

Trans Ruthenium(II) Complexes with NH-Bridged Tetradentate Symmetric and Asymmetric Polypyridyl Ligands

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Received May 15, 2002

NH-Bridged tetradentate ligands were synthesized to achieve stable trans Ru(II) bis(polypyridyl) complexes. The polypyridyl part of the ligand was either symmetric, as in *N,N*-bis(1,10-phenanthroline-2-yl)amine (phen-NH-phen), or asymmetric, as in *N*-(1,10-phenanthroline-2-yl)-*N*-(6-yl-dipyridyl[2,3-*a*:2',3'-*c*]phenazine)amine (dppz-NH-phen). Protonation of phen-NH-phen with trifluoroacetic acid and the subsequent reaction with RuCl₃ yield *trans*-[Ru(phen-NH-phen)Cl₂]. The chloro ligands in this compound can easily be replaced by stronger ligands, such as CH₃CN and DMSO. In this way, complexes *trans*-[Ru(phen-NH-phen)(CH₃CN)(DMSO)](PF₆)₂ (**1**), *trans*-[Ru(phen-NH-phen)(DMSO)₂](PF₆)₂ (**2**), and *trans*-[Ru(phen-NH-phen)(CH₃CN)₂](PF₆)₂ (**3**) were obtained. X-ray structures were determined for **1** and **3**. Following a procedure similar to that used with phen-NH-phen, the complex *trans*-[Ru(dppz-NH-phen)(CH₃CN)₂](PF₆)₂ (**4**) was obtained. To our knowledge, this is the first reported trans ruthenium(II) bis(polypyridyl) complex with two different polypyridyl ligands in the equatorial plane.

Ruthenium polypyridyl complexes have been extensively studied for many years, in part because of their potential use in solar energy conversion processes.¹ A majority of the reported ruthenium complexes containing two bipyridyl and two monodentate ligands (e.g., [Ru(bpy)₂(X)(Y)]ⁿ⁺) display a *cis* geometry. Only a few *trans* complexes have been described.² Possible explanations for the *cis* preference have been theoretically analyzed.³ Kinetic effects as well as repulsion between α hydrogens in opposite polypyridyl ligands were invoked. Moreover, most of the reported *trans*

complexes show thermal and/or photochemical instability.^{2c} Nevertheless, a *trans* configuration is likely to be advantageous in order to avoid through-space back electron transfer^{2g} after metal to ligand charge transfer (MLCT) excitation. On the other hand, asymmetric complexes with different polypyridyl moieties in the equatorial plane would have the additional advantage of generating donor and acceptor centers, which should increase the photoinduced charge separation capacity of the molecule. To our knowledge, all *trans* ruthenium(II) bis(polypyridyl) complexes reported to date possess identical polypyridyl ligands in the equatorial plane.

In the present communication, we report the synthesis of several *trans* ruthenium(II) complexes with two NH-bridged polypyridyl-based tetradentate ligands: the symmetric ligand *N,N*-bis(1,10-phenanthroline-2-yl)amine (phen-NH-phen) and the asymmetric ligand *N*-(1,10-phenanthroline-2-yl)-*N*-(6-yl-dipyridyl[2,3-*a*:2',3'-*c*]phenazine)amine (dppz-NH-phen).

The *N,N*-bis(1,10-phenanthroline-2-yl)amine ligand (phen-NH-phen) was first reported by Ogawa et al.⁴ by coupling 2-chloro-1,10-phenanthroline with 2-amino-1,10-phenanthroline. However, no complexation chemistry has been reported to date with this ligand. In the present work, the ligand was obtained as its delocalized tautomer^{4,5} by heating 2-chloro-1,10-phenanthroline⁶ in the presence of ammonia at 250 °C for 8 h, as reported for the dichloro derivative,⁵ or as reported by Ogawa et al., but by using 2-bromo-1,10-phenanthroline⁷ instead. The asymmetric ligand dppz-NH-phen was obtained in a high yield by coupling of the corresponding dppz-bromo derivative with 2-amino-1,10-

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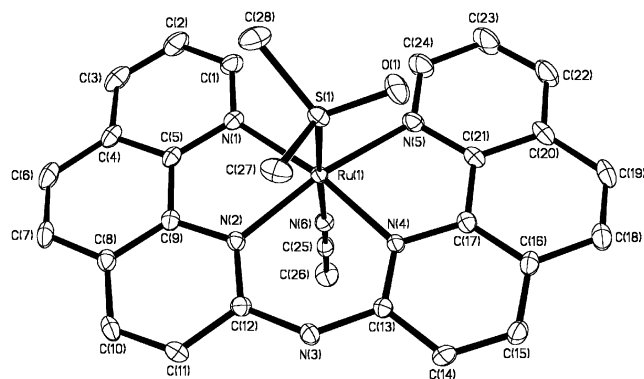


Figure 1. ORTEP view (30% probability) of the structure of the *trans*-[Ru(phen-NH-phen)(CH₃CN)(DMSO)]²⁺ cation (1).

phenanthroline. Complexes with tetradentate ligands generated by the condensation of two different polypyridyl units permit both to overcome H–H repulsion effects and to possess donor and acceptor centers in a *trans* geometry.

