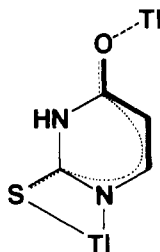


probably differ in strength. The Tl-N bond length is similar to that observed in $(\text{Me}_2\text{TlPhen})^+$ ¹⁸ and $\text{Me}_2\text{Tl}(\text{L-PHE})$ ^{19a} and shorter than in the other N-bonded compounds that have been studied,^{8,19b} suggesting this to be a relatively strong bond. The distance $d(\text{Tl-S})$ is intermediate between the two $d(\text{Tl-S})$ distances in $\text{Me}_2\text{TlSC}_6\text{H}_5$,²⁰ in which the sulfur forms asymmetrical Tl-S-Tl bridges, and decidedly shorter than in $\text{Me}_2\text{TlS}_2\text{COCH}_3$,²¹ a relatively stable bond again being indicated. The length of the Tl-O bond, on the other hand, is considerably greater than in other compounds,^{19,20} falling within the range considered appropriate for weak bonds in complexes of dimethylthallium(III) with polydentate ligands.⁸ The structure of the ligand differs considerably from that of free H_2Tl , which in the solid state adopts the lactam-thione form.²² Loss of a proton and combination with Me_2Tl^+ brings about a lengthening of the C-O and C-S bonds, though without their reaching values corresponding to single bonds (1.50 and 1.79 Å, respectively²³). These changes suggest the following charge distribution in the dimethylthallium(III) compound:



Vibrational and NMR Spectra. In the vibrational spectra the wavenumbers of the significant stretching vibrations of the complexed ligand²⁴ agree with the kind of coordination described above. With respect to the free ligand, the bands corresponding to stretching of the ring or the thioamide group remain unchanged or shift to slightly higher wavenumbers, where as that band with the most $\nu(\text{C}=\text{S})$ character shifts to lower wavenumbers.²⁵ The C-Tl-C stretching bands²⁶ appear very close together at wavenumbers lower than those reported for other systems, and two new bands that show up in the low-wavenumber region²⁷ may possess $\nu(\text{Tl-O})$ and $\nu(\text{Tl-S})$ contributions.

The compound $\text{Me}_2\text{Tl}(\text{HTu})$ is insoluble in water and in organic solvents of low dielectric constants but dissolves in DMF and DMSO. Its characteristics in DMSO- d_6 were investigated by using ^1H and ^{13}C NMR and IR spectroscopy. The existence of bands attributable to $\nu(\text{C}=\text{O})$ close to those found in the solid suggests the presence of the lactam form in solution, and the broad ^1H NMR band at 11.7 ppm²⁸ must accordingly be attributed to the nondeprotonated NH group. The ^{13}C NMR signals appear at positions between those found in S-methylated and N-methylated 2-thiouracils,²⁹ except for the C(2) signal, which

practically coincides with the corresponding signal in the N-(1)-methylated derivative.²⁹ This may be due to the greater electron-accepting capacity of the thallium atom in the complex, which must have an unshielding effect tending to oppose the shielding caused by the ligand's partial change toward the thiol form. These NMR data suggest that in solution the ligand remains coordinated to the metal via the sulfur atom and one of the nitrogen atoms, but they offer no grounds for judging whether the C=O group takes part in the bond, and for reasons already mentioned it is unadvisable to base such a judgement upon the IR data.²⁵

The methyl signals of the organometallic part of the complex appear in ^1H and ^{13}C NMR spectra at 0.88 and 23.24 ppm, respectively. The coupling constants $^2J(\text{Tl-H})$ and $^1J(\text{Tl-C})$ are 420 and 3033 Hz, respectively.³⁰ These values are not notably different from those reported for the other Me_2Tl^+ complexes with sulphydrated ligands, in which the C-Tl-C group is practically linear.³¹ If coupling takes place fundamentally via Fermi contact contribution³² depending on the degree to which the thallium s orbitals participate in the bond, then the organometallic moiety of $\text{Me}_2\text{Tl}(\text{HTu})$ would appear to adopt a more open configuration in solution than in the solid state.

