

Electrochemistry of ruthenium(II) complexes of 8-aminoquinoline

Megan K. O'Neill, Alfred Francois Trappey, Paul Battle, Christopher L. Boswell, David N. Blauch*

Department of Chemistry, Davidson College, Davidson, NC 28035 USA

Email: [dblauch@davidson.edu](mailto:dblauch@ davidson.edu)

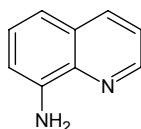
Supplementary Information

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A. Synthetic Methods

The 8-aminoquinolineruthenium(II) complexes were found to be air sensitive, and thus all procedures were performed under nitrogen and the complexes were stored under vacuum. Chemicals were of reagent grade and used without additional purification. $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was prepared by the published procedure.¹ Elemental analyzes were performed by Quantitative Technologies Inc. Mass spectrometry was performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of South Carolina.



8-aminoquinoline (NH_2Q)

$[\text{Ru}(\text{NH}_2\text{Q})_3](\text{PF}_6)_2$

A solution of 8-aminoquinoline (0.97 g, 6.7 mmol) in 95% ethanol (32 cm^3) was added to a solution of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ (0.99 g, 2.0 mmol) dissolved in water (30 cm^3). The resulting solution was heated under reflux for 20 hr. A solution of ammonium hexafluorophosphate (2.6 g, 16 mmol) dissolved in water (7 cm^3) was added to the hot reaction mixture. The resulting mixture was cooled on an ice bath and filtered. The orange solid was washed with 2 x 5 cm^3 water and dried under vacuum. The crude product was dissolved in hot acetone (10 cm^3), water (15 cm^3) was added, and the solution was boiled to remove the acetone. The mixture was cooled in an ice bath, and the re-precipitated product was isolated by filtration, washed with 3 x 5 cm^3 water, and dried under vacuum, yielding $[\text{Ru}(\text{NH}_2\text{Q})_3](\text{PF}_6)_2$ (1.24 g, 74%) as an impure orange solid.

$[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

The crude $[\text{Ru}(\text{NH}_2\text{Q})_3](\text{PF}_6)_2$ (1.04 g, 1.27 mmol) was dissolved in acetone (30 cm^3), and the solution was filtered to remove a small amount of insoluble brown impurity. The dark red filtrate was cooled to room temperature and treated with a solution of tetra(*n*-butyl)ammonium chloride (2.8 g, 10 mmol) in acetone (15 cm^3). The resulting mixture was cooled in an ice bath and filtered. The red solid was washed with 3 x 5 cm^3 acetone and dried under vacuum. In order to remove the last traces of the tetra(*n*-butyl)ammonium salts, the solid was stirred in boiling acetone, cooled in an ice bath and filtered. The residue was washed with 3 x 10 cm^3 acetone and dried under vacuum, yielding $[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.415 g, 74%) as a red solid. (Found: C, 51.0; H, 4.4; N, 12.8. Calc. for $\text{C}_{27}\text{H}_{28}\text{Cl}_2\text{N}_6\text{O}_2\text{Ru}$: C, 50.6; H, 4.4; N, 13.1); m/z (ESI) 267.1 (23%) (M^{2+} . $\text{C}_{27}\text{H}_{24}\text{N}_6\text{Ru}$ requires 267.1), 287.6 (33) ($\text{M}^{2+} + \text{CH}_3\text{CN}$. $\text{C}_{29}\text{H}_{27}\text{N}_7\text{Ru}$ requires 287.6), 389.1 (100) ($\text{M}^{2+} - \text{NH}_2\text{Q} - \text{H}^+$. $\text{C}_{18}\text{H}_{15}\text{N}_4\text{Ru}$ requires 389.0), 533.2 (54) ($\text{M}^{2+} - \text{H}^+$. $\text{C}_{27}\text{H}_{23}\text{N}_6\text{Ru}$ requires 533.1).

