

# Electronic Structure of the "Molecular Light Switch" $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ (dppz = Dipyrido[3,2-*a*:2',3'-*c*]phenazine). Cyclic Voltammetric, UV/Vis, and EPR/ENDOR Study of Multiply Reduced Complexes and Ligands

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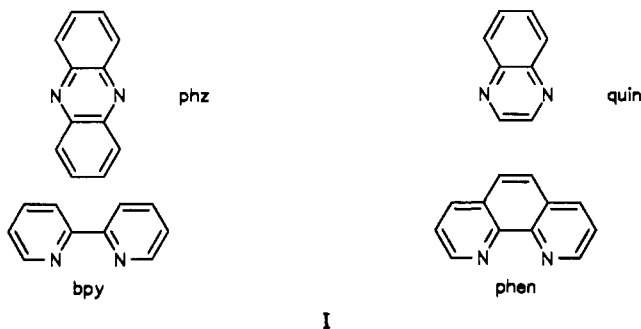
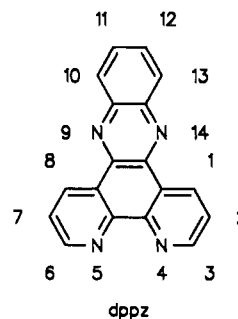
The chelate ligand dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz), its 1,1,12-dimethyl derivative dmdppz, and corresponding complexes with  $[\text{Ru}(\text{bpy})_2]^{2+}$  were studied in multiply reduced states by low-temperature cyclic voltammetry and UV/vis and EPR spectroscopy. The (dm)dppz ligands are reduced in two reversible steps, followed by a very moisture-sensitive third step. Highly resolved EPR and <sup>1</sup>H-ENDOR spectra of the intermediate anion radicals were obtained and analyzed. The results are interpreted using a HMO/McLachlan perturbation approach of  $\pi$  spin populations and orbital energies. Three low-lying unoccupied  $\pi$  molecular orbitals can be identified as phenazine-type ( $b_1$ , lowest) and as the  $\psi(b_1)$  and  $\chi(a_2)$  orbitals of the  $\alpha$ -diimine moiety. Complexes with the N(4),N(5)-bound  $[\text{Ru}(\text{bpy})_2]^{2+}$  fragment show at least six reversible one-electron reduction steps in rigorously dried DMF at 200 K; the first four persistent reduced states were characterized by EPR and UV/vis spectroscopy. The EPR spectra of the first three reduced states of the complexes show a signal which proves the occupation of the phenazine-localized  $\pi^*$  orbital of (dm)dppz by a single electron, the stepwise reduction of the bpy ligands resulting in temperature-dependent intensity loss of that EPR signal. The very basic quadruply reduced state exhibits EPR characteristics which are typical for Ru(II)-bound  $\alpha$ -diimine anion radicals. All assignments are supported by UV/vis spectra and analyses of redox potential values. Because the very easily protonated higher reduced states are not sufficiently persistent for EPR and UV/vis characterization, further assignments could thus be based only on the analysis of redox potential values. The particular composite electronic structure of the complexes with differing redox and "optical" orbitals is related to their "light switch" behavior, i.e. to the absence of luminescence quenching in a nonaqueous environment.

## Introduction

Stable luminescent probes for nonpolar microenvironments such as micelles or (bio)polymers in aqueous solution are sought after materials.<sup>1,2</sup> Among the host of ruthenium(II) "polypyridine" complexes,<sup>3</sup> the dicationic  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$  ( $1^{2+}$ ) (bpy = 2,2'-bipyridine and dppz = dipyrido[3,2-*a*:2',3'-*c*]phenazine) with an apparently untypical electronic structure<sup>4,5</sup> was found to act as a fairly selective "molecular light switch" for DNA<sup>6</sup> and in micellar solutions.<sup>7</sup> The metal-to-ligand charge-transfer (MLCT) luminescence is quenched in water but not in aqueous solutions due to a possibly specific<sup>6</sup> intercalation of the phenazine portion into a hydrophobic pocket. Emission also occurs in nonaqueous but weakly protic solvents such as ethanol.<sup>5</sup>

The special ligand dppz contains features both of an  $\alpha$ -diimine chelate ligand, the 2,2'-bipyridine or 1,10-phenanthroline (phen)

part,<sup>8</sup> and of a 1,4-diazine,<sup>9</sup> i.e. the phenazine (phz) or quinoxaline (quin) moiety (I).<sup>4</sup> Thus, it is not immediately obvious what



MLCT excited states are available for long-wavelength photo-

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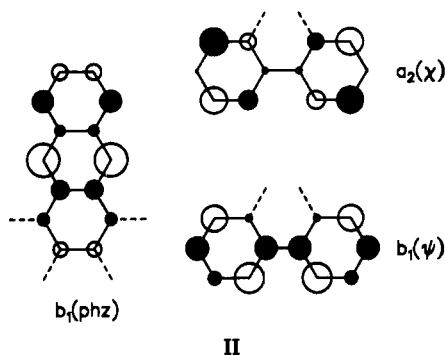
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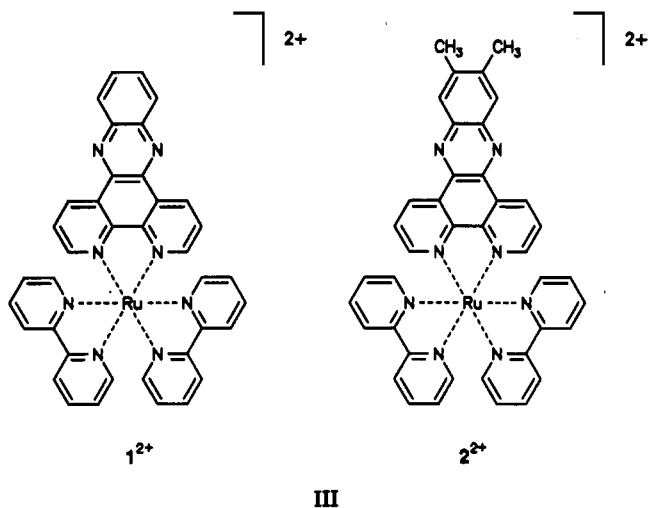
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emission. Low-lying unoccupied  $\pi^*$  molecular orbitals can be of the phenazine-centered type,  $b_1(\text{phz})$ , or of the  $\chi(a_2)$  or  $\psi(b_1)$  character of the  $\alpha$ -diimine part (II);<sup>10</sup> the latter two unoccupied MOs are particularly close for 1,10-phenanthroline and derivatives.<sup>8</sup>



While a Hückel MO calculation of dppz has suggested<sup>4a</sup> that the  $b_1(\text{phz})$  is the LUMO of the ligand, the situation could be different in  $N(4),N(5)$ -coordinated complexes where the  $\alpha$ -diimine-bound metal can stabilize  $\chi$  and especially  $\psi$ . Previous studies suggested that  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$  is made up of two "electronically independent" units, a  $[\text{Ru}(\text{bpy})_3]^{2+}$ -like chromophore and a phenazine-like electron acceptor.<sup>4,5</sup> We have therefore used a HMO perturbation approach in order to mimic metal coordination at  $N(4),N(5)$  and thus obtain an approximate energetic response of all three low-lying  $\pi^*$  MOs. Similarly, the HMO/McLachlan  $\pi$  spin populations of the dppz anion radical were obtained as a function of the Coulomb integral parameter at these coordinating centers.<sup>11</sup> The calculated data were used to assign hyperfine coupling constants as obtained from ENDOR-assisted EPR spectra of the reduced ligand  $\text{dppz}^{\cdot-}$ , of its 11,12-dimethyl analogue  $\text{dmdppz}^{\cdot-}$ , and of various reduced states of the complexes  $1^{2+}$  and  $2^{2+}$  (I, III).<sup>6b</sup> The successive occupation



of various empty MOs of dppz and bpy in the complexes on reduction was further studied by UV/vis absorption spectroscopy, i.e. spectroelectrochemically.

### Experimental Section

**Materials.** dppz and  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ , the latter as the bis-(hexafluorophosphate) salt,<sup>6b</sup> were synthesized according to literature procedures<sup>5,12</sup> from 1,10-phenanthroline-5,6-dione<sup>5</sup> (pdo) or the complex

$[\text{Ru}(\text{bpy})_2(\text{pdo})](\text{PF}_6)_2^{13a}$  and 1,2-diaminobenzene (cf. the procedures for the dimethyl derivatives below). The purity was checked by <sup>1</sup>H-NMR spectroscopy<sup>5</sup> and elemental analysis.

