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Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Preparation, Characterization, and Photophysical Properties of Covalently Linked Binuclear and Tetranuclear Ruthenium Bipyridyl Complexes

W. F. Wacholtz, R. A. Auerbach, and R. H. Schmehl*

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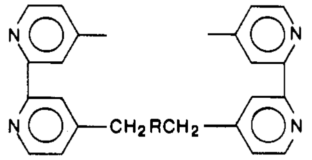
A series of covalently linked ruthenium bipyridyl complexes have been prepared by using the ligand 1,4-bis[2-(4′-methyl-2,2′-bipyridyl-4-yl)ethyl]benzene (b-b). From $[(dmb)_2Ru(b\text{-}b)]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) were prepared the symmetrically bridged complexes $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$. The spectroscopic properties and electrochemical behavior of these complexes were examined and compared to those of similar mononuclear complexes. Self-quenching of the luminescence of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is observed under low-intensity excitation. The complex $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ also shows adsorption onto Pt-disk electrodes upon reduction in cyclic voltammograms. The preparation of the unsymmetrically bridged complexes $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ where decb is 4,4′-bis(carboxyethyl)-2,2′-bipyridine is also reported. Efficient intramolecular quenching of the emission of the $[(dmb)_2Ru(b\text{-}b)]$ center of both $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{2+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ occurs. Excitation spectra of the two complexes establishes energy transfer as the principal mode of quenching.

Introduction

In the past decade the chromophore $[Ru(bpy)_3]^{2+}$ has been used as a sensitizer for numerous excited-state redox processes both in homogeneous solution and in the presence of organizing assemblies such as micelles, vesicles, and a variety of colloids.[1] In systems that serve to aggregate $[Ru(bpy)_3]^{2+}$ such that large local concentrations of the chromophore are obtained, evidence for self-quenching of the excited complex is obtained.[2-7] For example, association of $[Ru(bpy)_3]^{2+}$ with sodium dodecyl sulfate in the premicellar region results in observation of a rapid, multiexponential decay when the concentration of $[Ru(bpy)_3]^{2+}$ is large.[3] Rapid luminescence decay for $[Ru(bpy)_3]^{2+}$ has also been observed under certain conditions in the local environment of clays,[4b,5] cellulose,[4c] and silica.[4a] In such systems it is difficult to distinguish self-quenching processes from quenching by impurities incorporated into or associated with the colloidal medium. In homogeneous solutions of $[Ru(bpy)_3]^{2+}$ there are a few reports of self-quenching in concentrated solutions;[8] however, extremely large concentrations of the chromophore are required and analysis of the self-quenching is limited to luminescence lifetime measurements. The mechanism of the self-quenching is believed to be a combination of annihilation of two excited chromophores and quenching by ground-state $[Ru(bpy)_3]^{2+}$.[8] Another approach to examining potential self-quenching in this system is to prepare and spectroscopically examine covalently linked aggregates of $[Ru(bpy)_3]^{2+}$ in dilute solutions.

Recently we have prepared the covalently linked bipyridine ligand b-b. The ligand has been used for the in situ preparation of the mixed iron–ruthenium cluster $\{[(bpy)_2Ru(b\text{-}b)]_3Fe\}^{8+}$, which exhibits efficient quenching of the luminescence of the ruthenium bipyridyl centers by the iron bipyridyl complex at the center of the cluster.[9] This work presents the preparation, characterization, and photophysics of the dinuclear and tetranuclear ruthenium(II) clusters $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, respectively (dmb = 4,4′-dimethyl-2,2′-bipyridine). Two mixed ligand complexes, having one or more ruthenium centers coordinated to two 4,4′-bis(carboxyethyl)-2,2′-bipyridine (decb) ligands and the bridging b-b are also described. The photophysical properties of the dinuclear and tetranuclear clusters having identical chromophores provide evidence for self quenching only in the tetranuclear cluster in acetonitrile solutions. The complexes with two distinct chromophores exhibit intramolecular quenching of the higher energy chromophore of the complex. Mechanistic aspects of the intramolecular quenching are discussed.



= b-b; R = *p*- $CH_2C_6H_4CH_2$

Table I. Analytical Data

complex	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
$[(dmb)_2Ru(b\text{-}b)]^{2+\,b}$	54.65	54.66	4.43	4.28	9.11	9.49
$[(dmb)_2Ru(b\text{-}b)\text{-}Ru(dmb)_2]^{4+\,b}$	48.27	48.16	3.95	4.08	8.45	8.30
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+\,b}$	49.42	48.13	4.00	4.27	8.24	7.98
$[(dmb)_2Ru(b\text{-}b)Ru\text{-}(decb)_2]^{4+\,c}$	47.22	47.55	3.83	3.90	7.81	7.57
$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+\,c}$	48.25	49.40	3.93	3.93	7.04	7.45

[a] Analysis of PF_6^- salts as anhydrous powders. [b] Analyzed by Galbraith Laboratories, Knoxville, TN. [c] Analyzed by MicAnal, Tucson, AZ.

