Notes

Dipyrido[4,3-*b*;5,6-*b*]acridine Derivatives and Their Ruthenium(II) Complexes

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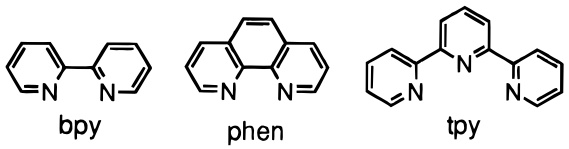
Introduction

Two of the most common bidentate chelating ligands employed in coordination chemistry are 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen).[2] The latter may be considered



as a 3,3′-etheno-bridged derivative of the former. The steric requirements of both ligands are very similar, and differences in the properties of their metal complexes may be mostly attributed to electronic differences arising from the greater electronegativity of phen. The next higher homologue of bpy is 2,2′;6,2″-terpyridine (tpy), which behaves as a tridentate chelator but enjoys many of the same coordination properties as bpy. The coordination chemistry of the analogous 3,3′-etheno-bridged derivatives of tpy has not yet been explored. This report will present the preparation and properties of these derivatives and their complexation with Ru(II).

Experimental Section

Nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million downfield from Me_4Si.[3] Electronic spectra were obtained on a Perkin-Elmer 330 spectrophotometer. Low-temperature emission spectra and luminescence lifetimes were obtained according to a method described previously.[4] Cyclic voltammograms were recorded using a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder according to a procedure described previously.[5] All solvents were freshly distilled reagent grade, and all melting points are uncorrected.

Literature procedures were followed for the preparation of 8-amino-7-quinolinecarbaldehyde,[6] 5,6,7,8-tetrahydroquinol-8-one,[7] 1,2,7,8-tetrahydrodipyrido[4,3-*b*;5,6-*b*]acridine (**1**),[8] and $[Ru(\mathbf{1})_2](PF_6)_2$.[9]

1,2-Dihydrodipyrido[4,3-*b*;5,6-*b*]acridine (2). A mixture of 8-amino-7-quinolinecarbaldehyde (0.172 g, 1 mmol), 5,6,7,8-tetrahydroquinol-8-one (0.147 g, 1 mmol), and saturated ethanolic KOH (0.5 mL) in absolute ethanol (15 mL) was heated at reflux under Ar for 15 h. After cooling, water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave a crude material which was purified by chromatography on alumina, eluting with MeOH−EtOAc (1:4) to give, after recrystallization from $CHCl_3$−ether, 1,2-dihydrodipyrido[4,3-*b*;5,6-*b*]acridine (0.26 g, 92%): mp > 300 °C; ^{1}H NMR ($CDCl_3$) reported in Table 1; ^{13}C NMR ($CDCl_3$) δ 151.3, 149.6, 148.7, 148.6, 146.1, 144.8, 136.6, 136.4, 136.3, 134.8, 133.5, 128.6, 128.5, 126.9, 126.0, 124.1, 124.9, 27.5, 27.3; IR ($CHCl_3$) 1650, 1530, 1510, 1455, 1400, 1380, 950, 850 cm^{-1}.

Dipyrido[4,3-*b*;5,6-*b*]acridine (3). A mixture of **2** (190 mg, 0.67 mmol) and 10% Pd/C (90 mg) in freshly distilled nitrobenzene (8 mL) was heated at 150−170 °C for 2 h. After cooling, the reaction mixture was chromatographed on alumina (20 g), eluting with EtOAc followed by MeOH/EtOAc (1:3). The reddish material thus obtained was further purified by recrystallization from CH_2Cl_2/Et_2O (1:20) to provide 151 mg (80%) of **3**: mp 257−258 °C (lit.[10] mp 258 °C); ^{1}H NMR ($CDCl_3$) reported in Table 1; ^{13}C NMR ($CDCl_3$) δ 149.5, 146.0, 145.0, 137.2, 136.1, 129.7, 128.1, 127.3, 127.1, 124.4.