$[\text{Ru}(\text{bpy})_2(\text{dppz})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ . Anal. Calc for  $\text{C}_{38}\text{H}_{28}\text{F}_{12}\text{N}_8\text{O}_2\text{P}_2\text{Ru}$  ( $M_r = 985.68$ ): C, 45.41; H, 2.78; N, 11.15. Found: C, 44.90; H, 2.67; N, 10.80.

**11,12-Dimethyldipyrido[3,2-*a*:2',3'-*c*]phenazine (dmdppz)** was prepared according to established procedures<sup>12</sup> from 1,10-phenanthroline-5,6-dione<sup>5</sup> and 1,2-diamino-4,5-dimethylbenzene in ethanol. Anal. Calc for  $\text{C}_{20}\text{H}_{14}\text{N}_4$  ( $M_r = 310.33$ ): C, 77.41; H, 4.54; N, 18.05. Found: C, 76.98; H, 4.47; N, 18.11. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  2.60 (s,  $\text{CH}_3$ ), 7.77 (dd,  $\text{H}^{2,7}$ ), 8.06 (s,  $\text{H}^{10,13}$ ), 9.23 (d,  $\text{H}^{3,6}$ ), 9.60 ppm (d,  $\text{H}^{1,8}$ );  $J(2,3;6,7) = 3.9$  Hz,  $J(1,2;7,8) = 8.1$  Hz.

$[\text{Ru}(\text{bpy})_2(\text{dmdppz})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ : An 83-mg (0.09-mmol) amount of  $[\text{Ru}(\text{bpy})_2(\text{pdo})](\text{PF}_6)_2^{13a}$  obtained via  $\text{H}_2\text{SO}_4/\text{HNO}_3$  oxidation of  $[\text{Ru}(\text{bpy})_2(\text{phen})](\text{PF}_6)_2^{13b}$  was dissolved in 30 mL of ethanol, 13 mg (0.1 mmol) of 1,2-diamino-4,5-dimethylbenzene was added, and the mixture was heated under reflux for 5 min. Addition of water to the cooled solution precipitated the red product, which was recrystallized from water/ethanol (1/1) to yield 70 mg (77%) of a monohydrate. Anal. Calc for  $\text{C}_{40}\text{H}_{32}\text{F}_{12}\text{N}_8\text{P}_2\text{ORu}$  ( $M_r = 1031.75$ ): C, 46.57; H, 3.12; N, 10.85. Found: C, 46.90; H, 3.12; N, 10.31.

**Tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ )** was prepared from  $n\text{-Bu}_4\text{NCl}$  and  $\text{NH}_4\text{PF}_6$ , recrystallized five times from ethanol, and dried at 140 °C under vacuum for at least 24 h.

Very dry *N,N*-dimethylformamide (DMF) for cyclic voltammetry at negative potentials was purified by azeotropic distillation with benzene at atmospheric pressure, subsequent vacuum distillation, and treatment with sodium anthracene for at least 4 days. Thus purified DMF was then vacuum-distilled directly into the dried electrochemical cell or into a dried Schlenk tube containing supporting electrolyte and dehydrated (135 °C) substrate. This procedure allowed routine measurements extending to  $-3.5$  V vs the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple.

**Apparatus and Procedures.** Cyclic voltammetric measurements were performed in a one-compartment three-electrode cell<sup>14</sup> with a 0.7-mm<sup>2</sup> platinum working electrode and a silver wire quasi-reference electrode. At the end of measurements, ferrocene was added to the sample as a reference. A PAR 273 potentiostat and a PA-3 polarograph (Laboratorni pístroje Prague) were employed for the experiments.

EPR and ENDOR spectra were recorded using a Varian E-4 or a Bruker ESP 300 system. The anion radicals of the ligands were generated for ENDOR measurements by reacting them with potassium in THF in the presence of  $\text{K}^+$ -complexing [2.2.2]-cryptand in sealed glass tubes. Electrochemical generation of singly reduced species (ligands and complexes) in situ was possible using cells of described design.<sup>15,27b</sup> Multiply reduced species were generated for EPR measurements by preparative electrolysis at the appropriate potential in a three-compartment cell, separated by glass frits, with a Pt gauze working electrode (ca. 200 mm<sup>2</sup>), a Pt gauze auxiliary electrode, and a silver wire quasi-reference electrode. The volume of the working electrode compartment was ca. 10 mL. The number of added electrons was confirmed by integration of the current. The possibility of decomposition was checked by taking a cyclic voltammogram after electrolysis with the help of a second Pt working electrode (0.7 mm<sup>2</sup>).

UV/vis absorption spectra of reduced species were measured in an optically transparent thin-layer electrolytic (OTTLE) cell described elsewhere.<sup>16</sup> Chemical reversibility of the process was checked by reoxidation after the measurements on reduced species. The spectra were recorded on a HP 8452A diode array spectrometer.

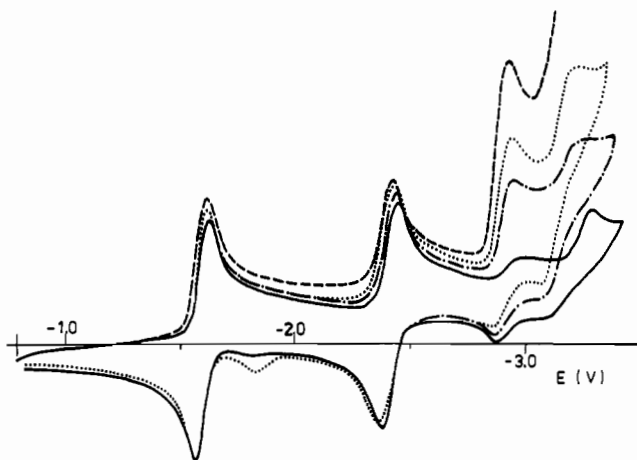
HMO/McLachlan and CNDO/S calculations of  $\pi$  spin populations  $\rho_\pi$  and EPR coupling constants  $a_x$  were carried out using standard programs and parameters ( $\lambda = 1.2$  and  $Q = 2.3$  mT for the McConnell equation  $a = Q(\rho_\pi)$ ).<sup>8,18</sup> EPR spectral simulations were performed with extended versions (W. Bruns, University of Stuttgart) of available<sup>8,17</sup> programs. Transition energies and oscillator strengths were calculated

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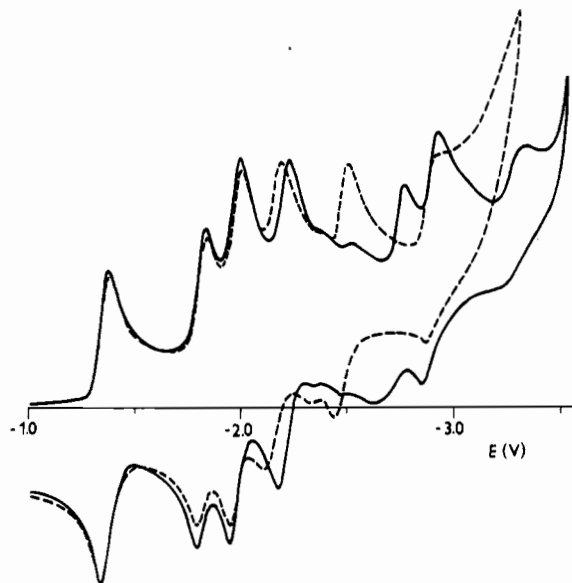
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**Figure 1.** Cyclic voltammograms of dppz ( $5 \times 10^{-4}$  M) at 200 K in dry DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  (—) and after stepwise addition of traces of water (---, ---, ---, approximately  $10^{-3}$  M) (potentials in volts vs  $\text{Fc}/\text{Fc}^+$ ).



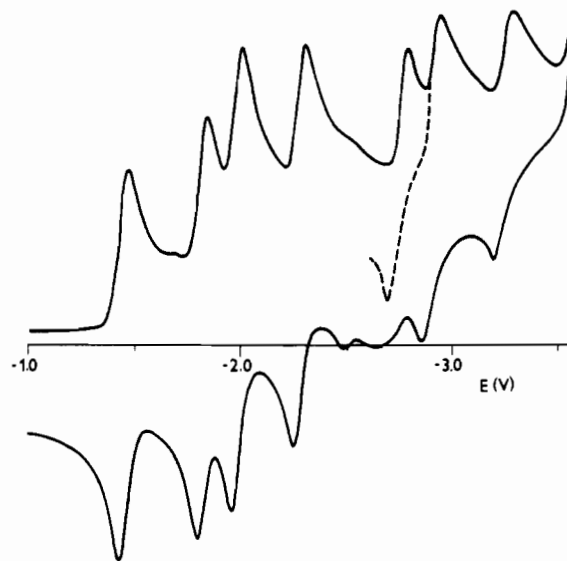
**Figure 2.** Cyclic voltammograms of complex  $1^{2+}$  ( $10^{-3}$  M) at 200 K in dry DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  (—) and after addition of traces of water (---) (potentials in volts vs  $\text{Fc}/\text{Fc}^+$ ).

by the semiempirical CNDO/S method<sup>18</sup> followed by configuration interaction. AM1<sup>19</sup>-optimized geometries were used as input for the calculation.

