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ESR Study of Reduced Monosubstituted Ruthenium(II) Diimine Complexes

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The electrochemically reduced monosubstituted diimine complexes $[Ru(bpy)(CN)_4]^{2-}$, $[Ru(bpm)(CN)_4]^{2-}$, and $[Ru(bpz)(CN)_4]^{2-}$ have been characterized by electron spin resonance spectroscopy. Well-resolved hyperfine structure (hfs) was observed in all three complexes, and coupling constants were calculated from the observed spectra. The hyperfine coupling constants derived from the ESR spectra indicate that the electronic spin density is largely localized within the π^* orbitals of the reduced species. Emission spectra, solvatochromic absorption spectra, and cyclic voltammetry data are also presented and discussed.

Introduction

The unique photochemical properties of the π-electron diimine complexes of Ru(II) have generated a considerable amount of attention over the last decade.[1] The utility of these complexes in applications varying from catalysis to electron and energy transfer has generated a vast array of characterization techniques aimed at developing a full understanding of the low-lying ($d-\pi^*$) excited states in these complexes. Through an extension of Koopman's theorem, this low-lying excited state has been studied via electrochemical reduction of the ground state complex.[2] Coupled with UV/visible spectroscopy and resonance Raman studies, the ESR method revealed evidence for a spatially isolated, single-ligand redox orbital.[3−6] Moreover, ESR evidence in the form of temperature-dependent line broadening was observed, suggesting an intramolecular ligand−ligand "hopping" mechanism in these complexes.[7]

The failure to observe hyperfine structure in the singly- and doubly-reduced tris-diimine complexes[8] has been attributed to a pseudo-spin-rotational $1/T_2$ broadening in which the pseudorotation is brought about by the interligand "hopping" mechanism.[7] Study of triply-reduced and mixed-ligand species enabled a more thorough investigation of each redox orbital. In both instances, the barrier to intramolecular, interligand electron "hopping" is large, forcing a more highly ligand-localized charge-transfer electron excited state. The observation of hyperfine structure in both the triply reduced[8] and the mixed-ligand species[9−11] confirmed the validity of this model. Although the barrier to "hopping" is large in these systems, varying degrees of anisotropic line broadening persist, yielding impaired resolution of the hyperfine splittings.[8]

In the current study, ESR spectra of the one-electron reduction products of three tetracyano, mono(diimine) Ru(II) complexes are presented in which the diimine ligands are 2,2′-bipyridine (bpy), 2,2′-bipyrimidine (bpm), and 2,2′-bipyrazine (bpz). An attempt was also made to characterize the tetraamine analog, $[Ru(NH_3)_4(bpy)](PF_6)_2$. From these results, further characterization of the important charge-transfer excited state of the trisubstituted analogs was made possible via a more thorought understanding of the intraligand electron spin distribution in the single π-electron diimine ligand.

Experimental Section

Materials. The ligands bpy and bpm were purchased commercially (Aldrich), and used without further purification. The ligand bpz was prepared by a literature method.[12] Tetrabutylammonium hydroxide was purchased commercially (Aldrich), as was tetrabutylammonium hexafluorophosphate (TBAH, Eastman Kodak), which was recrystalized once from water and three times from HPLC grade methanol. HPLC grade *N,N*′-dimethylformamide (DMF, Aldrich) was glass-distilled distilled at 10 Torr of nitrogen which was dried by slow passage through a high-surface area liquid nitrogen trap. All other solvents used were at least spectrophotometric grade.

The potassium salts, $K_2[Ru(L)(CN)_4]$, were made in accordance with a literature preparation of the $K_2[Ru(bpy)(CN_4]$ complex.[13] In the case of L = bpz it was necessary to add a small amount of methylene chloride to the water−methanol mixture to aid in the dissolution of the ligand. The tetrabutylammonium salts of these complexes were made by adding a 10-fold excess of tetrabutylammonium hydroxide (aqueous solution) to the potassium salt followed by column chromatography on an aqueous Sephadex LH-20 column. This step was necessary in order to render the salts soluble in DMF.[13] Purity of the resulting material was confirmed by comparison of the luminescence generated at two different excitation wavelengths. The tetraamine complex, $[Ru(NH_3)_4(bpy)](PF_6)_2$ was prepared by a literature method.[14]

Methods. Absorption spectra were acquired on a CARY-14 UV/visible spectrometer equipped with an OLIS computer interface. Emission spectra were acquired with a Photon Technologies LS-100 spectrometer.