Acknowledgment. This research was supported by a grant from the Spanish CAICYT. We also thank the CSIC (Spain) and, in Brazil, FAPESP and CNPq for exchange facilities.

Registry No. $\text{Me}_2\text{Tl}(\text{HTu})$, 110511-21-2; H_2Tl , 141-90-2; Me_2TlOH , 53759-11-8.

Supplementary Material Available: A table of thermal parameters (1 page); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027

Synthesis and Spectroscopic Characterization of the Purple Tris(phenanthrenequinone diimine)ruthenium(II) Ion

Anna Marie Pyle and Jacqueline K. Barton*

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There has been considerable attention focused on the optical and electronic properties of ruthenium(II) polypyridyl complexes and on their rich excited-state chemistry because of their possible application in the design of photochemical sensitizers for solar energy conversion.¹⁻³ The intense coloration and stability of the ruthenium(II) diimine complexes furthermore provide uniquely sensitive photophysical probes for solids, for surfaces, and, in our own laboratory, for biopolymers.^{4,5} While the detailed characterization of the ground- and excited-state electronic structures of bipyridyl and phenanthroline complexes of ruthenium(II) has proceeded, little attention has been given to other diimine complexes of ruthenium(II). We have examined complexes of the phenanthrenequinone diimine ligand to explore new photochemical

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 (27) Other signals in the ^1H and ^{13}C NMR spectra (ppm from TMS): 5.71 d [H(5)] and 742 d [H(6)] ($J_{5,6} = 6.7$ Hz); 176.8 [C(2)], 163.1 [C(4)], 106.3 [C(5)], and 150.8 [C(6)].

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electron transfer agents and to develop new photophysical probes for biopolymers.

Metal complexes containing the 9,10-phenanthrenequinone diimine (phi) ligand are relatively rare, and although there are a few examples of these species in the literature, their properties remain relatively undefined.⁶⁻¹⁰ Owing to the substantial π -acidity and extended aromaticity of the ligands, intense charge-transfer transitions might be expected at a lower energy than those for the corresponding $M(\text{bpy})_3^{2+}$ complexes, an advantage for photochemical sensitization. Furthermore, metal complexes of this type lend themselves well to the study of biological molecules. The ligand is planar with a large hydrophobic surface that extends far away from the metal. At the same time, imine protons on the ligand can hydrogen bond with Lewis base substrates or templates. The phi ligand therefore provides a rich proton source near the metal center in addition to the substantial π -electron-acceptor capability.

We report here the synthesis and spectroscopic characterization of two new $M(\text{phi})_n$ complexes: $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ and $\text{Zn}(\text{phi})\text{Cl}_2$. The complexes display novel spectroscopic features and rich coloration at low energies. In the case of the ruthenium(II) complex, the aromatic exocyclic imine functionality leads to spectroscopic features that are sensitive to hydrogen bonding and that may be characteristic of a delocalized charge-transfer framework.

Experimental Section

Ligand Synthesis. 9,10-Phenanthrenequinone bis((trimethylsilyl)imine) (silylphi) was synthesized from 9,10-phenanthrenequinone (Aldrich) and sodium bis(trimethylsilyl)amide (Fluka) as described by Tuchtenhagen and Ruhlmann.¹¹ Important modifications to this synthesis include a reaction temperature of no greater than 65 °C and a final phenanthrenequinone concentration of 0.08 M. Under these conditions, orange crystalline silylphi was obtained in 37% yield and stored under nitrogen. The phenanthrenequinone diimine ligand (phi) was generated and chelated in situ by combining the silylated imine ligand with an ethanolic solution of metal chloride by using a modification of Schlosser's method.¹²

$[\text{Ru}(\text{phi})_3]\text{Cl}_2$. A 1.025-g sample of 9,10-phenanthrenequinone bis((trimethylsilyl)imine) (2.9 mmol) dissolved in 75 mL benzene was added to a vigorously stirring suspension of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ (Alfa Products; 0.355 g, 0.73 mmol) in 25 mL of EtOH and 75 mL of benzene. All solvents were dried and distilled under nitrogen before use. This mixture was heated at 65 °C for 1 h until a rich purple solution was generated. The reaction vessel was then opened to the air. After the crude reaction mixture was filtered, it was cooled and evaporated to a small volume. $\text{Ru}(\text{phi})_3\text{Cl}_2$ was precipitated with diethyl ether and collected on a frit.