## Results

The ligands dppz and dmdppz and their complexes undergo reduction in several one-electron steps (Figures 1–3). Whereas the first two reduction waves of each ligand are fully reversible at room temperature, the third reduction step is irreversible under those conditions. There are two partly reversible components of the third reduction wave observable at 200 K, whose intensity increases markedly with the moisture content of the solvent.

The  $[\text{Ru}(\text{bpy})_2]^{2+}$  complexes  $1^{2+}$  and  $2^{2+}$  show a total of seven one-electron reduction steps at 200 K in DMF, in addition to the metal-centered oxidation (Figures 2 and 3, Table I). The higher number of observable reversible reduction processes in comparison to a previous report<sup>5</sup> for  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$  is attributable to the use of rigorously dried DMF. Whereas the first three reduction processes are not too strongly affected by traces of water, the potentials of the fourth and especially of the fifth reduction step are distinctly dependent on such moisture effects. The addition

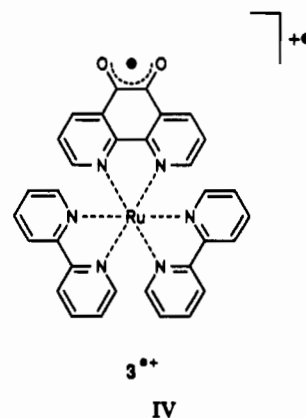


**Figure 3.** Cyclic voltammograms of complex  $2^{2+}$  ( $10^{-3}$  M) at 200 K in dry DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  with two different turning points:  $-3.50$  V, —;  $-2.88$  V, --- (potentials in volts vs  $\text{Fc}/\text{Fc}^+$ ).

of very small amounts of water to a dry DMF solution of  $1^{2+}$  and  $2^{2+}$  leads to the anodic shift of the fourth couple by about 50 mV and to the appearance of a new fifth couple, shifted by about 200 mV to less negative potentials relative to the positions of the original couple (Figure 2, Table I). In very dry DMF at 200 K, reversible sixth and partly irreversible seventh reduction waves to the tetra- and pentaanions become observable for the complexes (Figure 3).

The singly reduced paramagnetic forms, the anion radicals of the ligands, were generated for EPR/ENDOR spectroscopy using potassium and  $\text{K}^+$ -complexing [2.2.2]-cryptand in THF solution. A highly resolved EPR spectrum of  $\text{dppz}^{\cdot-}$  is shown in Figure 4 together with its computer simulation. The coupling constants employed in the simulation and summarized in Table II were extracted in part from  $^1\text{H}$ -ENDOR spectra (Figure 4C) and assigned in conjunction with HMO/McLachlan-calculated  $\pi$  spin populations (see Table II and Figure 9).

The rather well-resolved EPR spectrum of a singly reduced complex,  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{+\cdot}$  ( $1^{+\cdot}$ ), as generated electrochemically in dichloromethane/0.1 M  $\text{Bu}_4\text{NPF}_6$  is shown in Figure 5, accompanied by a computer simulation (data in Table II). In contrast to  $1^{2+}$  or  $2^{2+}$ , the *o*-semiquinone complex  $[\text{Ru}(\text{bpy})_2(\text{pdo})]^{+\cdot}$  ( $3^{+\cdot}$ ) (structure IV) of the precursor material<sup>13</sup> shows



only one unresolved line with a 0.4-mT peak-to-peak line width and  $g = 2.0023$ . ENDOR spectroscopy of these paramagnetic complexes was not possible due to high saturation levels.

The EPR measurements of the doubly and triply reduced forms of  $1^{2+}$  in DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  produced spectra which were virtually identical to those of the singly reduced form, albeit with

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Table I. Half-Wave Potentials<sup>a</sup> *E* for the Oxidation (<sup>ox</sup>*E*) and the Reduction (<sup>r</sup>*E*) of Ligands and Complexes in DMF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>

species	<sup>ox</sup> <i>E</i>	<sup>I</sup> <i>E</i>	<sup>II</sup> <i>E</i>	<sup>III</sup> <i>E</i>	<sup>IV</sup> <i>E</i>	<sup>V</sup> <i>E</i>	<sup>VI</sup> <i>E</i>	<sup>VII</sup> <i>E</i>
dppz (293 K)		-1.60	-2.49	-2.99 <sup>b</sup>				
dppz (200 K)		-1.58	-2.40	-2.91/-3.30 <sup>b,c</sup>				
[Ru(bpy) <sub>2</sub> (dppz)] <sup>2+</sup> (293 K)		-1.36	-1.79	-1.99	-2.31	-2.53 <sup>d</sup> /-2.74 <sup>e,e</sup>	-2.97 <sup>b</sup>	
[Ru(bpy) <sub>2</sub> (dppz)] <sup>2+</sup> (200 K)		-1.35	-1.81	-1.97	-2.20	-2.48 <sup>d</sup> /-2.72 <sup>e,e</sup>	-2.88	-3.28
[Ru(bpy) <sub>2</sub> (dppz)] <sup>2+</sup> (293 K, moist)		-1.35	-1.78	-1.99	-2.25	-2.54 <sup>f</sup>	-2.94 <sup>b,f</sup>	
[Ru(bpy) <sub>2</sub> (dppz)] <sup>2+</sup> (200 K, moist)		-1.35	-1.81	-1.96	-2.14	-2.46 <sup>f</sup>	-2.89 <sup>f</sup>	
[Ru(bpy) <sub>2</sub> (dppz)] <sup>2+</sup> (293 K, moist) <sup>g</sup>	+0.85	-1.44	-1.87	-2.07	-2.29	-2.55 <sup>f</sup>		
dmdppz (293 K)		-1.71	-2.56	-3.03 <sup>b</sup>				
dmdppz (200 K)		-1.66	-2.46	-2.93/-3.26 <sup>b,c</sup>				
[Ru(bpy) <sub>2</sub> (dmdppz)] <sup>2+</sup> (293 K)	+0.85 <sup>g</sup>	-1.45	-1.80	-2.00	-2.37	-2.55 <sup>d</sup> /-2.79 <sup>e,e</sup>	-3.03 <sup>b</sup>	
[Ru(bpy) <sub>2</sub> (dmdppz)] <sup>2+</sup> (200 K)		-1.46	-1.83	-1.99	-2.29	-2.50 <sup>d</sup> /-2.72 <sup>e,e</sup>	-2.91	-3.24
[Ru(bpy) <sub>2</sub> (dmdppz)] <sup>2+</sup> (293 K, moist)		-1.45	-1.80	-2.00	-2.36	-2.62 <sup>f</sup>	-2.95 <sup>b,f</sup>	
bpy <sup>h</sup>		-2.55	-3.25 <sup>e</sup>					

<sup>a</sup> From cyclic voltammetry at 100 mV/s;  $E = 1/2(E_{pa} + E_{pc})$  in V vs ferrocene/ferrocenium couple. <sup>b</sup> Irreversible step; cathodic peak potential given. <sup>c</sup> Complementary waves; cf. text. <sup>d</sup> Small wave; reversible. <sup>e</sup> Partly irreversible. <sup>f</sup> Protonated form; cf. text. <sup>g</sup> Measured in acetonitrile. <sup>h</sup> Reference 14.

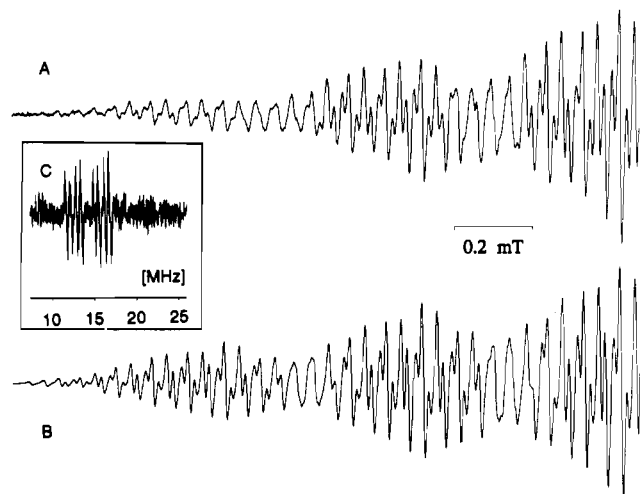


Figure 4. EPR spectrum of dppz<sup>•-</sup> at 293 K, generated with K and [2.2.2]-cryptand in THF (A), and computer simulation with the values from Table II and a line width of 0.01 mT (B). The <sup>1</sup>H-ENDOR spectrum of dppz<sup>•-</sup> at 260 K is shown in the insert (C).

lowered intensity ( $\approx 30\%$  at 300 K,  $\approx 60\%$  at 210 K, and  $\approx 90\%$  at 190 K for the neutral complex **1**;  $\approx 12\%$  at 300 K,  $\approx 20\%$  at 210 K, and  $\approx 26\%$  at 190 K for the monoanionic form **1**<sup>-</sup>). Additional signals, especially for 2,2'-bipyridine anion radical ligands, were not observed down to 190 K. The fourth reduction to the dianionic complex **1**<sup>2-</sup>, on the other hand, produces a broad ( $\Delta H_{pp} = 1.45$  mT), featureless EPR signal at  $g = 1.9928$ .