$[Ru(2)_2](PF_6)_2$. A mixture of **2** (0.35 g, 1.2 mmol) and $RuCl_3 \cdot 3H_2O$ (0.13 g, 0.5 mmol) in ethanol/H_2O (1:1, 10 mL) was heated under argon at reflux for 18 h. After cooling, the solid was removed by filtration and NH_4PF_6 (0.37 g, 2 mmol) in water (2 mL) was added to precipitate the complex. Filtration gave a crude material which was chromatographed on alumina, eluting with CH_3CN. After recrystallization from CH_3CN/toluene (1:1), the complex was obtained as an orange-red solid (0.44 g, 85%): mp > 300 °C; ^{1}H NMR ($CDCl_3$) reported in Table 1; ^{13}C NMR (CD_3CN) δ 156.3, 156.0, 153.2, 153.0, 151.1, 145.8, 139.0, 138.3, 137.4, 136.5, 131.5, 131.4, 131.4, 129.7, 128.4, 128.1, 126.4, 27.2, 26.2; IR (KBr) 1540, 1380, 1350, 1200, 1170, 880, 820 cm^{-1}. Anal. Calcd for $C_{38}H_{26}F_{12}N_6P_2Ru \cdot H_2O$: C, 46.77; H, 2.87; N, 8.61. Found: C, 46.40; H, 2.85; N, 8.55.

$[Ru(3)_2](PF_6)_2$. A mixture of **3** (45 mg, 0.16 mmol) and $RuCl_3 \cdot 3H_2O$ (14 mg, 0.058 mmol) in EtOH/H_2O (1:1, 4 mL) was treated as described for **2**. The resulting complex was purified by chromatography on 15 g of Al_2O_3, eluting with CH_3CN/toluene (1:1). The complex was obtained as a red solid (45 mg, 81%): mp >300 °C; ^{1}H NMR ($CDCl_3$) reported in Table 1; IR (KBr) 1540, 1370, 1210, 1090, 900, 830 cm^{-1}. Anal. Calcd for $C_{38}H_{22}F_{12}N_6P_2Ru$: C, 47.85; H, 2.31; N, 8.81. Found: C, 47.33; H, 2.47; N, 9.09.

Synthesis

The target ligands are all derivatives of dipyrido[4,3-*b*;5,6-*b*]acridine (**3**) that possess varying degrees of unsaturation in the two fused benzo rings. The tetrahydro derivative **1** was previously described.[8]

The dihydro derivative **2** was prepared from the Friedländer condensation of 8-amino-7-quinolinecarbaldehyde (**4**) with 5,6,7,8-tetrahydro-8-quinolone (**5**). We recently developed a convenient preparation for **4** that allows facile access to a variety of 1,10-phenanthroline derivatives.[6]

(1) (a) University of Houston. (b) Tulane University
(2) (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: San Diego, CA, 1992. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(3) The NMR atom-numbering scheme designates the quinoline nitrogen as atom 1, and each successive nonbridgehead carbon atom on the periphery of the molecule is then numbered sequentially proceeding away from the bay region of the molecule. Atoms identical by symmetry are designated only once.
(4) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117.
(5) Goulle, V.; Thummel, R. P. *Inorg. Chem.* **1990**, *29*, 1767.
(6) (a) Hung, C.-Y.; Wang,T.-L.; Shi, Z.; Thummel, R. P. *Tetrahedron* **1994**, *50*, 10685. (b) Riesgo, E.; Jin, X.; Thummel, R. P. *J. Org. Chem.* **1996**, *61*, 3017.
(7) Thummel, R. P.; Lefoulon, F.; Cantu, D.; Mahadevan, R. *J. Org. Chem.* **1985**, *50*, 3824.
(8) Thummel, R. P.; Jahng, Y. *J. Org. Chem.* **1985**, *50*, 2407.
(9) Thummel, R. P.; Jahng, Y. *Inorg. Chem.* **1986**, *25*, 2527.

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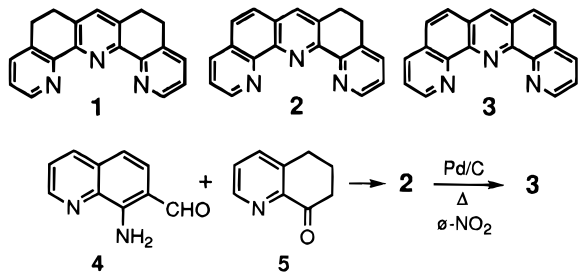


The parent compound **3** was previously prepared in 16% yield by a double Skraup reaction with 4,5-diaminoacridine.[10] Considerable difficulties were reported in the ultimate preparation of this material. With **2** in hand, we hoped that simple dehydrogenation would afford **3**. Normally such a conversion can be readily effected with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); however, DDQ treatment of **2** led to none of the expected product. Similarly, catalytic dehydrogenation with palladium on charcoal was ineffective unless the reaction was run in nitrobenzene.[11] Besides acting as a polar, high-boiling solvent, nitrobenzene permitted a disproportionation to occur, providing an 80% yield of **3** along with a corresponding amount of aniline.