Experimental Section

Reagents and Materials. 4,4′-Dimethyl-2,2′-bipyridine (dmb) was purchased from Reilly Tar and Chemical (Indianapolis, IN) and was used as received. 4,4′-Bis(carboxyethyl)-2,2′-bipyridine (decb) was prepared according to literature methods.[10] 1,4-Bis[2-(4′-methyl-2,2′-bipyridyl-4-yl)ethyl]benzene (b-b) was prepared as described elsewhere.[9] *cis*-Dichlorobis(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) ($Ru(dmb)_2Cl_2$) was prepared by literature methods substituting ethanol for dimethylformamide as solvent.[11] *cis*-Dichlorobis(4,4′-bis(carboxyethyl)-2,2′-bipyridine)ruthenium(II) ($Ru(decb)_2Cl_2$) was prepared by a modification of the literature procedure, using ethanol as solvent rather than DMF.[10] Ruthenium trichloride trihydrate ($RuCl_3{\cdot}3H_2O$) was supplied by Alfa Products (Danver, MA) and was used without further purification. Silver tetrafluoroborate ($AgBF_4$) was supplied by Aldrich Chemical Co. and was used as received. All solvents were reagent grade and were used without further purification except where otherwise noted. Acetonitrile used in electrochemical measurements (Burdick and Jack-

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son) was refluxed over CaH_2 and distilled immediately prior to use. Microanalyses were performed by either Galbraith Laboratories (Knoxville, TN) or MicAnal (Tuscon, AZ); analytical data are provided in Table I.

Syntheses. $[Ru(dmb)_2(b\text{-}b)](PF_6)_2$ and $[Ru(decb)_2(b\text{-}b)](PF_6)_2$. A solution of b-b ($9.9 \times 10^{-4}$ mol) in 50 mL of ethanol was brought to reflux under an atmosphere of nitrogen. A solution of the cis chloro complex ($[Ru(dmb)_2Cl_2]$ or $[Ru(decb)_2Cl_2]$) (4.96×10^{-4} mol) in 10 mL of ethanol was added slowly to the colorless solution. Upon complete addition of the complex, the resulting solution was refluxed for 2 h. The reaction mixture was evaporated to dryness, the solid was redissolved in distilled water, and the mixture was filtered to remove excess unreacted ligand. Saturated aqueous NH_4PF_6 was added dropwise to the filtrate, precipitating the product as an orange powder. The filtered, dried product was chromatographed on neutral alumina (activity I) with pure acetonitrile as eluent. Two luminescent orange bands eluted with the mononuclear complex eluting first near the solvent front. The second band was attributed to the dinuclear complex ($[(dmb_2Ru(b\text{-}b)Ru(dmb)]^{4+}$; vide infra) and appears only as a minor contaminant in the reaction. TLC on alumina plates using a 1:1 CH_3CN:toluene mixture was used to determine the absence of impurities (principally the dinuclear complex). For $[(dmb)_2Ru(b\text{-}b)]^{2+}$ $\lambda_{max} = 460 \pm 2$ nm ($\epsilon = 14\,000 \pm 100$ M^{-1} cm^{-1}). $[(decb)_2Ru(b\text{-}b)]^{2+}$ was not isolated but was used in further synthetic steps as the crude chloride salt.

$[Ru(dmb)_2(b\text{-}b)Ru(dmb)_2](PF_6)_4$. A solution of b-b (118 mg, 2.52×10^{-4} mol) in 25 mL of ethanol was brought to reflux under nitrogen. To this was added a solution of $[Ru(dmb)_2Cl_2]$ (272 mg, 5.03×10^{-4} mol) in 25 mL of ethanol, and the solution was refluxed for 12 h. The reaction mixture was evaporated and worked up as described above to yield an orange powdered PF_6^- salt. The powdered complex was chromatographed on acidic alumina (activity I) with pure acetonitrile as eluent. Two bands eluted: a purple nonluminescent band eluted with the solvent front (unreacted $[Ru(dmb)_2Cl_2]$) and an orange luminescent complex. TLC on alumina was used to verify that the product was the dinuclear complex (R_f 0.4 for $[Ru(dmb)_2(b\text{-}b)Ru(dmb)_2]^{4+}$ and R_f 0.6 for $[(dmb)_2Ru(b\text{-}b)]^{2+}$). $\lambda_{max} = 460 \pm 2$ nm ($\epsilon = 27\,800 \pm 200$ M^{-1} cm^{-1}).