The UV/vis absorption spectra of multiply reduced ligands (dm)dppz<sup>0/-/2-</sup> and of complexes **1**<sup>2+-n</sup> and **2**<sup>2+-n</sup> ( $n = 1-4$ ) were studied in DMF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. Series of spectra are shown in Figures 6 and 7; the maxima are summarized in Tables III and IV. Energies and transition probabilities were obtained by CNDO/S calculations for dppz and dppz<sup>2-</sup> (Table III). Methyl substitution at C(11), C(12) slightly shifts the transitions to longer wavelengths.

$\pi$  molecular orbital perturbation calculations based on the CNDO/S<sup>18</sup> and on the Hückel MO/McLachlan<sup>8</sup> approximations were carried out in order to obtain energies of low-lying unoccupied MOs of dppz (Figure 8) and the  $\pi$  spin populations of the singly occupied MO of dppz<sup>•-</sup> (Figure 9, Table II). Both methods show the same character of the orbitals as depicted in Figure 8. The perturbation involved a change of the Coulomb integral parameter  $h_N$  at the chelating nitrogen centers N(4), N(5) while the parameter  $h_N'$  of the 1,4-diazine nitrogen atoms N(9), N(14) was held constant at 0.5.

## Discussion

**Singly Reduced Forms of the Ligands.** The first reduction of dppz and dmdppz occurs at potentials which are close to that of

phenazine.<sup>4,5</sup> A cathodic shift of about 100 mV upon going from dppz to its 11,12-dimethyl derivative dmdppz supports the suggestion<sup>4</sup> that the added electron occupies an orbital  $b_1(\text{phz})$  localized at the phenazine moiety of the molecule. The EPR spectra of the anion radicals formed are dominated by a 1:2:3:2:1 quintet with about a 0.5-mT coupling constant for two equivalent <sup>14</sup>N nuclei (Figure 4), which is close to the <sup>14</sup>N hyperfine splitting of 0.515 mT for the phenazine anion radical proper.<sup>20a,b</sup> The <sup>14</sup>N coupling constants of 1,10-phenanthrolines<sup>8</sup> or 2,2'-bipyridines<sup>21</sup> and their complexes are generally smaller ( $< 0.4$  mT); the appearance of one large value  $a(^{14}\text{N}) > 0.5$  mT thus confirms the  $b_1(\text{phz})$  character of the singly occupied MO.

The remaining <sup>1</sup>H coupling parameters were determined from ENDOR spectra (Figure 4C); their tentative assignment in Table II is based on calculated HMO/McLachlan spin populations at  $h_N = h_N' = 0.5$  (Figure 9) and on the established hyperfine splittings of phenazine and quinoxaline anion radicals.<sup>20</sup> The largest proton coupling is readily assigned to positions 10 and 13 on the basis of HMO calculations (Figure 9) and previously noted effects of the decrease of  $\alpha(\text{peri})$  coupling after methyl substitution in the  $\beta$  position.<sup>20c</sup> The EPR splitting at positions 11 and 12 of dppz<sup>•-</sup> is virtually identical with the easily EPR- and ENDOR-identifiable CH<sub>3</sub> coupling of dmdppz<sup>•-</sup>. The other, smaller splittings can be safely assigned only after selective deuteration. While one proton coupling seems to be too small in (dm)dppz<sup>•-</sup> to be detected, the  $\alpha$ -diimine <sup>14</sup>N coupling was identified via optimization of computer-simulated ESR spectra (Figure 4B). The value of about 0.02 mT for N(4), N(5) in (dm)dppz<sup>•-</sup> confirms that the metal *can* interact with the  $b_1(\text{phz})$  orbital, if only to a rather low extent.

The one-electron reduction of (dm)dppz changes the absorption spectra in a distinct manner. Whereas the characteristically structured transitions (Figure 6) between 350 and 400 nm of the neutral forms are reduced in intensity, there are two new band systems: One is in the visible region with a maximum around 580 nm and some short-wavelength shoulders; the other is in the UV region at a maximum around 330 nm with a long-wavelength shoulder (Figure 6, Tables III and IV). While these new features resemble bands which are found in singly reduced phenazine (maxima at 551 and 375 nm)<sup>22</sup> or quinoxaline (maxima at 606 and 345 nm),<sup>22</sup> the spectra of the anion radicals of 2,2'-bipyridine with maxima around 585 and 398 nm (narrow, intense)<sup>22,23</sup> and of 1,10-phenanthroline (maxima at 657 and 388 nm)<sup>22</sup> look

- (20) (a) Henning, J. C. M. *J. Chem. Phys.* **1966**, *44*, 2139. (b) Eloranta, J.; Salo, E.; Mäkinen, S. *Acta Chem. Scand., Ser. A* **1980**, *34*, 427. (c) Kaim, W. *J. Chem. Soc., Perkin Trans.* **1984**, 1767. (d) For complexes, see: Kaim, W. *Chem. Ber.* **1982**, *115*, 910.  
 (21) Kaim, W. *Chem. Ber.* **1981**, *114*, 3789.  
 (22) Shida, T. *Electronic Absorption Spectra of Molecular Ions*; Elsevier: Amsterdam, 1988.  
 (23) Krejčík, M.; Vlček, A. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *313*, 243.

Table II. EPR/ENDOR Coupling Constants  $a$  (mT) and  $g$  Factors of Reduced Ligands and Complexes

radical	$g^a$	$a$						
		N(9,14)	H(10,13)	H(11,12)	H(2,7)	H(3,6)	N(4,5)	H(1,8)
dppz <sup>•-</sup> (calc) <sup>b</sup>		0.612	0.214	0.081	0.041	0.018	0.009	-0.014
dppz <sup>•-</sup> (calc) <sup>c</sup>		0.374	0.157	0.116	0.060	0.043	0.020	0.005
dppz <sup>•-d</sup>	2.003 21	0.505	0.183	0.143	0.094	0.056	0.021	<0.007
dppz <sup>•-e</sup>			0.184	0.143	0.095	0.055		<0.005
dmdppz <sup>•-</sup> (calc) <sup>c</sup>		0.365	0.135	0.154	0.062	0.041	0.020	0.005
dmdppz <sup>•-d</sup>	2.003 27	0.504	0.162	0.145 <sup>f</sup>	0.092	0.054	0.021	<0.006
dmdppz <sup>•-e</sup>			0.148	0.148 <sup>f</sup>	0.093	0.054		<0.005
[Ru(bpy) <sub>2</sub> (dppz)] <sup>•+</sup> (calc) <sup>g</sup>		0.587	0.200	0.076	0.069	-0.018	0.039	-0.036
[Ru(bpy) <sub>2</sub> (dppz)] <sup>•+d</sup>	2.003 36	0.48	0.13	0.07 <sup>h</sup>	0.07 <sup>h</sup>	0.07 <sup>h</sup>	0.07 <sup>h</sup>	<0.03
[Ru(bpy) <sub>2</sub> (dmdppz)] <sup>•+d</sup>	2.003 39	0.47	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>	<i>h</i>

<sup>a</sup>  $\pm 2 \times 10^{-3}$ . <sup>b</sup> From HMO/McLachlan calculation ( $\lambda = 1.2$ ,  $h_N = 0.5$ ,  $Q = 2.3$  mT;  $a = Q\rho_\pi$ ). <sup>c</sup> From CNDO/S calculation. <sup>d</sup> EPR data from simulation (293 K). <sup>e</sup> <sup>1</sup>H-ENDOR values (220 K). <sup>f</sup> Methyl protons. <sup>g</sup> From HMO/McLachlan perturbation of dppz<sup>•-</sup> ( $\lambda = 1.2$ ,  $h_{N(9,14)} = 0.5$ ,  $h_{N(4,5)} = 0.9$ ,  $Q = 2.3$  mT). <sup>h</sup> Insufficient resolution.