For the synthesis of the precursor [Ru(tetradentate ligand)-Cl₂] complexes, the ligands were dissolved in trifluoroacetic acid and precipitated with diethyl ether as the corresponding protonated trifluoroacetate salts,⁸ which subsequently are converted in more than 80% yield to *trans*-[Ru(phen-NH-phen)Cl₂] and *trans*-[Ru(dppz-NH-phen)Cl₂], respectively, by reaction with RuCl₃ in ethyleneglycol at 190 °C.

The complex *trans*-[Ru(phen-NH-phen)(CH₃CN)(DMSO)](PF₆)₂ (**1**) was obtained in 90% yield by reaction of the dichloro compound with acetonitrile in DMSO in the presence of AgPF₆. In a similar way, the complex *trans*-[Ru(phen-NH-phen)(DMSO)₂](PF₆)₂ (**2**) was isolated by heating the dichloro compound at 120 °C in DMSO in the presence of AgPF₆ (91% yield). *trans*-[Ru(phen-NH-phen)(CH₃CN)₂](PF₆)₂ (**3**) and *trans*-[Ru(dppz-NH-phen)(CH₃CN)₂](PF₆)₂ (**4**) were attained in more than 85% yield in the reaction of the corresponding dichloro complexes with a 2:1 DMF/CH₃CN mixture in the presence of AgPF₆.

All complexes were characterized by conventional techniques, including ¹H NMR. X-ray suitable crystals of the hexafluorophosphate salts of **1** and **3** were grown by slow evaporation from acetonitrile/toluene solutions.

The molecular structure of **1** is shown in Figure 1. The ruthenium center adopts a six-coordinate geometry with the equatorial plane occupied by four coplanar phenanthroline nitrogens and acetonitrile and S-bonded DMSO in axial positions. The octahedral coordination shows considerable distortion due to both the unsymmetric axial substitution (Ru–N₆ = 2.064 Å, Ru–S₁ = 2.235 Å) and different Ru–N distances to the opened (Ru–N₁ = 2.108 Å, Ru–N₅ = 2.113 Å) and to the closed (Ru–N₂ = 2.026 Å, Ru–N₄ = 2.025 Å) side of the tetradentate ligand. The short Ru–S distance is indicative of strong π-back-bonding from the metal to the DMSO. This is also reflected by the ¹H NMR spectrum of this complex, where the signal of the DMSO protons (1.85 ppm) is shifted upfield compared to those of free DMSO (2.49 ppm).

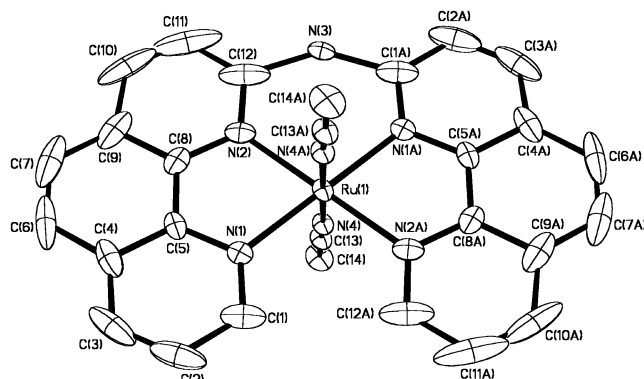


Figure 2. ORTEP view (30% probability) of the structure of the *trans*-[Ru(phen-NH-phen)(CH₃CN)₂]²⁺ cation (3).

Each phenanthroline moiety is nearly planar, tilted in respect to each other by an angle of 10.11°. In this complex, the steric repulsion between α hydrogens in opposite phenanthrolines is relieved by forming a higher angle to the open part of the ligand, allowing the phenanthrolines to be planar. A similar arrangement was reported for the complex [Ni(diphen)(H₂O)Cl]Cl.⁶ It is interesting to note that the bridging nitrogen displays an almost trigonal planar geometry (C₁₂–N₃–C₁₃ = 132.73°). This is also reflected by the bridging nitrogen–phenanthroline distances (N₃–C₁₂ = 1.383 Å and N₃–C₁₃ = 1.386 Å), which are intermediate between a single and a double carbon–nitrogen bond, implying certain π bonding character between N₃ and C₁₂ and C₁₃.

In compound **2**, the ¹H NMR spectrum in DMSO-*d*₆ shows that, in solution, this complex consists of a mixture of S–O, S–S, and O–O bonded DMSO molecules. This is in agreement with previously reported bis(DMSO) bis(polypyridyl) ruthenium(II) complexes.^{2c} In CD₃CN, the ¹H NMR spectrum of **2** is identical to that of compound **1** (except for the absence of the CH₃CN signal), indicating that one of the DMSO molecules is replaced by CD₃CN.