Solid $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ was washed with acetone to remove several blue byproducts¹³ and then with diethyl ether to remove organic material resulting from in-air decomposition of excess ligand. After several diethyl ether precipitations from ethanol solutions, $\text{Ru}(\text{phi})_3\text{Cl}_2$ was washed with H_2O to give a final yield of 51%. Samples were often further purified by cellulose column chromatography.

The ^1H NMR spectrum of $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ is indicative of a symmetrical, D_3 metal chelate with resonances at 7.6 (2 H, triplet), 8.22 (1 H, doublet), 8.8 (1 H, doublet), and 14.2 ppm (1 H, singlet imine). This is confirmed by elemental analysis. Anal. Calcd for $[\text{Ru}(\text{phi})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 62.38; H, 3.99; N, 10.39; Ru, 12.90. Found: C, 62.29; H, 4.21; N, 10.0; Ru, 13.10. Fast atom bombardment (FAB) mass spectroscopy of $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ showed a strong $\text{Ru}(\text{phi})_3^{2+}$ molecular ion of M_r 719 with the next largest peak being the $\text{Ru}(\text{phi})_2^{2+}$ fragment at M_r 514. Infrared

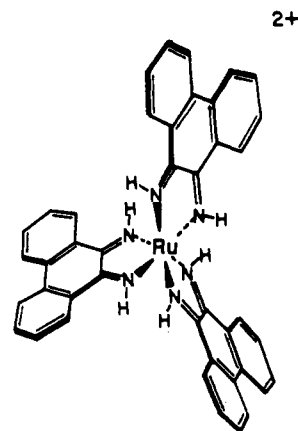


Figure 1. $\text{Ru}(\text{phi})_3^{2+}$.

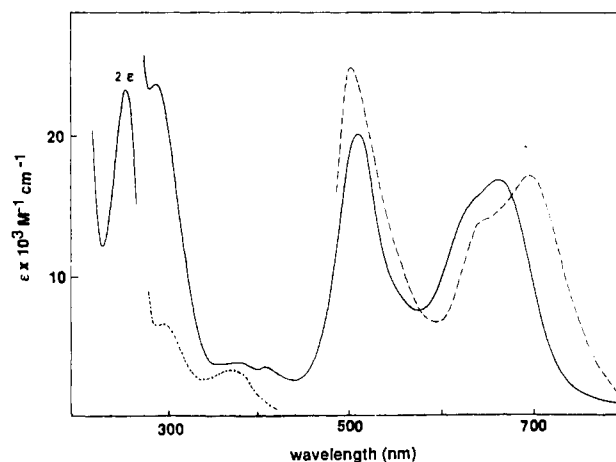


Figure 2. Absorption spectra of $\text{Ru}(\text{phi})_3^{2+}$ in ethanol (—) and from 500 to 800 nm in HMPA (---). Absorption spectrum of $\text{Zn}(\text{phi})\text{Cl}_2$ in DMF from 275 to 425 nm (···) is not to scale.

spectroscopy revealed characteristic imine N—H stretches at 3274 and 3167 cm^{-1} and a C=N stretch at 1497 cm^{-1} .

$\text{Zn}(\text{phi})\text{Cl}_2$. The zinc complex was synthesized as described for $[\text{Ru}(\text{phi})_3]\text{Cl}_2$. Yellow $\text{Zn}(\text{phi})\text{Cl}_2$ was filtered directly out of the reaction mixture in quantitative yield and washed with diethyl ether, H_2O , and acetone. Anal. Calcd for $\text{Zn}(\text{phi})\text{Cl}_2 \cdot 1/3\text{C}_6\text{H}_6$: C, 52.15; H, 3.29; N, 7.60; Cl, 19.23. Found: C, 52.14; H, 3.71; N, 7.21; Cl, 18.50. The molecular ion by FAB was the $\text{Zn}(\text{phi})\text{Cl}^+$ cation of M_r 307 as expected for the proposed structure.