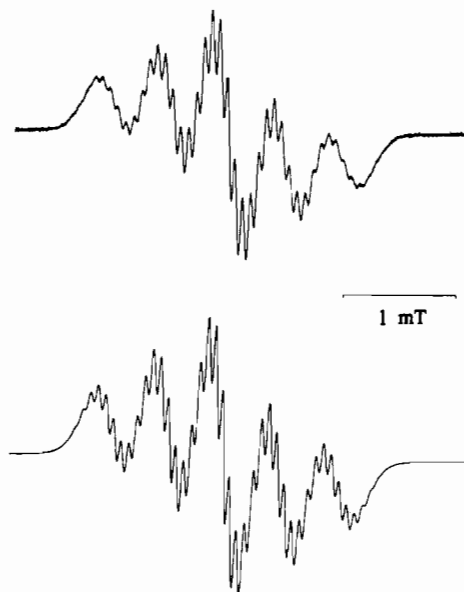


Figure 5. EPR spectrum of 1<sup>•+</sup> at 293 K, generated electrochemically in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (top), and computer simulation with the values from Table II and a line width of 0.072 mT (bottom).

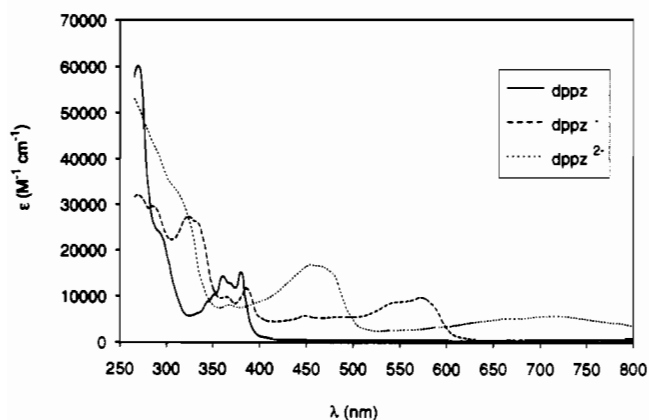


Figure 6. UV/vis spectra from spectroelectrochemistry of the ligand dppz in DMF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

distinctly different. Summarizing, the first electron added clearly enters the phenazine-based  $b_1$  orbital (Figure 8).

**Doubly Reduced Forms of the Ligands.** The approximately 0.8 V difference between the first and the second reduction wave is a typical value for 1,4-diazines.<sup>24</sup> It is therefore believed that the second added electron also occupies  $b_1$ (phz).

Spectroelectrochemically, the (dm)dppz<sup>2•-</sup> ions are distinguished by a very broad long-wavelength band with a maximum around

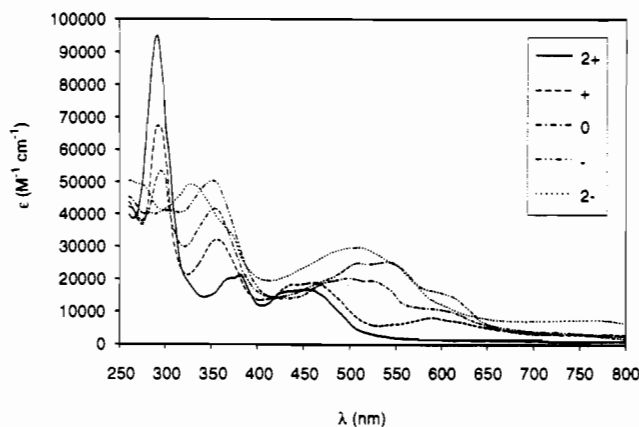
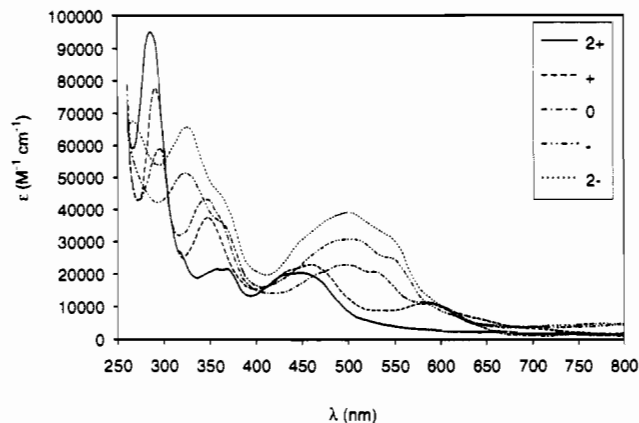


Figure 7. UV/vis spectra from spectroelectrochemistry of the complexes 1<sup>2•+</sup> (top) and 2<sup>2•+</sup> (bottom) in DMF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

710 nm, by a larger composite band with a flattened top centered at 460 nm, and by a shoulder at 315 nm (Figure 6). The original, characteristically structured bands for the HOMO-LUMO transition between 350 and 400 nm have expectedly disappeared on double occupation of the LUMO; the double-humped bands have shifted from about 580 nm in the anions to about 460 nm in the dianions. The high-energy shift and intensity increase of these bands suggest that they are due to transitions from the occupied  $b_1$ (phz) orbital to higher unoccupied molecular orbitals.

Reduction beyond the dianionic state of the ligands produced two waves with a combined intensity corresponding to about one electron in the dry electrolyte (Figure 1). The strong increase of these waves on addition of moisture suggests protonation of the highly basic trianions, either at the  $\alpha$ -diimine or at the 1,4-diazine site.

**Singly Oxidized Forms of the Complexes.** In acetonitrile/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, both complexes 1<sup>2•+</sup> and 2<sup>2•+</sup> are reversibly oxidized to Ru(III) species at +0.85 V vs Fc/Fc<sup>+</sup>, a potential close to that

(24) Cf.: Schultz, A.; Kaim, W. *Chem. Ber.* 1991, 124, 129.

Table III. UV/Vis Data for dppz,  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ , and Their Reduced Forms<sup>a</sup>

dppz	dppz <sup>-</sup>	dppz <sup>2-</sup>	dppz(calc)	dppz <sup>2-</sup> (calc)	$[\text{Ru}(\text{bpy})_2(\text{dppz})]^n$				
					$n = 2+$	$n = +$	$n = 0$	$n = -$	$n = 2-$
290 (sh)	287	287 (sh) 311 (sh)	284 ( <sup>1</sup> B <sub>1</sub> , w <sup>b</sup> ) 287 ( <sup>1</sup> A <sub>1</sub> )	303 ( <sup>1</sup> B <sub>1</sub> ) 306 ( <sup>1</sup> A <sub>1</sub> )	285 317 (sh)	289	295		
340 (sh)	322							325	321
350 (sh)	332 (sh)					347	347	342	
359			353 ( <sup>1</sup> B <sub>1</sub> )		357		360 (sh)	365 (sh)	360 (sh)
367 (sh)	363	367	367 ( <sup>1</sup> A <sub>1</sub> )		367				
379	384		379 ( <sup>1</sup> B <sub>2</sub> , w)						
	450	456		426 ( <sup>1</sup> B <sub>1</sub> )	435 (sh) 451	435 (sh) 456	460 (sh)		
	545	475 (sh)		496 ( <sup>1</sup> A <sub>1</sub> )			495 535	508 565	497 550 (sh)
	572					588	588	588 (sh)	
		719 (b <sup>c</sup> )				650 (b, sh)			≈800

<sup>a</sup> From spectroelectrochemistry. <sup>b</sup> Weak transition. <sup>c</sup> Broad band.

Table IV. UV/Vis Data for dmdppz,  $[\text{Ru}(\text{bpy})_2(\text{dmdppz})]^{2+}$ , and Their Reduced Forms<sup>a</sup>

dmdppz	dmdppz <sup>-</sup>	dmdppz <sup>2-</sup>	$[\text{Ru}(\text{bpy})_2(\text{dmdppz})]^n$					
			$n = 2+$	$n = +$	$n = 0$	$n = -$	$n = 2-$	
275	275 293		292	293	296	299		
300 (sh)	330 342 (sh)	300 (sh) 321 (sh)	319 (sh)			325 (sh) 342		330
344 (sh)								
352 (sh)				358	355			
360 (sh)								
369		369	368 (sh)		365 (sh)	362 (sh)		368 (sh)
379	374		381					
390	395		432 (sh)	430 (sh)				
	454 (sh)	465	460	465	477 (sh)			
	549 (sh)	484 (sh)			500	505		500
	586			594	535	545		545 (sh)
		706 (b <sup>b</sup> )			596	605 (sh)		780 (b)

<sup>a</sup> From spectroelectrochemistry. <sup>b</sup> Broad band.