A sample of $[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ that had partially oxidized in air gave m/z (ESI) 267.0 (43%) (M^{2+} . $\text{C}_{27}\text{H}_{24}\text{N}_6\text{Ru}$ requires 267.1), 287.5 (100) ($\text{M}^{2+} + \text{CH}_3\text{CN}$. $\text{C}_{29}\text{H}_{27}\text{N}_7\text{Ru}$ requires 287.6), 294.6 (23) ($\text{M}^{2+} + \text{O} - 2\text{H} + \text{CH}_3\text{CN}$. $\text{C}_{29}\text{H}_{25}\text{N}_7\text{ORu}$ requires 294.6), 274.0 (10) ($\text{M}^{2+} + \text{O} - 2\text{H}$. $\text{C}_{27}\text{H}_{22}\text{N}_6\text{ORu}$ requires 274.0), 533.1 (11) ($\text{M}^{2+} - \text{H}^+$. $\text{C}_{27}\text{H}_{23}\text{N}_6\text{Ru}$ requires 533.1). The $\text{M}^{2+} + \text{O} - 2\text{H}$ species may be attributable to oxidation of 8-aminoquinoline to 8-nitrosoquinoline. Similar reactivity has been observed in other amineruthenium(II) complexes where imine or nitrile formation is structurally blocked.^{2,3}

$[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{Q})](\text{PF}_6)_2$

8-Aminoquinoline (0.46 g, 3.2 mmol) and $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (1.02 g, 1.96 mmol) were dissolved in 50/50 ethanol/water (50 cm^3), and the solution was heated under reflux for 28 hr. A solution of ammonium hexafluorophosphate (2.03 g, 12 mmol) in water (5 cm^3) was added to the hot reaction solution, and the resulting mixture was cooled on an ice bath and filtered. The red residue was washed with 2 x 10 cm^3 water and dried under vacuum. The crude solid was stirred with boiling water, and filtered while hot. After cooling in an ice bath, the solid was recovered by filtration and stirred with boiling ethanol. The ethanolic mixture was filtered while hot, and the filtrate was cooled in an ice bath and filtered. The residue was washed ethanol and dried under vacuum, yielding $[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{Q})](\text{PF}_6)_2$ as a red solid. (Found: C, 40.9; H, 2.4; N, 9.7. Calc. for $\text{C}_{29}\text{H}_{24}\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}$: C, 41.1; H, 2.8; N, 9.9); m/z (ESI) 279.1 (100%) (M^{2+} . $\text{C}_{29}\text{H}_{24}\text{N}_6\text{Ru}$ requires 279.1), 557.0 (14) ($\text{M}^{2+} - \text{H}^+$. $\text{C}_{29}\text{H}_{23}\text{N}_6\text{Ru}$ requires 557.1).

B. Spectroscopic Results

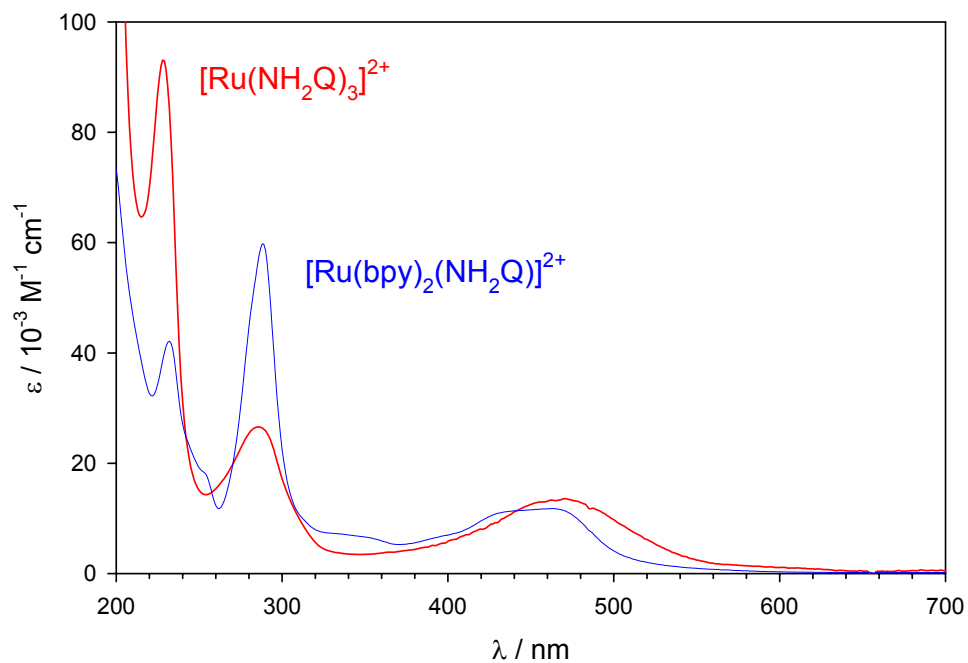


Fig. S1 Ultraviolet-visible spectra of $[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2$ (red curve) and $[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{Q})](\text{PF}_6)_2$ (blue curve) in water.