Cyclic voltammetry (CV) and bulk electrolysis were performed in a Vacuum Atmospheres glovebox under a nitrogen atmosphere using

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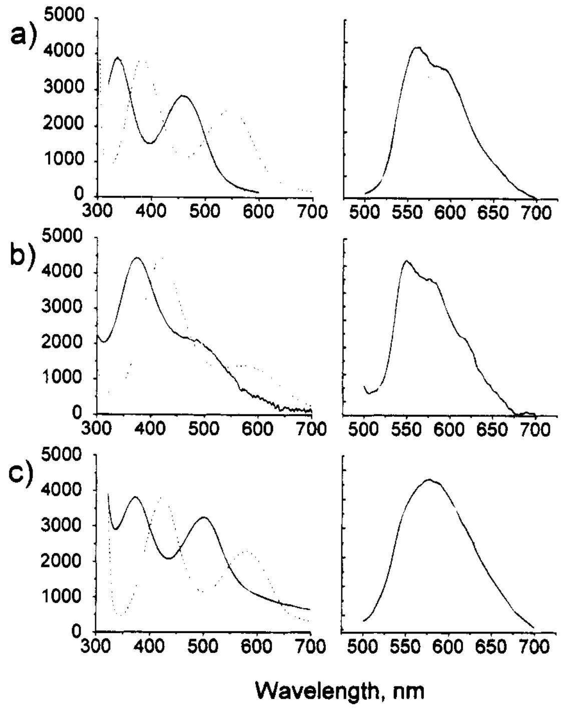

Figure 1. Absorption (left) in EtOH (—) and DMF (- -) and emission (right) of $(N[(CH_2)_3CH_3]_4)_2[Ru(L)(CN)_4]$ with L = bpy (a), L = bpm (b), and L = bpz (c). Absorptivity scale is molar extinction coefficient. Emission intensities are arbitrary.

a three-compartment H-cell with ~0.1 mM solutions. CV measurements were all reproduced in a single-compartment argon-purged cell (EG&G, Princeton Applied Research). A platinum wire electrode served as the working electrode for CV measurements, a platinum wire mesh served as the auxiliary electrode, a platinum flag served as the bulk electrolysis electrode, and a saturated calomel electrode (in the argon-purged cell) or a silver/silver ion pseudoreference electrode (in the glovebox) was employed. Cyclic voltammetry of the ferrocene/ferrocenium redox couple was performed after each experiment to calibrate the pseudo-reference electrode. Bulk electrolyses were carried out at a potential 100 mV negative of the cathodic wave for each complex, and cyclic voltammetry was performed after electrolysis to ensure the stability of the reduced complex.

ESR X-band spectra were acquired on a Bruker ESP 300 spectrometer equipped with an ER 4111 variable temperature controller. Simulation of acquired spectra were performed with software written by Kirste.[15]

Results

Absorption and emission spectra for the three tetrabutylammonium tetracyano–monodiimine complexes are presented in Figure 1. As with the potassium salts, dramatic solvatochromism was observed for these complexes, presumably induced by the strong-field cyanide ligands. The absorbance of the $[Ru(NH_3)_4(bpy)](PF_6)_2$ species is reported elsewhere.[14] The $[Ru(NH_3)_4(bpy)](PF_6)_2$ complex is nonluminescent.