The ruthenium(II) complexes of **1**−**3** were prepared in the normal fashion by heating 2 equiv of ligand with $RuCl_3 \cdot 3H_2O$ in aqueous ethanol. These complexes were precipitated as their hexafluorophosphate salts and unambiguously identified by ^1H and ^{13}C NMR.

Properties

The ^1H NMR chemical shift data for the ligands and their Ru(II) complexes are presented in Table 1. Ligand **2** may be considered as having a saturated half which corresponds to ligand **1** and an unsaturated half which corresponds to ligand **3**. The chemical shift data for corresponding protons on these three molecules are very consistent with a variation of ≤0.07 ppm for all aromatic protons. The central proton H7 is most sensitive to the increasing unsaturation, and its chemical shift moves downfield by 0.58 ppm as one progresses both from **1** to **2** and from **2** to **3**.

Table 1. ^1H NMR Chemical Shift Data[a] for Dipyridoacridine Ligands and Their Ru(II) Complexes[b,c]

cmpd	H2	H3	H4	H5/H6	H7	H8/H9	H10	H11	H12
1					7.44	3.01	7.56	7.23	8.72
2	9.13	7.60	8.22	7.72	8.02	3.19/3.06	7.60	7.28	8.75
3	9.10	7.64	8.16	7.79/7.64	8.60				
$[Ru(\mathbf{1})_2]^{2+}$					7.83	3.49/3.38	7.62	7.03	7.17
$[Ru(\mathbf{2})_2]^{2+}$	7.56	7.27	8.35	8.37/8.17	8.59	3.74/3.49	7.67	6.97	7.12
$[Ru(\mathbf{3})_2]^{2+}$	7.48	7.25	8.41	8.65/8.27	9.44				

[a] Reported in ppm downfield from internal Me_4Si; ligands measured in $CDCl_3$ and complexes in CD_3CN. [b] For NMR numbering scheme, see ref 3. Protons which are equivalent by symmetry have been omitted for clarity. [c] Values for **1** are taken from ref 8 and values for $[Ru(\mathbf{1})_2]^{2+}$ are taken from ref 9.

The complexes of **1**−**3** show chemical shift changes which reflect both the electronegativity of the attached carbon and local anisotropic effects. The protons *ortho* and *meta* to the chelating nitrogen shift upfield, and the *para* proton shifts downfield. The largest effect is for the *ortho* proton so that H2 and H12 for $[Ru(\mathbf{1})_2]^{2+}$ shift upfield by 1.55 ppm while for $[Ru(\mathbf{3})_2]^{2+}$ these same protons shift upfield by 1.62 ppm. For $[Ru(\mathbf{2})_2]^{2+}$ the shifts are 1.57 and 1.63 ppm for the comparable protons. This large shift results from these protons being held over the shielding face of the central pyridine ring of the orthogonal ligand. In the complexes, the central proton H7 is once again diagnostic of the increasing delocalization of the system, shifting downfield by 0.76 ppm in going from $[Ru(\mathbf{1})_2]^{2+}$ to $[Ru(\mathbf{2})_2]^{2+}$ and 0.85 ppm in going from $[Ru(\mathbf{2})_2]^{2+}$ to $[Ru(\mathbf{3})_2]^{2+}$.

Table 2. Half-Wave Potentials for Dipyridoacridine Ligands and Their Ru(II) Complexes[a]

cmpd	$E_{1/2}$(oxidn)	$E_{1/2}$(redn)	
1		−2.11[b]	
2		−1.89[b]	
3		−1.65[b]	
$[Ru(\mathbf{1})_2]^{2+}$	1.2 l (80)	−1.35 (80)	−1.63 (120)
$[Ru(\mathbf{2})_2]^{2+}$	1.28 (60)	−1.11 (100)	−1.34 (110)
$Ru(\mathbf{3})_2]^{2+}$	1.35 (100)	−0.94 (100)	−1.12[b]
$[Ru(tpy)_2]^{2+}$	1.27 (60)	−1.27 (60)	−1.51 (67)

[a] Potentials are in volts vs SCE for acetonitrile solutions, 0.1 M in TBAP, recorded at 25 ± 1 °C at a sweep rate of 200 mV/s. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses. [b] Irreversible; potential is given for the cathodic wave.