The ^1H NMR of $\text{Zn}(\text{phi})\text{Cl}_2$ is slightly complicated by the fact that it dissolves only in coordinating solvents such as DMSO or DMF. Upon dissolution, the tetrahedral structure changes to octahedral as two molecules of solvent bind cisoid to the metal center. The resulting species has several isomers and a C_1 symmetry that renders each proton non-equivalent. Although imine protons are especially affected by the different steric environment of the isomers, there is an integral of two imine protons for each eight aromatic protons. C—H resonances in DMF: 8.52 (1 H, doublet), 8.36 (1 H, doublet), 8.21 (2 H, multiplet), 7.74 (1 H, triplet), 7.55 (2 H, triplet), 7.39 ppm (1 H, mult). N—H resonances: 12.35 (1 H, s), 12.0 ($1/3$ H, s), 11.8 ($1/3$ H, s), 11.6 ppm ($1/3$ H, s).

Instrumentation. Ultraviolet-visible absorption experiments were performed by using a Varian-Cary 219 spectrophotometer and ^1H NMR measurements on a Varian VXR-300 spectrometer. Cyclic voltammetry was conducted by using an IBM voltammograph and recorder. Flash photolysis experiments were made with a YAG laser, monitored with an optical multichannel analyzer interfaced to a PDP 11/23.

Results and Discussion

Synthesis and Characterization. The complex $\text{Ru}(\text{phi})_3^{2+}$ can be synthesized from the silylated phi ligand in greater than 51% yield. Alternate synthetic schemes, involving metal reduction and concomitant oxidation of coordinated diaminophenanthrene, were less reproducible and gave poor yield. $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ is a stable molecule that does not decompose upon exposure to air or by continuous irradiation with visible light. The ligand is not similarly stable but instead rapidly condenses to the dimeric phenanthro-

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- (13) Blue ruthenium species are produced in great quantity if the reaction is allowed to reflux too long or if concentrated solutions of $\text{Ru}(\text{phi})_3^{2+}$ are allowed to stand for long periods of time. Chromatography has shown these species to be variable and high in molecular weight. Deep blue ruthenium species have been observed previously and formulated either as clusters or ligand-bridged multinuclear species.¹⁴
- (14) Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1791.

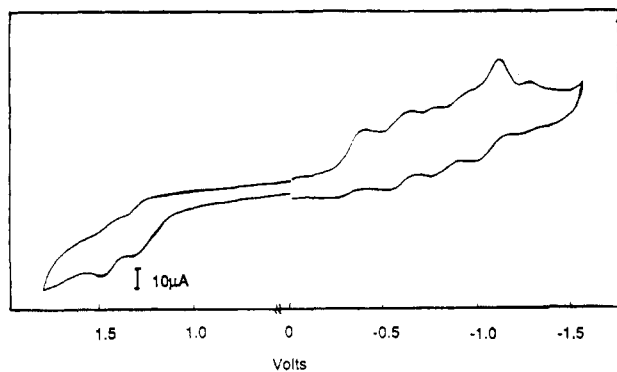


Figure 3. Cyclic voltammogram of $\text{Ru}(\text{phi})_3(\text{PF}_6)_2$ in acetonitrile. All measurements taken at 100 mV/s scan speed, V versus SCE. The featureless oxidative scan between 0 and 0.5 V is not shown.

imidazole. Hence spectral comparisons between coordinated ruthenium complexes and free ligand cannot be easily accomplished. The zinc complex was therefore synthesized to provide a spectroscopic analogue for the coordinated ligand. Despite reflux with high ligand concentrations, only the mono- ϕ zinc adduct formed.

