. The more octahedral complex **2**, however, has almost the same ^{3}MLCT energy as **1** but shows a longer lifetime. Because the chromophoric ligand is the same (with the same degree of emission spectral distortion, electronic coupling, etc.), we tentatively attribute this to a stronger ligand field in **2**.

In summary, Ru^{II} complexes **1** and **2** are the first reported examples where dqp ligands with a close to 180° bite angle have been combined with tridentate ligands with an N^C^N donor set. The strong donor set in these complexes leads to broad and intense absorptions over much of the visible region, even broader than those observed for related N_5C complexes. Combined with the preferred geometries and nanosecond excited-state lifetimes, the favorable absorption properties render these types of complexes as promising new chromophores for a multitude of applications.

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Supporting Information Available: Synthetic details, X-ray crystal data, COSY spectra, cyclic voltammograms, transient absorption traces for **1** and **2**, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Complex **2** is slowly oxidized when exposed to air, as indicated by a green impurity in thin-layer chromatography and broad signals in NMR ascribed to the presence of the paramagnetic Ru^{III} species. For the NMR experiment, this was conveniently suppressed by the addition of a small amount of $NaBH_4$.

(13) Complex **2** shows a very weak emission above 800 nm that was not quantified.

(14) Borgström, M.; Ott, S.; Lomoth, R.; Bergquist, J.; Hammarström, L.; Johansson, O. *Inorg. Chem.* **2006**, *45*, 4820–4829.