Table S1 Spectroscopic properties of ruthenium(II) complexes of 8-aminoquinoline in water

$[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2$		$[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{Q})](\text{PF}_6)_2$	
$\lambda_{\text{max}} / \text{nm}$	$\epsilon / \text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{max}} / \text{nm}$	$\epsilon / \text{M}^{-1} \text{cm}^{-1}$
228	93100	232	42100
286	26600	288	59800
471	13600	463	11800
		440 (sh)	

C. Electrochemical Methods and Results

Electrochemical measurements were performed with a PAR 273A or Bioanalytical Systems Epsilon potentiostat using a single-compartment cell equipped with a glassy carbon disk working electrode (0.0707 cm^2) and a platinum counter electrode. Spectroelectrochemical measurements were performed using an indium tin oxide coated glass working electrode (Delta Technologies) and an HP 8453 diode-array UV-Vis spectrometer. Potentials were recorded vs a Ag/AgCl reference electrode. Measurements were obtained at $21 \pm 1 \text{ }^\circ\text{C}$, and all measurements were performed under nitrogen.

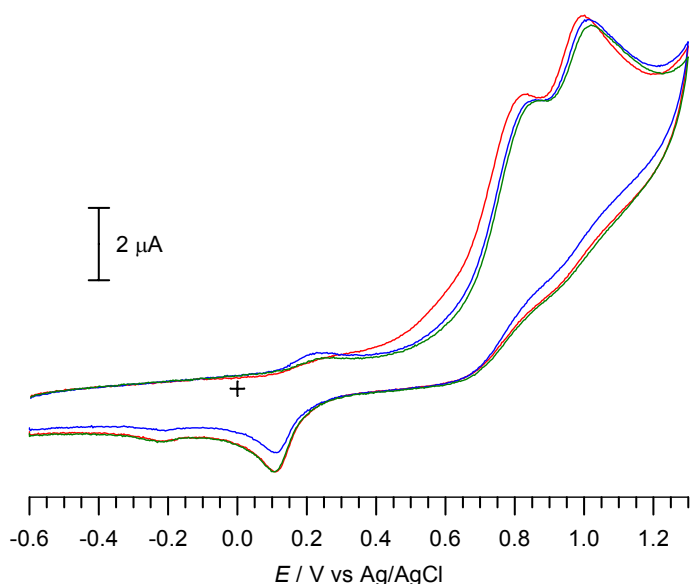


Fig. S2 Cyclic voltammograms of 0.62 mM $[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{Q})](\text{PF}_6)_2$ in pH 5.04 acetate buffer. Electrode was freshly polished and curves represent first (red), second (blue), and third (green) sequential scans. Sweep rate is 25 mV sec^{-1} .