Cyclic voltammetry for these complexes in DMF/TBAH is presented in Figure 2. Table 1 gives peak potentials and half-wave potentials for the three complexes. In all cases, the half-wave potentials for the one-electron reduction were approximately 0.7 V more negative than the first half-wave potential for the corresponding tris(diimine) complexes, presumably due to the large negative charge existent in the unreduced mono complex. Bulk electrolysis was carried out at a potential 100 mV negative of the cathodic peak in each case. Although absorption spectra were not acquired for the reduced species, in all cases the solution turned dark brown in color upon complete reduction, analogous again to the behavior of the tris analogs. Cyclic voltammetry was successfully performed on the $[Ru(NH_3)_4(bpy)](bpy)](PF_6)_2$ complex, but post-electrolysis cyclic voltammetry revealed that the reduced species was unstable.

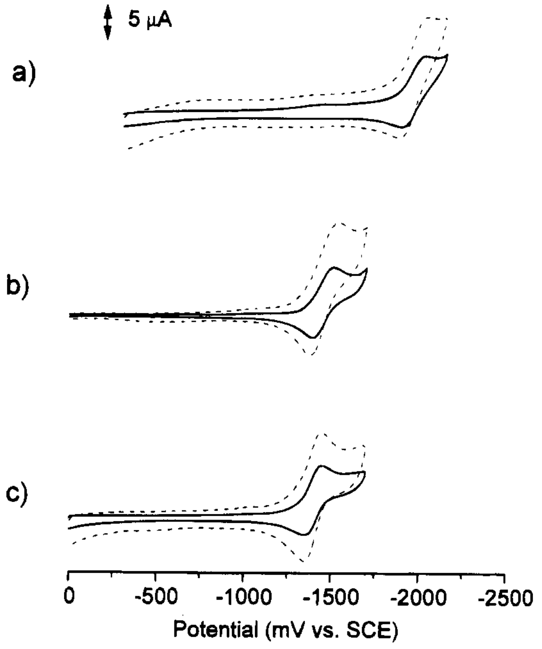

Figure 2. Cyclic voltammograms of $(N[(CH_2)_3CH_3]_4)_2[Ru(L)(CN_4]$ in DMF/TBAH solution with L = bpy (a), L = bpm (b), and L = bpz (c), at 100 mV/s (—) and 400 mV/s (- -).

Table 1. Redox Wave Potentials of Mono(diimine) Tetracyano Complexes (in V)[a]

species	E_a vs $Fc^{+/0}$	E_c vs $Fc^{+/0}$	$E_{1/2}$ vs $Fc^{+/0}$
$Ru[(bpy)(CN)_4]^{2-}$	−2.42	−2.50	−2.46
$Ru[(bpm)(CN)_4]^{2-}$	−2.05	−2.12	−2.09
$Ru[(bpz)(CN)_4]^{2-}$	−1.96	−2.04	−2.00

[a] Polarization rate = 100 mV/s.

ESR spectra for the three reduced tetracyano complexes are presented in Figure 3. In all cases, hfs was exhibited by the reduced species. Moreover, no temperature dependence in the peak to peak line width of the $S = {}^1/_2$ spectrum was observed in the operational temperature range from ~100–350 K, as was expected due to the absence of electron "hopping." The coupling constants for the three species are presented in Table 2.

Discussion

The observation of hfs in all three of the reduced monodiimine complexes validates the argument that the lack of hfs in the polydiimine moieties is due to the pseudorotational broadening brought about by the interligand hopping process. The hfs coupling constants provide insight to the electronic structure of these species, aiding in the description of the structure of the excited states of the tetracyano mono(diimine) complexes. Due to the ligand localized nature of the MLCT state in the tris(diimine) analogs, this argument can be extended to describe the structure of the tris analogs as well, which cannot be directly characterized by ESR hfs due to the interligand hopping process. ESR data on the tris analogs has shown that the diimine ligand orbitals in these complexes consist of nearly degenerate and noncommunicating orbitals.[7] Reduction products of the trisubstituted complexes exhibit ESR temperature-dependent line