The electrochemical half-wave potentials for the ligands and their Ru(II) complexes were measured in acetonitrile, and the data are presented in Table 2. For the ligands, the observed changes occur in regular increments, shifting toward more positive potential with increasing delocalization of the ligand. The reduction potential increases by +0.22 V in going from **1** to **2** and by +0.24 V in going from **2** to **3**. The first and second reduction potentials for the corresponding complexes increase by approximately the same amounts. The oxidation potential corresponds to the removal of an electron from a metal t_{2g} orbital and hence is less sensitive to the nature of the ligand; nevertheless, an increment of +0.07 V is observed as one proceeds along the series of complexes of **1**−**3**.

Table 3 records the electronic absorption and luminescence data for the ligands and their Ru(II) complexes. The complexes show a steadily increasing bathochromic shift for their longest wavelength absorption as the ligand varies from **1** to **3** (see Figure 1). The change is +22 nm in going both from **1** to **2** and from **2** to **3**, and a relatively steady increase in intensity is associated with this progression. The long-wavelength absorption of such complexes is normally assigned to a metal-to-ligand charge transfer (MLCT) from a metal t_{2g} orbital to a ligand π^* orbital. In this series of complexes, the change in energy of the MLCT transition is influenced by two competing factors. The relative energies of the metal dπ levels are reflected by the oxidation potentials of the complexes. The observed increase in these oxidation potentials from +1.21 to +1.35 V indicates that the dπ levels are stabilized in going from complex **1** to complex **3**. In the absence of changes in the ligand π^* levels, this lowering of the dπ levels would result in an increase in the energy of the MLCT transition between complexes **1** and **3**. The controlling factor in this series, however, is the stabilization of the ligand π^* levels which occurs as the degree of unsaturation increases. This stabilization is likewise indicated by the increasing ease of reduction of the complexes from −1.35 to −0.94 V. There is now a significant body of evidence which correlates the absorption maxima for MLCT transitions with the difference between the first oxidation and first reduction potentials for a series of similar complexes.[12−14] While the

(10) Koft, E.; Case, F. H. *J. Org. Chem.* **1962**, *27*, 865.
(11) Braude, E. A.; Linstead, R. P.; Wooldrige, K. R. H. *J. Chem. Soc.* **1954**, 3586.
(12) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(13) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg.Chem.* **1983**, *22*, 1617.

Table 3. Electronic Absorption and Luminescence Data for Dipyridoacridine Ligands and Their Ru(II) Complexes

cmpd	absorption[a] λ_{max} nm (ϵ)				emission λ_{max} nm	lifetime, μs
1	243 (21 500)	298 (10 300)	328 (16 500)	340 (18 500)	424[b]	
2	269 (18 500)	304 (25 500)	339 (11 900)	358 (12 400)	423[b]	
3	243 (16 500)	303 (35 700)	340 (3800)	350 (3200)	422[b]	
$[Ru(\mathbf{1})_2]^{2+}$	312 (47 100)	360 (41 300)	478 (14 100)		650[c]	8.6
$[Ru(\mathbf{2})_2]^{2+}$	300 (52 200)	350 (55 100)	500 (15 400)		655[c]	9.3
$[Ru(\mathbf{3})_2]^{2+}$	306 (133 500)	455 (9 600)	522 (17 800)		701[c]	17.6
$[Ru(\mathbf{6})_2]^{2+}$	293 (71 400)	335 (41 400)	498 (13 900)		656[c]	
$[Ru(tpy)_2]^{2+}$	310 (71 600)	330 (32 900)	475 (16 200)		598[c]	

[a] Recorded in CH_3CN. [b] Approxately 1.2×10^{-4} M CH_2Cl_2 with excitation at 300 nm. [c] Recorded in EtOH/MeOH (4:1) at 77 K with excitation at the long wavelength absorption maximum.