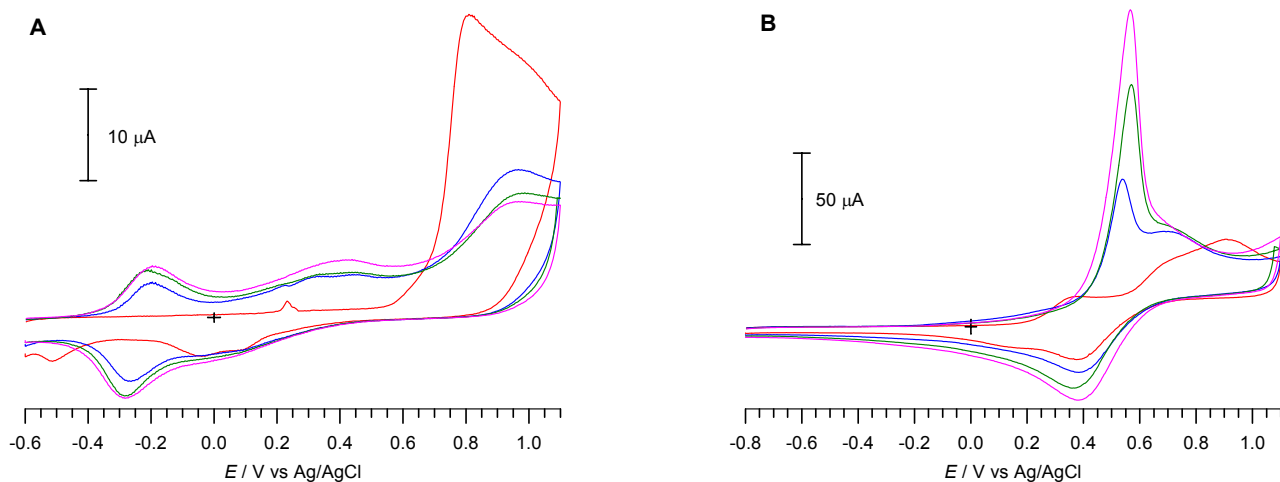


Fig. S3 Cyclic voltammograms for 1.2 mM NH_2Q (A) and 1.1 mM $[\text{Ru}(\text{NH}_2\text{Q})_3]\text{Cl}_2$ (B) in pH 2.51 chloroacetate buffer. Electrode was freshly polished and curves represent the first (red), second (blue), third (green), and fourth (pink) sequential scans. Sweep rate is 50 mV sec^{-1} .

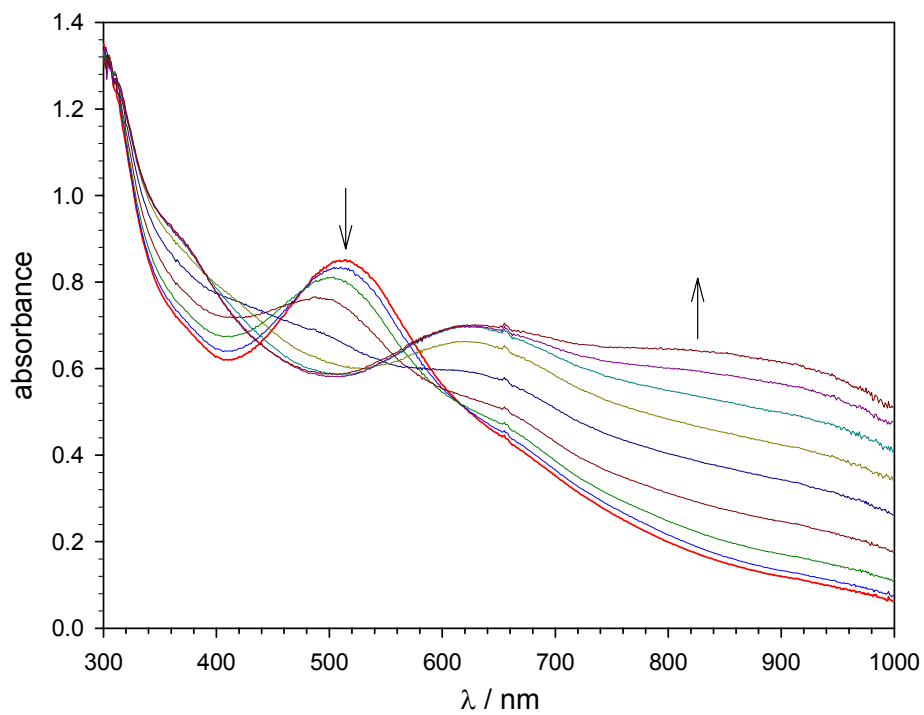


Fig. S4 Spectra of poly-Ru(NH₂Q)₃²⁺ coated ITO electrode in pH 9.82 acetate buffer at -0.9 (red curve), -0.6, -0.5, -0.4, -0.3, -0.2, -0.1, 0, and 0.1 V (brown curve) vs Ag/AgCl.

D. Computational Methods and Results

Density functional theory computations employing Becke's three-parameter hybrid functional⁴ using the Lee, Yang, and Parr correlation function⁵ (b3lyp) were performed using the Gaussian 03 software package⁶. The split-valence ecp basis set of Stevens, Basch, Krauss, and Jasien⁷ with polarization functions on the second-row nonmetals, cep-121g(d), was used for all computations. Wave function stability calculations were performed to confirm that ground state wave functions had been obtained. Frequency computations were performed to verify that each optimized geometry corresponded with an energy minimum (no imaginary frequencies). Energies and oscillator strengths for electronic transitions were obtained using non-equilibrium time-dependent density functional theory (TD-DFT).