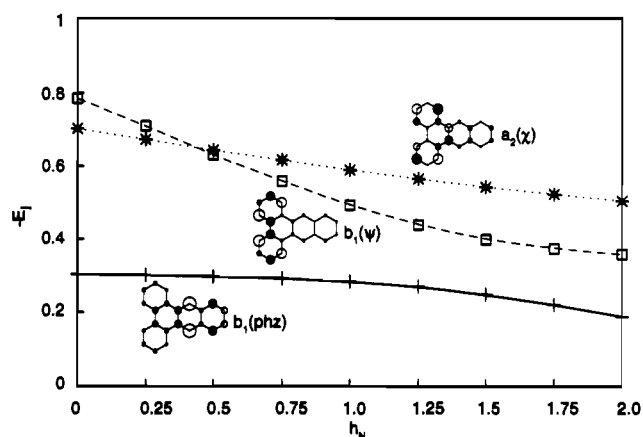


Figure 8. HMO energies of the three lowest unoccupied  $\pi$  molecular orbitals of dppz as a function of the Coulomb integral parameters  $h_N = h_{N(4),N(5)}$  ( $h_{N(9),N(14)} = 0.5$ ; all  $k_{CC} = k_{CN} = 1.0$ ). Graphical representation of squared MO coefficients  $c_E^2$  is given for all  $h_{N(4,5,9,14)} = 0.5$ .

of tris(bipyridine)ruthenium(II/III).<sup>3</sup> The result that dimethylation at C(11),C(12) leaves the oxidation potential completely unchanged (Table I) suggests very little electronic coupling between the phenazine moiety of (dm)dppz and the coordinating lone pairs of the nitrogen centers in the  $\alpha$ -diimine part.

**Singly Reduced Forms of the Complexes.** The first reduction of the complexes  $1^{2+}$  and  $2^{2+}$  occurs at potentials which are rather close (ca. 0.25 V) to those of the free ligands (Table I). In typical Ru(II) "polypyridine" complexes,<sup>3</sup> this reduction potential dif-

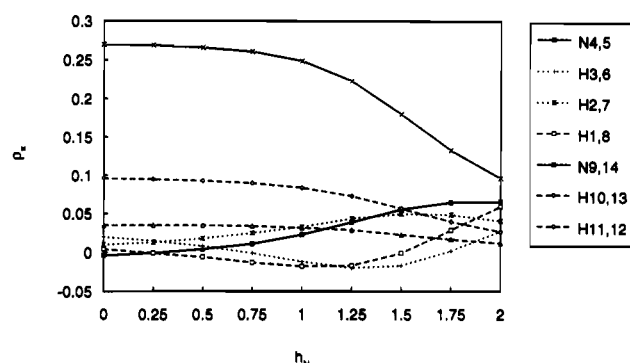


Figure 9. HMO/McLachlan  $\pi$  spin populations  $\rho_\pi$  of dppz<sup>-</sup> as a function of perturbation at N(4),N(5) (perturbation parameter  $h_N$ ;  $h_{N(9,14)} = 0.5$ ).

ference  ${}^1E(\text{complex}) = {}^1E(\text{ligand})$  is larger than 0.5 V.<sup>14,26</sup> We conclude<sup>5,25</sup> that the singly occupied molecular orbital (SOMO) has little contribution from the centers which bind the dipositive metal. The SOMO could then be either the  $b_1(\text{phz})$  or a metal-stabilized  $a_2(x)$  MO of the (dm)dppz ligand (Figure 8). However, the metal coordination should primarily stabilize  $b_1(\psi)$  with its large MO coefficients at the metal-coordinating centers N(4)

- (25) (a) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* 1987, 26, 415. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* 1990, 29, 1898.  
(26) (a) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* 1986, 108, 3578. (b) Ernst, S. D.; Kaim, W. *Inorg. Chem.* 1989, 28, 1520.

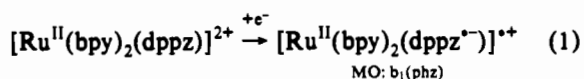
and N(5) (Figure 8). We thus believe that it is still the  $b_1(\text{phz})$  which is singly occupied in the complexes  $[\text{Ru}(\text{L})(\text{bpy})_2]^{2+}$ . Another argument from cyclic voltammetry concerns the difference in  $^1E$  between dppz and dm dppz complexes, which is of the same order of magnitude (0.1 V) as for the free ligands (Table I).

The same conclusion follows from the unusually good resolution of the EPR spectrum of  $1^{2+}$  (Figure 5). In most instances, the EPR spectra of singly reduced ruthenium(II) "polypyridine" complexes were found to be very poorly resolved or even totally featureless because of electron hopping<sup>27a</sup> or because of significant amounts of spin delocalization from the radical ligand to the metal and to coligands.<sup>27b</sup> In addition to the EPR line-broadening effects caused by the presence of a heavy-metal center, the resulting large number of small EPR coupling constants has been held responsible<sup>27b</sup> for extensive overlap of lines and poor overall resolution. Such effects should be minimal, however, if the unpaired electron is confined to a part of the radical ligand which is weakly coupled to the metal complex fragment.

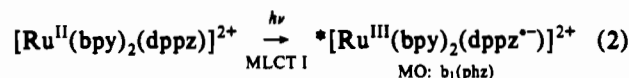
The very small interaction of the unpaired electron with ruthenium(II) ( $\xi \approx 1200 \text{ cm}^{-1}$ ) results in  $g$  factors of 2.003 36 ( $1^{2+}$ ) and 2.003 39 ( $2^{2+}$ ), which are very close to those for the free ligand radical anions (2.003 21 and 2.003 27, respectively). Most complexes  $(\text{L}^-)\text{Ru}(\text{L})(\text{bpy})_2$  have  $g$  factors deviating considerably from the  $g$  value of free  $\text{L}^-$ .<sup>27,28</sup> Although the EPR resolution for  $1^{2+}$  and  $2^{2+}$  does not allow a complete, unambiguous analysis (Figure 5), the N(9),N(14) hyperfine splittings could be easily determined and proved to be just slightly lower than the corresponding coupling constants of the ligand anion radicals (Table II). Thus, the relatively high EPR resolution and the good correspondence between ligand radical anions and their complexes with respect to  $g$  factors and to major coupling constants confirm that it is still the  $b_1(\text{phz})$  orbital which is occupied by the first electron in complexes of (dm)dppz.

Spectroelectrochemically, the singly reduced complexes  $1^{2+}$  and  $2^{2+}$  show intense bands at 590 and 350 nm which can be attributed to bound (dm)dppz<sup>•-</sup>. The bands at 460 and 430 nm are typical for  $\text{Ru}(\text{II}) \rightarrow \text{bpy}$  metal-to-ligand charge-transfer (MLCT) transitions<sup>3</sup> whereas the band at about 290 nm belongs to an internal transition of bound, nonreduced bpy.<sup>23</sup> These features and a structured band between 350 and 390 nm of neutral bound (dm)dppz are also found in the nonreduced complexes  $1^{2+}$  and  $2^{2+}$  (Figures 6 and 7, Tables III and IV).

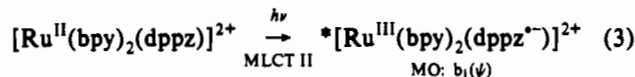
Previous work<sup>4,5</sup> has already touched upon the question which arises in the case of the singly reduced complexes described here. Specifically, the discrepancy between redox potential differences and transition energies at the absorption maxima led to the assumption that the redox and the "optical" orbitals may be different.<sup>5</sup> This conclusion is supported by the MO energy calculations and orbital characteristics (Figure 8): While  $b_1(\text{phz})$  is always the lowest unoccupied MO and as such available for the first two reductions (1), the  $\pi^*$  orbital with the highest



MO coefficients at the metal-coordinating centers N(4),N(5) is the slightly higher lying  $b_1(\psi)$ , the "bpy"-type  $\pi^*$  orbital. The term "optical" is misleading insofar as the (probably) lowest-energy MLCT transition (2) from ruthenium(II) to  $b_1(\text{phz})$  of dppz is also an optical process which, however, is not detectable in the absorption spectra because of very low intensity and overlap

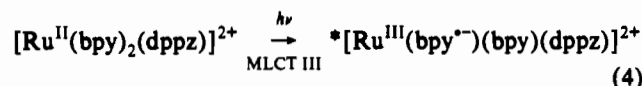


by the more intense MLCT II band (3). Small oscillator strength



for such a symmetry-allowed transition (2) indicates poor overlap at the metal/ligand "interface",<sup>26</sup> which is a result of the small MO coefficients at N(4),N(5) of  $b_1(\text{phz})$  (Figure 8).