$\text{Ru}(\text{phi})_3\text{Cl}_2$ is a vivid purple molecule with a rich absorption spectrum. A representation of its structure is shown in Figure 1. The electronic spectrum of $\text{Ru}(\text{phi})_3^{2+}$, along with that of $\text{Zn}(\text{phi})\text{Cl}_2$, is given in Figure 2. The ruthenium complex shows three intense transitions in the visible region, at 510 nm ($\epsilon_{\text{max}} = 18\,200 \text{ M}^{-1} \text{ cm}^{-1}$), 640 nm ($\epsilon_{\text{max}} = 13\,600 \text{ M}^{-1} \text{ cm}^{-1}$), and 660 nm ($\epsilon_{\text{max}} = 15\,200 \text{ M}^{-1} \text{ cm}^{-1}$). Assignment of the transitions is aided by comparison to the spectrum of $\text{Zn}(\text{phi})\text{Cl}_2$, which, by virtue of its d^{10} electron configuration, exhibits only $\pi-\pi^*$ transitions and should approximate the electronic behavior of the air-sensitive phenanthrenequinone diimine ligand. As can be seen in Figure 2, the zinc complex shares with the ruthenium species transitions at 380 nm ($\epsilon_{\text{Zn}} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{Ru}} = 4000 \text{ M}^{-1} \text{ cm}^{-1}$), 300 nm ($\epsilon_{\text{Zn}} = 4500 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{Ru}} = 22\,500 \text{ M}^{-1} \text{ cm}^{-1}$), and 256 nm ($\epsilon_{\text{Zn}} = 50\,000 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{Ru}} = 45\,000 \text{ M}^{-1} \text{ cm}^{-1}$). These higher energy $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ transitions may therefore be assigned as $\pi-\pi^*$ on the basis of their similarity to those of $\text{Zn}(\text{phi})\text{Cl}_2$. The broad intense transitions for the ruthenium complex at longer wavelengths (510, 640, and 660 nm) may be assigned in contrast as charge-transfer transitions.

Cyclic voltammetry reveals multiple electrochemical reduction steps and oxidations in the ruthenium complex (Figure 3). Electrochemical oxidation of $[\text{Ru}(\text{phi})_3](\text{PF}_6)_2$ in acetonitrile is irreversible. Oxidation potentials of 1.23 and 1.42 eV versus SCE were observed at a scan speed of 100 mV/s. Of the six reduction potentials observed at -0.38, -0.60, -0.75, -0.95, -1.11, and -1.28 eV, only those at -0.60, -1.11 and -1.28 eV were found to be reversible. A standard of $[\text{Ru}(\text{phi})_3](\text{PF}_6)_2$ showed first redox potentials of -1.31 and +1.30 V, respectively. As may be expected, the increased π -acidity of the ϕ ligand compared to that of bipyridyl or phenanthroline leads to substantially decreased reduction potentials for the $\text{Ru}(\text{phi})_3^{2+}$ complex.

Possible emission from $[\text{Ru}(\text{phi})_3]\text{Cl}_2$ was monitored at pH 1-11, in various solvents and at 77 K. No emission was observed from 350 to 800 nm. The lack of emission is understandable in view of the short lifetime of the excited state. The transient excited-state absorption spectrum ($\lambda_{\text{max}} = 440 \text{ nm}$), measured by flash photolysis, revealed a lifetime of $\leq 6 \text{ ns}$, the length of the laser pulse.

The excited-state energy of $\text{Ru}(\text{phi})_3^{2+}$ appears to be highly dependent on the molecular environment. Small changes in pH, salt concentration, or solvent lead to large variations in the λ_{max} of the charge-transfer (CT) bands. As can be seen in Figure 4, this solvent dependence contrasts sharply the little solvatochromism observed for $\text{Ru}(\text{bpy})_3^{2+}$.¹⁵ Most significantly, the energy of the 660-nm charge-transfer band (CT1 in ethanol) decreases linearly