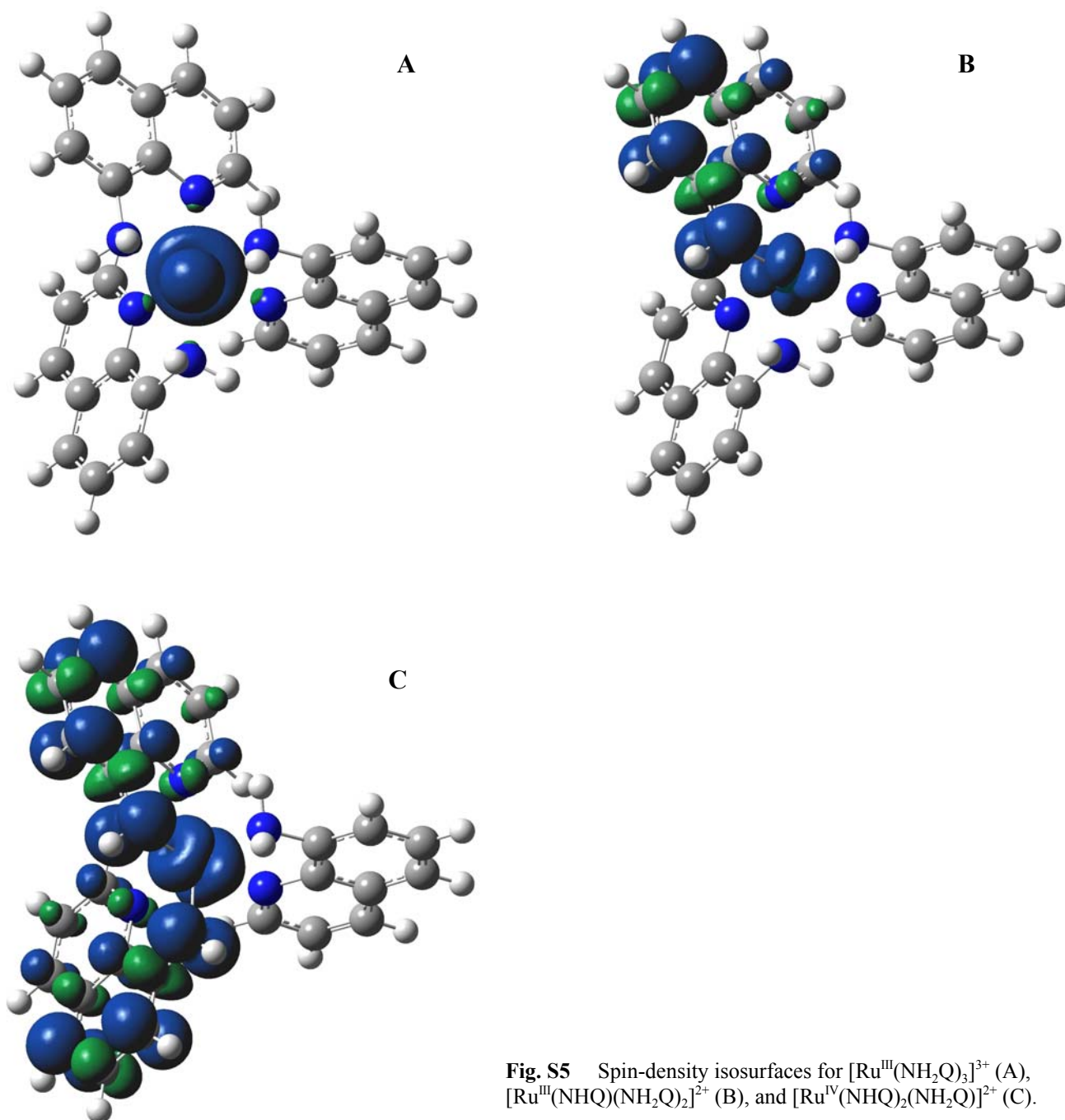


Fig. S5 Spin-density isosurfaces for $[\text{Ru}^{\text{III}}(\text{NH}_2\text{Q})_3]^{3+}$ (A), $[\text{Ru}^{\text{III}}(\text{NHQ})(\text{NH}_2\text{Q})_2]^{2+}$ (B), and $[\text{Ru}^{\text{IV}}(\text{NHQ})_2(\text{NH}_2\text{Q})]^{2+}$ (C).

E. References

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