The structure of **3** is shown in Figure 2. In this case, the opened side and the closed side of the ligand appear equivalent because of disorder generated by an opposite stacking arrangement of both sides of the ligand in the crystal with a crystallographic inversion center at ruthenium. As a result, the distances from the ruthenium center to the phenanthroline nitrogens (Ru–N₁ = 2.055 Å, Ru–N₂ = 2.050 Å) lie between the distances to the opened and closed sides in compound **1**. The phenanthroline moieties are rigorously planar, and the axial acetonitriles are linear with a nitrogen–ruthenium bond distance of 2.026 Å.

Compound **4** was characterized by ¹H NMR (DMSO-*d*₆, 400 MHz, Figure 3). The aromatic portion of the spectrum consists of the sum of the phen and dppz moieties (Figure 4). It is interesting to note that the proton in position 6' (10.44 ppm) of the phenanthroline portion of dppz is located downfield with respect to the protons in positions 4 (dppz, 9.97 ppm) and 4' (9.83 ppm).

This behavior is opposed to that of previously reported dppz-type ligands⁹ and complexes with dppz-type ligands,^{9,10} and it is not observed in free dppz-NH-phen. The deshielding

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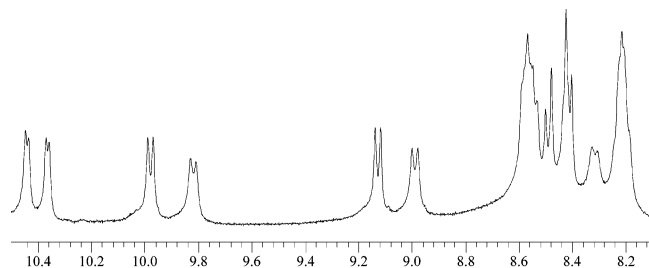


Figure 3. ^1H NMR spectrum of *trans*-[Ru(dppz-NH-phen)(CH₃CN)₂](PF₆)₂ in DMSO-*d*₆.

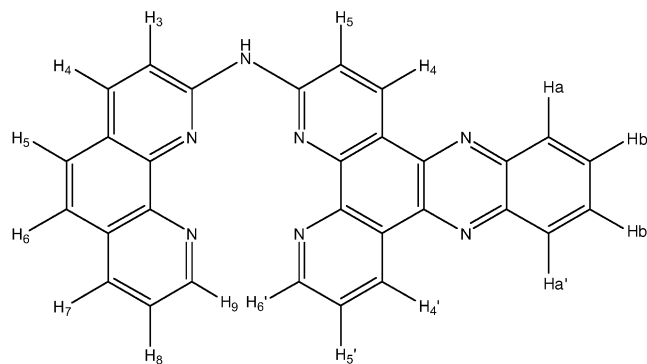


Figure 4. dppz-NH-phen ligand.

generated by the ruthenium center is higher for protons 6' and 9 (10.36 ppm) than for protons 4 (dppz) and 4'.

The absorption spectra of **1–4** exhibit metal to ligand charge transfer (MLCT) and ligand centered (LC) bands. All complexes show very intense absorption over the whole 200–400 nm region. This can mostly be attributed to the strongly delocalized nature of the ligands that results in a series of π and π^* orbitals which are very close in energy. The corresponding spectrum for each complex presents a set of π – π^* overlapping bands in the UV and visible regions with the corresponding metal to ligand charge transfer bands.

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Table 1. Calculated (Intraligand) and Experimental (Complex **3**) Absorption Maxima

calcd excitation energy (nm)	assignment	λ_{max} (nm) complex 3	assignment
337	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	430	MLCT
309	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	343	LC
275	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	313	LC
255	$\pi \rightarrow \pi^*$	274	LC
247	$\pi \rightarrow \pi^*$	254	LC
232	$\pi \rightarrow \pi^*$	241	LC
225	$\pi \rightarrow \pi^*$	216	LC
211	$\pi \rightarrow \pi^*$		

In the complexes with the phen-NH-phen ligand, the assignment of the absorption bands was performed by comparison of the spectra of the complexes with the theoretically calculated absorption spectrum for the phen-NH-phen ligand. The geometry of the ligand was taken from the X-ray structure of compound **1** (omitting the metal and the axial ligands) and used as input for the Hyperchem program.¹¹ A CI ZINDO/S calculation was performed (22 occupied and 22 unoccupied orbitals, 969 configurations). Table 1 shows the theoretical intraligand bands, the experimental bands for complex **3** in acetonitrile, and the assignments of the bands.

The results reported in this communication are very promising with regard to the synthesis of *trans* geometry complexes. Follow up work is in progress to synthesize new *trans* donor–acceptor assemblies by coupling differently functionalized 2-amino- and 2-chloro-phenanthroline-type compounds. A study of the excited state behavior of the obtained complexes is also in progress.

Acknowledgment. Projects Fondecyt 2000048 and Fondecyt Líneas Complementarias 8980007 and the Georgia Institute of Technology supported this work.

Supporting Information Available: X-ray crystallographic information, experimental procedures, elemental analysis, ^1H NMR data. This material is available free of charge in the Internet at <http://pubs.acs.org>.

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