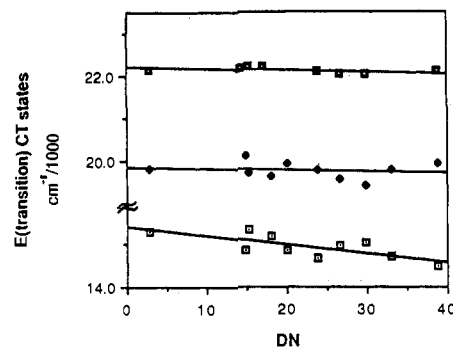


Figure 4. Plot of hydrogen-bonding solvatochromism as measured by the shift in energy of CT bands with donor number (DN); (■) $\text{Ru}(\text{bpy})_3^{2+}$ (from ref 15), $y = 22.2 - 0.004x$; (◆) $\text{Ru}(\text{phi})_3\text{Cl}_2$, CT3, $y = 19.8 - 0.004x$; (□) $\text{Ru}(\text{phi})_3\text{Cl}_2$, CT1, $y = 15.4 - 0.02x$. Measurements were obtained in the following solvent array (DN in parentheses): nitromethane (2.7), dioxane (14.8), propylene carbonate (15.1), water (18.0), THF (20.0), tributyl phosphate (23.7), DMF (26.6), DMSO (29.8), pyridine (33.1), HMPA (38.8).

as the Lewis base character, or donor number (DN),¹⁶ of the solvent increases. CT1 is one component of a double-structured absorption commonly found among ruthenium diimine complexes. Curiously, it is only the CT1 absorption and not its companion band at 640 nm (CT2) that displays hydrogen-bonding solvatochromism with Lewis bases. The two seemingly fused bands at low DN seem to move apart in energy as the DN increases, and the CT1 band red shifts to as much as 700 nm in HMPA. The energy of the 510-nm band (CT3) fluctuates with solvent, but like the MLCT bands of $\text{Ru}(\text{bpy})_3^{2+}$, this fluctuation is not linear with DN. Thus the CT2 and CT3 transitions of $\text{Ru}(\text{phi})_3^{2+}$ are not sensitive to hydrogen bonding and must be of distinctly different character than the lowest energy CT1 band, which fluctuates between 650 and 700 nm as the strength of hydrogen-bonding interactions increases. Such solvatochromic behavior lends itself well to the application of the complex as a photophysical probe, because the energy of bands like CT1 becomes a sensitive indicator of the metal environment and possible hydrogen bonding interactions.

The spectral characteristics of $\text{Ru}(\text{phi})_3^{2+}$ reveal several novel and unexpected features of the electronic structure of the complex. Perhaps most interesting is the lowest energy charge-transfer transition, CT1, centered at 660 nm in ethanolic solution. This transition is among the lowest energy transitions thus far observed for monomeric ruthenium(II) species.¹⁷ Blue ruthenium species have been reported previously,¹⁴ but while their structures have remained elusive, all have been formulated as multinuclear species. The low-energy transitions in $\text{Ru}(\text{phi})_3^{2+}$ may arise in part from the coordination of the highly delocalized ϕ ligand. Coordinated phenazines and dicyanomethylene-substituted phenanthrolines represent other applications of an extended π -framework, yet for those the charge-transfer transitions are centered at wavelengths more than 100 nm shorter.¹⁸

Most curious however is the comparison to the mixed-ligand complex⁷ $\text{Ru}(\text{bpy})_2\text{phi}^{2+}$. The mixed species shows charge-transfer transitions at 450 and 525 nm, which may be attributed to localized charge transfer onto the bpy and ϕ ligands, respectively, in the excited state. Spectra of mixed-ligand polypyridyl complexes of ruthenium(II) have in general been the simple sum of spectra for the tris-chelate complexes, since the metal to ligand charge-transfer is localized in these systems.¹⁹ Also surprising is the short excited-state lifetime of $\text{Ru}(\text{phi})_3^{2+}$ and the solvent dependence of one of the low-energy transitions.

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(17) The additional intense band at 510 nm leads to the purple coloration in the complex. A comparable pair of low-energy transitions are found in the benzoquinone diimine derivative.⁸

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The distinctive spectral characteristics of $\text{Ru}(\text{phi})_3^{2+}$ might be understandable on the basis of a delocalized charge transfer onto the three ligands. The sequential lowering of the energy of the transition (150 nm change in wavelength)²⁰ with increasing substitution of phi ligands suggests such delocalization and stands in sharp contrast to spectral characteristics of the localized bipyridyl system, where the intensity rises but the energy of the charge-transfer band does not shift appreciably with increasing bpy substitution. This delocalization may also explain the intense low-energy transitions observed in other tris(α -diimine) complexes.^{8,21} The delocalized framework may, finally, also account for the short excited-state lifetime of the complex, owing to large spin-orbit coupling that would be inherent in a completely delocalized system. Alternatively, the excited state is sufficiently low in energy that it may be rapidly deactivated by coupling to the ground state.