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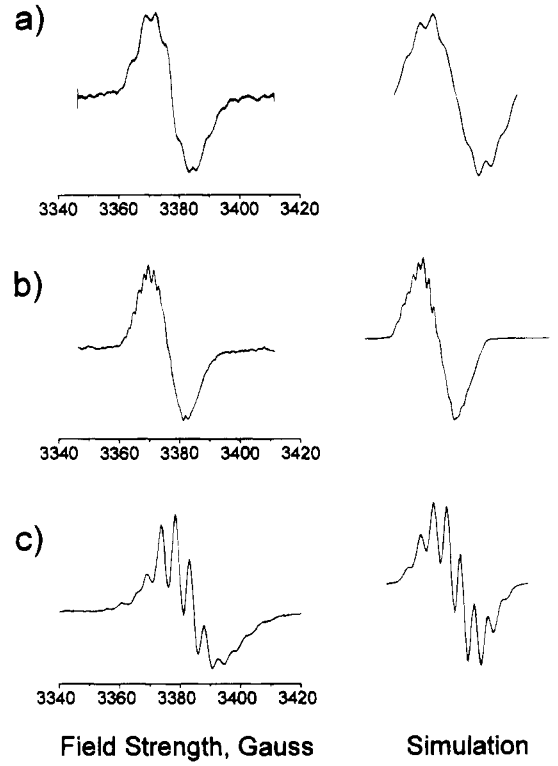

Figure 3. ESR spectra and simulations of one-electron reduction products (in DMF/TBAH solution) of $(N[(CH_2)_3CH_3]_4)_2[Ru(L)(CN)_4]$ with L = bpy (a), L = bpm (b), and L = bpz (c).

Table 2. Hyperfine Coupling Constants of Reduced Mono(diimine) Tetracyano Complexes (in mT)

species	*a*	*n*X	*n*
bpy[a]	0.115	2H	5,5′
	0.530	2H	4,4′
	0.575	4H	3,3′,6,6′
	0.265	2N	
$[Ru(bpy)(CN)_4]^{3-}$	0.54	2H	5,5′
g = 1.999	0.56	2N	
	0.30	Ru	
bpm[b]	0.137	4N	1,1′,3,3′
	0.47	2H	5,5′
$[Ru(bpm)(CN)_4]^{3-}$	0.147	2H	5,5′
g = 1.999	0.27	2N	1,1′
	0.15	Ru	
bpz[c]	0.55	2H	5,5′
	0.09	2H	3,3′,6,6′
	0.33	2N	1,1′
	0.05	2N	4,4′
$[Ru(bpz)(CN)_4]^{3-}$	0.47	2H	5,5′
g = 1.991	0.47	2N	1,1′
	0.11	Ru	

[a] Reference 18. [b] Reference 6. [c] Reference 5.

broadening for the one- and two-electron reduction products. However, to our knowledge, hfs in the three-electron reduction product for a homoleptic trisubstituted species has only been observed once previously at high temperature in DMSO.[8] Some question remained at that time whether the result was indicative of a perturbation upon the coupling constant by the DMSO solvent, or a temperature sensitive anisotropy in the **g** and/or **A** tensors. However, well-resolved hfs has been observed for the mixed-ligand complexes $Ru[(bpy)_2(L)]^{2+}$ (where L = bpz, bpm, and 4,4′-diester bpy), in which the barrier towards interligand "hopping" is large enough to eliminate broadening of the ESR line due to the pseudorotational spin interaction.[7,9-11]

The present results on the tetracyano, monodiimine species eliminate most of the questions which remain concerning the character and validity of the spatially isolated redox orbital model for all ruthenium diimine type complexes by providing a system in which no "hopping" process is possible. Furthermore, these results provide a technique for characterizing the effect of the ruthenium ion on the chelate orbitals of a variety of complexing ligands.