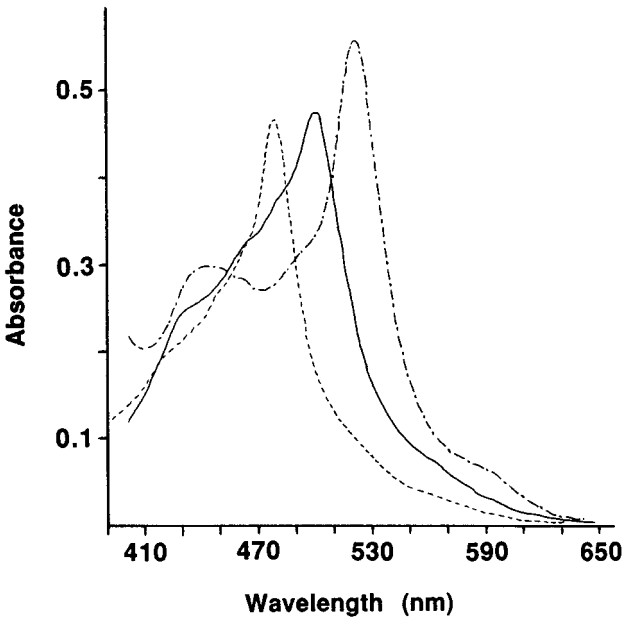
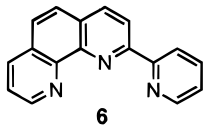


Figure 1. Electronic absorption spectra of dipyridoacridine Ru(II) complexes in CH_3CN: 3.25×10^{-5} M $[Ru(\mathbf{1})_2]^{2+}$, - - -; 3.07×10^{-5} M $[Ru(\mathbf{2})_2]^{2+}$, —; 3.11×10^{-5} M $[Ru(\mathbf{3})_2]^{2+}$, —•—.

correlation holds for this series, the exact nature of the three excited states is likely to differ substantially since the electron density distribution in the MLCT state should vary considerably for **1**−**3**. Ligands **1** and **3** have relatively high symmetry (both C_{2v}), while ligand **2** lacks symmetry about the central pyridine (C_s). As a result, the MLCT state of $[Ru(\mathbf{2})_2]^{2+}$ should be more localized on the unsaturated side of ligand **2**, while the other two complexes are likely to have a more uniform electron density distribution on ligands **1** and **3** in the MLCT state.

It is well-known that, while Ru(II) complexes of bpy are strongly luminescent and have long excited state lifetimes in solution at room-temperature, the structurally related tpy complexes exhibit virtually no luminescence in room temperature solution and have very short lifetimes. The absence of luminescence in the tpy complexes is believed to be related to the presence of ligand field (metal centered) excited states which have nearly the same energy as the emitting MLCT state.[15] A postulate of the present work was that, upon increasing the delocalization of the coordinating tpy derivative, the ligand π^* energy levels would be lowered without significantly affecting the ligand field and the energetic separation between the MLCT and LF states would increase, making luminescence more readily observable from the MLCT state. In fact, none of the Ru(II) complexes of ligands **1**−**3** exhibit significant luminescence in room-temperature solution. The 77 K luminescence maxima and lifetimes for the complexes are reported in Table 3. A peculiar observation is that the emission maxima for the complexes of **1** and **2** occur at nearly the same energy and have very similar vibronic band shapes. It is noteworthy that the MLCT absorption maximum of $[Ru(\mathbf{1})_2]^{2+}$ (478 nm) is nearly the same as that for $[Ru(tpy)_2]^{2+}$ (474 nm). If the absorption spectra in the matrix maintain this similarity, this suggests that the potential surface of the ^{3}MLCT state of $[Ru(\mathbf{1})_2]^{2+}$ is more distorted relative to the ground state than would be the case for $[Ru(tpy)_2]^{2+}$, thereby resulting in a lower energy emission maximum.

Ligand **2** may also be viewed as a dimethylene-bridged derivative of 2-(2-pyridyl)-1,10-phenanthroline (**6**). To examine



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the effects of this similarilty, we compared $[Ru(\mathbf{2})_2]^{2+}$ with the unbridged analogue $[Ru(\mathbf{6})_2]^{2+}$, which had been prepared earlier.[6] Both the absorption and luminescence properties of these two complexes are found to be very similar.