In summary, $\text{Ru}(\text{phi})_3^{2+}$ displays intense, unusual transitions at low energies. On the basis of a comparison with a zinc analogue, the transitions may be described as charge transfer in character. By comparison with a mixed-ligand complex of phi, a delocalized charge-transfer transition is suggested. Finally the dependence of the transitions on hydrogen bonding in addition to the rich intensity at long wavelengths renders the complex useful as a biophysical probe.

Acknowledgment. We thank Dr. C. V. Kumar for carrying out the flash photolysis experiments and Professor W. Rorer Murphy at Seton Hall University for the use of his cyclic voltammetry equipment and both for their helpful comments and suggestions. We are also grateful for the financial support of the National Science Foundation (Grants CHE-85-9580 and CHE-85-17354 and Alan T. Waterman Award) and the National Institute of General Medical Science (Grant GM33309).

Registry No. $[\text{Ru}(\text{phi})_3]\text{Cl}_2$, 110528-05-7; $\text{Ru}(\text{DMSO})_4\text{Cl}_2$, 59091-96-2; $\text{Zn}(\text{phi})\text{Cl}_2$, 110528-02-4; $[\text{Ru}(\text{phi})_3](\text{PF}_6)_2$, 110528-04-6; 9,10-phenanthrenequinone bis(trimethylsilyl)imine, 18054-46-1.

- (20) It is interesting that the transition centered at 510 nm in $\text{Ru}(\text{phi})_3^{2+}$ is not at all apparent in mixed-ligand complexes containing the phi ligand. Instead, the 525-nm transition in $\text{Ru}(\text{bpy})_2(\text{phi})^{2+}$ (presumably a result of localized charge transfer onto phi) is centered between the two transitions observed for the tris-substituted $\text{Ru}(\text{phi})_3^{2+}$ species. The visible spectrum of $\text{Ru}(\text{bpy})_2(\text{phi})^{2+}$ (data not shown) shows visible transitions centered at 472 and 572 nm, consistent with some degree of delocalization.
- (21) A similar delocalization may explain the intense visible transition in the ruthenium cage complex recently prepared by Sargeson et al. (personal communication).

Contribution from the Department of Chemistry,
George Mason University, Fairfax, Virginia 22030

Kinetic Study of Electron-Transfer Reactions of Sterically Constrained Bis(diimine) Complexes of Copper(II) and Copper(I) with Ruthenium Ammine Complexes

Keith M. Davies* and Brien Byers¹

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Although correlation of rate data through the Marcus relations has been satisfactorily achieved for many Cu(I)-Cu(II) electron-transfer reactions,²⁻⁷ attempts at determining Cu(I)-Cu(II)