The absorption spectrum of  $1^{2+}$ , formulated as (1), invites comparison with the excited-state absorption spectrum of  $^*[\text{L}^{2+}]$ , which was reported previously.<sup>5</sup> Of the bands at 558, 527, 430, and 385 nm, the last three occur at positions typical for  $^*[\text{Ru}(\text{bpy})_3]^{2+}$ ,<sup>5</sup> they can thus be associated with free (430 nm) or singly reduced bpy (385 and 527 nm),<sup>5,22,29</sup> as formed in the bpy-directed MLCT excitation process (4). The second band



above 500 nm in the excited-state absorption spectrum ( $\lambda_{\text{exc}}$  450 nm)<sup>5</sup> is then attributed to a transition to the  $b_1(\psi)$  orbital of bound dppz<sup>•-</sup> as formulated in the MLCT process (3). Since the MLCT bands for both major transitions (3) and (4) are closely spaced at 435 and 460 nm, the excitation at 450 nm<sup>5</sup> should give rise to absorption spectra of bound  $\text{bpy}^{\bullet-}$  and dppz<sup>•-</sup> ligands.

**Doubly Reduced Forms of the Complexes.** The alternative here is to put the second electron into the  $b_1(\text{phz})$   $\pi$  MO of dppz or into the lowest lying  $\pi^*$  orbital of one of the bpy coligands. The small potential differences of only 0.4 V between the first two reduction waves may be taken as a first argument against the former alternative; however, metal/ligand orbital mixing sometimes causes a distinct reduction of such potential differences in the complexes relative to the free ligands.<sup>28</sup> But the fact that the potential for the second reduction is not at all affected by the methylation at C(11),C(12) clearly points to a 2,2'-bipyridine ligand as site of the second reduction process. The absolute values of  $^1E$  are less negative than corresponding potentials<sup>26b,30</sup> for other  $\alpha$ -diimine complexes  $[\text{Ru}(\text{L})(\text{bpy})_2]^{2+}$ ; they are also rather close to  $^1E$  of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Both results indicate a very small interaction in the neutral complexes between the two single electrons, one on a bpy ligand and the other on the remote 1,4-diazine part of (dm)dppz<sup>•-</sup>.

UV/vis spectra of the neutral forms show bands at 590 and 350 nm, attributed to (dm)dppz<sup>•-</sup>, and a decreased internal ( $\pi \rightarrow \pi^*$ ) bpy transition at 295 nm.  $\text{Ru}(\text{II}) \rightarrow \text{bpy}$  transitions are only visible in the form of a shoulder around 460 nm because there are new bands with maxima at 535 and 500 nm, which are typical for the bpy anion radical.<sup>14,22</sup> The increase in the 340–350-nm band is also attributed to  $\text{Ru}(\text{II})$ -bound singly reduced 2,2'-bipyridine;<sup>14</sup> the expected but often very weak  $\text{bpy}^{\bullet-}$  transitions around 800 nm with their characteristic vibrational structure<sup>22,31</sup> were not detectable in this case. The UV/vis spectroelectrochemical results clearly suggest a localized description  $\text{Ru}(\text{L}^-)(\text{bpy}^{\bullet-})(\text{bpy})$ ,  $\text{L} = (\text{dm})\text{dppz}$ , for the neutral state.

The EPR results (Table II) for the doubly reduced form 1 with its even number of electrons are less conclusive: While a spectrum virtually identical to that of the singly reduced complex  $1^{2+}$  can be observed with reduced intensity, there was no signal detectable

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from a coordinated bpy anion radical down to 190 K. The presence of equivalent bpy and  $\text{bpy}^{\cdot-}$  in the complex allows electron hopping between these two intermediately coupled sites on the EPR time scale; considerable broadening is the usual consequence.<sup>27</sup> The broadened EPR signal from  $\text{bpy}^{\cdot-}$  should become even less detectable if an additional weak spin-spin interaction between the  $\text{bpy}^{\cdot-}/\text{bpy}$  system and the  $\text{dppz}^{\cdot-}$  radical ligand leads to a temperature-dependent reduction of EPR signal intensity as observed for the still well-resolved signal of coordinated  $\text{dppz}^{\cdot-}$ . The similarity of the hyperfine splitting pattern of singly, doubly, and triply (cf. below) reduced complexes is not unexpected, considering that free and metal-coordinated  $\text{dppz}^{\cdot-}$  have very similar spin distribution. The effect of the reduction of metal-bound bpy ligands is apparently too small to change the spin distribution perceptibly, the only effect being the reduction of signal intensity because of weak spin-spin interaction.

**Triply Reduced Forms of the Complexes.** The differences of about 0.16 V between the potentials for second and third reductions of the complexes are typical for consecutive electron uptake by two equivalent Ru(II)-bound bpy ligands and are attributed to Coulombic repulsion.<sup>3,14,26b,32</sup> The absolute values are virtually independent of methylation at positions 11 and 12 of the dppz ligand. UV/vis spectroelectrochemistry still reveals the  $\approx 590$ - and  $\approx 340$ -nm bands of  $(\text{dm})\text{dppz}^{\cdot-}$  and the (increased)  $\approx 550$ -,  $\approx 500$ -, and 325-nm features of coordinated  $\text{bpy}^{\cdot-}$ . The band at 290 nm, assigned to an intraligand transition of nonreduced bpy, has disappeared (Figures 6 and 7). An obvious formulation for the anion is thus  $[\text{Ru}^{\text{II}}(\text{L}^{\cdot-})(\text{bpy}^{\cdot-})_2]^-$ .

The EPR signal from this odd-electron species  $1^-$  is identical to the spectrum of the singly reduced from  $1^{+}$ , albeit at distinctly lower intensity. Additional signals from the two singly reduced 2,2'-bipyridine ligands are not observed down to 190 K. The reduction of intensity of the  $\text{dppz}^{\cdot-}$  EPR spectrum and the assumed broadening of the  $\text{bpy}^{\cdot-}$  signals are interpreted as a consequence of asymmetric three-center spin-spin coupling in which two  $\text{bpy}^{\cdot-}$  ligands in the anionic complex  $1^-$  affect the  $\text{dppz}^{\cdot-}$  ligand more than one coligated  $\text{bpy}^{\cdot-}$  in the neutral species  $1$ .

**Quadruply Reduced Forms of the Complexes.** The fourth one-electron reduction wave is dependent on the non-bpy ligand; i.e., the potential is about 0.1 V more negative for the complex of the more electron-rich  $\text{dm}\text{dppz}$  system (Table I). The potentials are also very sensitive to the moisture content of the solvent (Figure 2). The slight anodic shift of ca. 50 mV after what is assumed to be a rapid protonation by traces of water can be related to a considerably increased charge at the basic,  $\text{H}^+$ -accessible (see Figure 10) nitrogen sites N(9),N(14) in a doubly reduced  $(\text{dm})\text{dppz}$  ligand. The reversible protonation of  $\pi$ -electron-deficient heterocycles is known to cause anodic shifts of the reduction potential.<sup>33,34</sup> Another line of evidence for a formulation  $[\text{Ru}^{\text{II}}(\text{L}^{2-})(\text{bpy}^{\cdot-})_2]^{2-}$  comes from the difference of about 0.9 V between  $^1E$  and  $^4E$  which is the typical difference between first and second reduction of a 1,4-diazine<sup>9,24</sup> (cf. the free ligands, Table I).

In the UV/vis spectra of the highly reduced states  $1^{2-}$  and  $2^{2-}$ , there are intense bands with maxima at 500 and 325 nm and a weak broad band extending beyond 800 nm; all three features have been observed similarly for the doubly reduced free ligands (Figure 6 and 7). Bands due to  $\text{bpy}^{\cdot-}$  are visible at 340 nm and appear together with the 500-nm transition of  $(\text{dm})\text{dppz}^{2-}$  between 500 and 550 nm. The prominent peaks at 590 and 355 nm of  $(\text{dm})\text{dppz}^{\cdot-}$  have disappeared in the dianionic complexes.

In spite of its even electron count, the dianionic complex  $[\text{Ru}^{\text{II}}(\text{dppz}^{2-})(\text{bpy}^{\cdot-})_2]^{2-}$  exhibits an EPR signal. The spectrum is very different from that of Ru-coordinated  $\text{dppz}^{\cdot-}$ ; both the

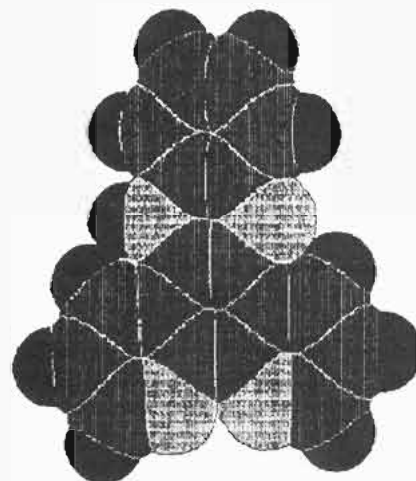


Figure 10. Space-filling model of monoprotated dppz, calculated with standard bond parameters.

broadness of the featureless line and the low  $g$  factor of 1.9928 are fully compatible with Ru(II)-bound  $\text{bpy}^{\cdot-}$ .<sup>27</sup> Apparently, the EPR signal is not significantly affected by spin-spin coupling<sup>27a</sup> between two  $\text{bpy}^{\cdot-}$  ligands in such a complex; the broadening interaction with the anion radical  $\text{dppz}^{\cdot-}$  is now no longer effective.