The agreement of the hyperfine structure of the tetracyano bpz and tetracyano bpm one-electron reduction products with those derived from the mixed ligand species $Ru[(bpy)_2(bpz)]^+$ and $Ru[(bpy)_2(bpm)]^+$ is good,[9,10] although the hfs for the mono compounds is not as well resolved as the previous hfs. The tetracyano complexes can be used to provide a first approximation for the tris diimine analogs, this despite the difference in charge on the species and the nature of the ancillary ligands. The redox orbital spin density of the diimine ligand appears essentially unaltered. In fact, the appearance of the mono-bpy ESR hyperfine structure is similar to that of the tris complex, at high temperature albeit with enhanced resolution. The moderate anisotropy present in each case is likely due to *g*-factor or hfs anisotropy, since T_1 line broadening does not occur as evidenced by the absence of temperature dependence.

The hfs coupling constants derived from the simulation of the mono-bpy ESR spectrum indicate a polarization of spin density, relative to the free ligand, at the 5 and 5′ carbon atoms and the nitrogen chelating atoms. This result is, of course, due to the presence of the Ru(II), and reiterates the findings of the study on mixed-ligand species.[9,10] Furthermore, the spin density on the Ru(II) itself is low, in concord with theoretical and empirical descriptions of the redox orbital in this class of metal complexes.[6,16,17] The bpm and bpz analogs give the same general result with respect to the intraligand spin distribution. The distribution is more ligand polarized in the bpm and bpz analogs, a result to be expected due to their lower lying π LUMO relative to bpy.

The electrochemical data indicate the usual qualitative hierarchy of reduction potentials in the sequence bpy < bpm < bpz. This series is a manifestation of the stabilization of the π^* state by enhanced metal-ligand bonding and ligand-metal backbonding in the ligands with lower lying π orbitals. The spin density on the chelating nitrogen atoms (estimated from the hfs coupling constants) follows the sequence bpy > bpz > bpm. An explanation for the misplacement of bpm in this sequence is suggested by the symmetry of the ligand. While the four nitrogens are equivalent in the free ligand, their equivalence is removed by complexation to the ruthenium ion, which in turn polarizes the electron density in the ligand orbitals. The electron density on the nonchelating nitrogens is not observed from the hfs coupling constants in the mixed-ligand mono-bpm study as well.[9]

Hirota *et al*[18] suggested, in a study on the excited state of the tetraethylammonium salt of the tetracyano mono-bpy complex, that the similarities in absorption and emission spectra of this salt and the tris bpy analog are an argument for the spatially isolated redox orbital model. The present results extend their argument in that the absorption and emission spectra of the bpm and bpz complexes (Figure 1) are also quite similar to those of the tris analogs.

The tetraamine complex, $[Ru(NH_3)_4(bpy)](PF_6)_2$, was unstable to bulk electrolysis, likely due to lower-lying d* orbitals in this

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moiety. Indeed, Hupp *et al.*[17] argued from their electrochemical data for significant metal/ligand orbital mixing of the tetraamine species $[Ru(NH_3)_4(bpy)](PF_6)_2$ and $[Ru(NH_3)_4(phen)](PF_6)_2$ (phen = 1,10-phenanthroline). The tetraamine moiety also fails to replicate the phosphorescence light-induced redox properties of the $Ru(bpy)_3^{2+}$ and of the tetracyano bpy complexes, also due to deactivation of the d−π* state via low-lying metal centered states.[18] Kobayashi and Kaizu drew the same conclusion from the observation that no luminescence is emitted by the tetraamine complexes.[19] Hence, it appears that the monosubstituted ruthenium diimine complexes will only mimic the MLCT properties of the tris analogs when very strong field ligands constitute the ancillary substituents.

In summary, the present study report hfs constants for the monosubstituted bpy, bpm, and bpz tetracyano ruthenium(II) complexes, which elucidate the nature of the redox-active excited state of these and the tris analogs of these complexes. Although the bpm and bpz hfs constants have been reported in the mixed-ligand species, resolution of the bpy hfs constants was not previously possible due to the hopping mechanism. The observation of hfs in the mono(diimine) moieties complements those observed in the mixed-ligand species, and supports the hopping model as the rationale for the inability to resolve hfs in the bis and tris analogs.

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