self-exchange electron-transfer rate constants in other instances have met with less success. For reactions involving the bis-(1,10-phenanthroline) and bis(2,2'-bipyridine) complexes of Cu(I) and Cu(II), in particular, where considerable structural differences exist between the two oxidation states, widely divergent estimates of the $\text{Cu}(\text{phen})_2^{+/2+}$ and $\text{Cu}(\text{bpy})_2^{+/2+}$ self-exchange rate constants have been obtained,^{3,8} depending upon the oxidation state of the copper complex in the cross reaction and the redox partner involved. For the corresponding 2,9-dimethyl-1,10-phenanthroline (dmp) complexes, where steric constraints imposed by the methyl substituents force a closer match in the geometry of the copper centers, the Marcus relations have been able to provide more consistent self-exchange rate constants as well as successfully correlate rate constants with thermodynamic driving force for several series of reactions.^{2,9,10} The weak driving-force dependence noted for the reduction of $\text{Cu}(\text{dmp})_2^{2+}$ by Ru(II) reductants⁵ and the finding¹¹ of saturation kinetics for the reactions of the sulfonyloxyphenyl substituted dmp complex $\text{Cu}(\text{dpmp})_2^{2+}$ (dpmp = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline) further illustrate the kinetic complexities that can result in labile Cu(I)-Cu(II) systems where changes in coordination number may accompany the activation process. We report here the kinetic redox behavior of two other sterically constrained bis(diimine) Cu(II) complexes. We have examined the reduction of the bis-(4,4',6,6'-tetramethyl-2,2'-bipyridine)copper(II) and bis(6,6'-dimethyl-2,2'-bipyridine)copper(II) complexes, $\text{Cu}(\text{tmbp})_2^{2+}$ and $\text{Cu}(\text{dmbp})_2^{2+}$, by a series of Ru(II) complexes, as well as the oxidation of the Cu(I) complex $\text{Cu}(\text{tmbp})_2^+$ by the Ru(III) oxidant *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{isn})_2]^{3+}$.

Experimental Section

Chemicals and Solutions. The ruthenium complexes $[\text{Ru}(\text{NH}_3)_3(\text{py})(\text{ClO}_4)_2]$ (py = pyridine), $[\text{Ru}(\text{NH}_3)_3(\text{isn})(\text{ClO}_4)_2]$ (isn = isonicotinamide), $[\text{Ru}(\text{NH}_3)_4(\text{bpy})(\text{ClO}_4)_2]$ (bpy = 2,2'-bipyridine), *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{isn})_2](\text{ClO}_4)_2$, and *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{isn})_2](\text{ClO}_4)_3$ were prepared by publishing procedures.^{12,13} Spectra of the ammine complexes were in good agreement with literature values. The ligand tmbp was synthesized by the procedure of Linnell¹⁴ and purified by vacuum sublimation (0.5 mm) and recrystallization from hexanes. The ligand dmbp was synthesized by the G. F. Smith Co. and recrystallized from hexanes prior to use. The purity and structure of the tmbp and dmbp ligands were confirmed by NMR. The complexes $\text{Cu}(\text{tmbp})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{tmbp})_2(\text{ClO}_4)_2$, and $\text{Cu}(\text{dmbp})_2\text{ClO}_4$ were prepared by the reported methods.¹⁵ Reactions were generally carried out in 20% methanol/80% water. Solutions of $\text{Cu}(\text{tmbp})_2^{2+}$ and $\text{Cu}(\text{dmbp})_2^{2+}$ were prepared by adding $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ to a 20-100-fold excess of ligand dissolved in methanol. MES (2-morpholinoethanesulfonic acid) was used to buffer reaction solutions at operational "pH" values measured with respect to aqueous reference standards. The 20% methanol/80% water solutions, after adjustment of the ionic strength to 0.10 M with LiCF_3CO_2 , were generally at "pH" 6.1. Such solutions were prepared immediately prior to their use in the kinetic experiments. The Cu(I) products showed an absorption maximum at 450 nm ($\epsilon = 6.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) characteristic of sterically constrained bis(diimine)copper(I) complexes. Solutions of the Cu(II) complexes absorb negligibly below 700 nm.

The reaction of $\text{Ru}(\text{NH}_3)_4(\text{isn})_2^{3+}$ with $\text{Cu}(\text{tmbp})_2^+$ was followed at pH 6.1 in 20% methanol/80% water and 0.10 M LiCF_3CO_2 by mixing, in the stopped-flow apparatus, a solution of the Cu(I) reductant containing 0.010 M sodium 2-morpholinoethanesulfonate at pH 8.3 with the Ru(III) oxidant in 0.010 M free acid buffer, 2-morpholinoethanesulfonic acid, at pH 3.8. $\text{Ru}(\text{NH}_3)_4(\text{isn})_2^{3+}$ was slowly reduced by the solvent ($t_{1/2} = 35 \text{ s}$) at pH 6.1.

- (1) Present address: Department of Chemistry, Texas A&M, University, College Station, TX.
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