**Higher Reduced States of the Complexes.** Whereas spectroscopic techniques could be used to interpret the first four reduced forms, the higher reduced species proved to be too reactive for such measurements. In very dry DMF at 200 K, both complexes are reduced at  $-2.72$  V to the trianions, followed by further reversible reduction steps to the tetra- and pentaanions at about  $-2.90$  and  $-3.25$  V, respectively (Figure 3). Controlled addition of moisture results in the emergence of alternative, anodically shifted waves for  $^nE$  (Figure 2), which are attributed to N(9),N(14)-protonated species. Formation of such 1,4-dihydro-1,4-diazine structures is supported by the established strong tendency of singly<sup>20c,35</sup> and especially of doubly reduced 1,4-diazines<sup>9,34</sup> to add protons to the highly charged nitrogen centers. In contrast to the triply reduced free ligands, the highly reduced complexes offer only the 1,4-diazine site for protonation; the result is a straightforward cyclic voltammetric behavior where one signal grows at the expense of the other on addition of water.

This aspect relates to the "light switch" function because, structurally, the  $(\text{dm})\text{dppz}$  molecules are distinguished by a partially impeded access of electrophiles to the potentially basic centers N(9) and N(14). The space-filling model of  $\text{dppzH}^+$  (Figure 10), which is based on standard bond parameters, illustrates this. As long as the molecule is essentially planar, the space occupation by H(8) and the peri-hydrogen H(10) allows only rather small electrophiles such as  $\text{H}^+$  to squeeze in and coordinate to N(9) (Figure 10). Proton quenching of MLCT luminescence is no longer possible if additional hydrophobic interactions around N(9) and N(14) prevent the access of  $\text{H}^+$ .

Starting from the dianion  $[\text{Ru}^{\text{II}}(\text{L}^{2-})(\text{bpy}^{\cdot-})_2]^{2-}$ , there are two alternatives for the next electron uptake: One interpretation (i) involves the triply reduced  $(\text{dm})\text{bpy}$  ligand and two singly reduced bpy molecules. Such a possibility is suggested by the less negative value of  $^5E$  when compared to corresponding values for other complexes  $[\text{Ru}(\text{L})(\text{bpy})_2]^{n+}$ ,<sup>14,30</sup> however, this effect could also be attributed to the rather small interaction between reduced bpy and "remotely" reduced  $(\text{dm})\text{dppz}$ . Another argument for (i) would be the sensitivity of this step toward water, which may be expected from a trianionic  $(\text{dm})\text{dppz}$  ligands (cf. the noncoordinated ligands). In any case, however, the fifth electron cannot enter a phenazine-based MO since  $b_1(\text{phz})$  is doubly occupied and  $b_1(\psi)$  (or  $a_2(\chi)$ ) has little contribution from N(9),N(14) (Figure 8). Furthermore,  $^4E$  already exhibits a moisture effect,

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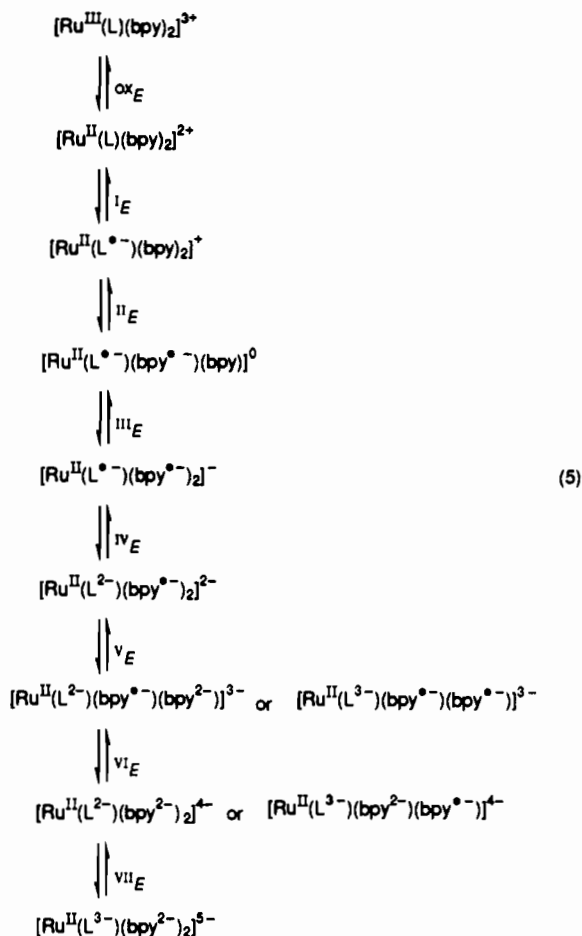


albeit to a lower extent. The fact that  ${}^{\vee}E$  is identical for both complexes at  $-2.27$  V is compatible both with an electron uptake into the  $b_1(\psi)$  orbital of (then trianionic) (dm)dppz and with formation of one bpy dianion.

This second alternative (ii), the further reduction of coordinated  $\text{bpy}^{\cdot-}$  ligands to  $\text{bpy}^{2-}$  at potentials  ${}^{\vee}E$  and  ${}^{\vee\text{I}}E$ , is strongly suggested by the pattern of reduction potentials. In particular, the small difference of about 0.16 V between  ${}^{\vee}E$  and  ${}^{\vee\text{I}}E$  is typical for consecutive reductions of two coordinated bpy ligands (cf. the differences  ${}^{\text{II}}E - {}^{\text{III}}E$ ;<sup>3,14,26,27a,28,30,32</sup> furthermore, the differences  ${}^{\text{IV}}E - {}^{\vee}E$  are similar to  ${}^{\text{I}}E - {}^{\text{II}}E$ . This parallelism would also suggest that the fifth and higher reduction steps correspond to localized processes as described comprehensively in (5). An argument against this alternative (ii) is that the potentials for the (irreversible) third (dm)dppz reduction in the free ligands ( ${}^{\text{III}}E$ ) and in the complexes ( ${}^{\vee\text{II}}E$ ) are similar; however, the binding of the dinegative complex fragment  $[\text{Ru}^{\text{II}}(\text{bpy}^{2-})_2]^{2-}$  to  $\text{L}^{2-}$  should hardly facilitate the further reduction of  $\text{L}^{2-}$  relative to the free-ligand situation.

**Summary.** Using a combined electrochemical, spectroscopic, and calculational approach, we have established that the dipyrido[3,2-*a*:2',3'-*c*]phenazine  $\pi$  system is distinguished by exhibiting three relatively low lying unoccupied molecular orbitals. The lowest-lying MO  $b_1(\text{phz})$  is localized in the phenazine section of the molecule. Occupation of this MO via multiple reduction or via a corresponding MLCT process (2) leads to the possibility of electrophilic addition at the then rather basic sites N(9),N(14); however, the special steric situation (Figure 10) allows primarily the access of protons as electrophiles. This selectivity for emission-quenching  $\text{H}^+$ <sup>3,36</sup> in an already partially hydrophobic heteroaromatic pocket is crucial for the "light switch" behavior<sup>6,7</sup> of the ruthenium complex  $1^{2+}$ , i.e. for the absence of water-induced luminescence quenching in hydrophobic microenvironments.

While electrochemical reduction of complexes  $1^{2+}$  and  $2^{2+}$  leads to the occupation of the second lowest  $\pi^*$  MO of (dm)dppz only at extremely negative potentials, the intense long-wavelength charge-transfer band of the dicationic complexes has to be assigned as  $d(\text{Ru}) \rightarrow b_1(\psi)$  (eq 3). Both the transitions to  $b_1(\text{phz})$  at lower energy and  $a_2(\chi)$ , presumably at higher energy, should have very little intensity due to their small orbital coefficients at the metal-



coordinating centers N(4),N(5). EPR spectroscopy has illustrated the weak but still existing intramolecular coupling between the charged, light-absorbing ruthenium tris chelate moiety and the partially hydrophobic, potentially intercalating quenching sites N(9),N(14) of the title complex.

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