The dipyrido-acridine derivative $[Ru(\mathbf{3})_2]^{2+}$ differs significantly from the other two complexes. The higher degree of unsaturation in this complex results in a significant decrease in the energy of the emission maximum. The complex also has a significantly longer luminescence lifetime (Table 3) than either of the two related complexes. In general, excited state nonradiative decay rate constants for complexes having similar MLCT excited states follow the energy gap rule whereby the nonradiative relaxation rate constant increases with a decrease in the excited state−ground state energy difference.[16,17] (The series of substituted tpy derivatives reported by Maestri and co-workers exhibit this trend.[15]) The longer lifetime for $[Ru(\mathbf{3})_2]^{2+}$ is interesting because it suggests that increasing unsaturation in terpyridine-like ligands is effective in decreasing excited state nonradiative relaxation rate constants. Recent work of Meyer and co-workers[18] has shown that diimine complexes having MLCT excited states with delocalization extending beyond the coordinated pyridine ring exhibit a smaller degree of excited state distortion. A decrease in the distortion of the excited state relative to the ground state results in a decrease of the electron−vibrational coupling constant, *S*. According to

(14) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.
(15) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg Chem.* **1995**, *34*, 2759.
(16) (a) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (c) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
(17) Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013.
(18) (a) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473. (b) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395.

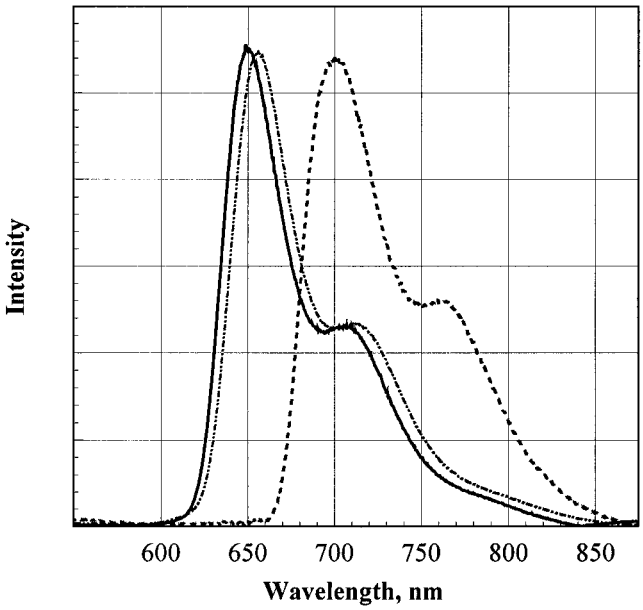

Figure 2. Emission spectra of dipyridoacridine Ru(II) complexes at 77 K in 4:1 ethanol/methanol glass, normalized and baseline corrected: $[Ru(\mathbf{1})_2)]^{2+}$, —; $[Ru(\mathbf{2})_2)]^{2+}$, ••—••; $[Ru(\mathbf{3})_2)]^{2+}$, - - -.

radiationless decay theory, decreases in S will result in decreases in the nonradiative decay rate constant[18b] and thus an increase in the excited state lifetime. A decrease in *S* is manifested in the emission spectrum by a decrease in the intensity of the lower energy vibronic bands relative to the zero−zero transition. As can be seen in Figure 2, such a decrease is not apparent for the series reported here. From the available data there is no clear explanation for this behavior.

Significant room-temperature luminescence is not observed for $[Ru(\mathbf{3})_2]^{2+}$ very likely because the ligand field states are lowered in energy along with the MLCT state for the ligand. This lowering is expected because the increased unsaturation of ligand **3** also increases its rigidity, which results in a lessened ability to attain an optimal "bite" angle upon coordination to the metal, leading to a smaller ligand field splitting. Therefore room-temperature emission is not observed because population of the LF state is still facile.

In summary, novel and straightforward syntheses of [4,3-*b*;5,6-*b*]dipyridoacridine and its dihydro derivative have been presented and the $[RuL_2]^{2+}$ complexes of these species have been prepared. The increasing delocalization which is embodied in the series **1**−**3** is appropriately reflected in the physical properties of the complexes. The energies of the emission maxima for the complexes do not show this incremental behavior. Ensuing studies will address other metal complexes of **2** and **3**.

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