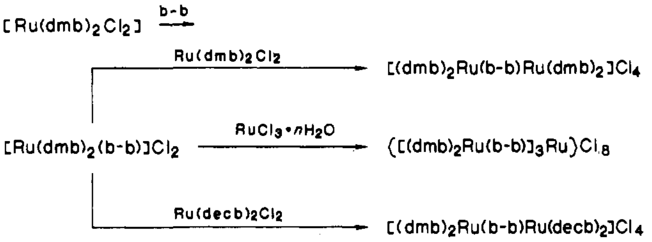
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}(PF_6)_8$. A solution containing $[Ru(dmb)_2(b\text{-}b)]Cl_2$ (300 mg, 2.97×10^{-4} mol) and $RuCl_3 \cdot H_2O$ (27.6 mg, 9.9×10^{-5} mol) in 50 mL of ethanol was heated at reflux under N_2 for 24 h. The reaction mixture was evaporated to dryness and the crude product was taken up in distilled water and chromatographed on a Sephadex G-10-120 column (2 cm × 20 cm) with distilled water as eluent. An orange emissive band eluted with the solvent front, and an orange luminescent band was retained by the column. The product complex was recovered by precipitation from the orange eluent using aqueous NH_4PF_6. TLC on alumina indicates the absence of the mononuclear starting complex ($[(dmb)_2Ru(b\text{-}b)]^{2+}$); the R_f of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is 0. $\lambda_{max} = 460 \pm 2$ nm ($\epsilon = 60\,200 \pm 200$ M^{-1} cm^{-1}).

$[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]$. A solution of $[Ru(decb)_2Cl_2]$ (174 mg, 2.25×10^{-4} mol) in 50 mL of ethanol was brought to a reflux under nitrogen. A solution of $AgBF_4$ (87.7 mg, 4.5×10^{-4} mol) in 10 mL of ethanol was added dropwise in the dark, and the resulting reaction mixture was stirred at reflux for 2 h. To this purple solution was added dropwise a solution of $[Ru(dmb)_2(b\text{-}b)]Cl_2$ (228 mg, 2.25×10^{-4} mol) in 25 mL of ethanol and the solution refluxed for an additional 6 h. The resulting reaction mixture was evaporated to dryness, the residue was redissolved in distilled H_2O, and the AgCl solid was removed by filtration through a fine-porosity frit. Saturated aqueous NH_4PF_6 was added dropwise to the filtrate, precipitating the product complex as an orange-brown powder. The filtered, dried product was chromatographed as described for the symmetrical complex ($[(dmb_2Ru(b\text{-}b)Ru(dmb)]^{4+}$). TLC on alumina as above indicates the presence of only $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ (R_f 0.5). $\nu_{CO} = 1730 \pm 10$ cm^{-1}. $\lambda_{max} = 464 \pm 2$ nm ($\epsilon = 21\,500 \pm 200$ M^{-1} cm^{-1}).

$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}(PF_6)_8$. A solution containing $[Ru(decb)_2(b\text{-}b)]Cl_2$ (200 mg, 1.60×10^{-4} mol) and $RuCl_3 \cdot H_2O$ (14.87 mg, 5.24×10^{-5} mol) in 50 mL of ethanol was brought to a reflux under N_2 atmosphere. After being heated at reflux for 36 h, the solution was evaporated to dryness. The workup was identical with that for the symmetrical tetranuclear complex ($\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$) described above; a dark powder was obtained. TLC on alumina as above indicates the absence of unreacted $[(decb)_2Ru(b\text{-}b)]^{2+}$ (R_f for $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is 0). $\nu_{CO} = 1730 \pm 5$ cm^{-1}. $\lambda_{max} = 364 \pm 2$ nm ($\epsilon = 59\,700 \pm 200$ M^{-1} cm^{-1}) and 482 ± 2 nm ($\epsilon = 72\,700 \pm 200$ M^{-1} cm^{-1}).

Apparatus. All UV-vis absorption spectra were recorded on a Hewlett-Packard 8451 single-beam diode-array spectrophotometer. IR spectra were obtained as KBr disks or mulls on NaCl plates and were recorded on a Perkin-Elmer Model 683 spectrophotometer. Emission spectra were recorded by using a Spex Industries Model 111C photon-counting fluorometer equipped with a 450-W Xe arc lamp (Osram) and a cooled PMT housing (Hammamatsu R928, select red sensitive). All emission spectra were corrected for PMT response. The absorbance of all solutions used in emission spectral measurements was <0.2 at the excitation wavelength. NMR spectra were obtained by using an IBM Instruments NR/200 FT NMR spectrometer with CD_3CN as both solvent and internal reference. Differential-pulse polarograms (DPP) were recorded on a Sargeant-Welch Model 4001 polarograph. Cyclic voltammograms were obtained as described previously.[12] Coulometric measurements were made by using an Electrosynthesis Corp. (ESC) Model 630 digital coulometer in series with an EG&G Princeton Applied Research Model 173 potentiostat. In all electrochemical measurements the sodium saturated calomel electrode (SSCE) served as reference with tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Luminescence lifetime measurements were obtained by using an apparatus described elsewhere.[12]

Scheme I



Results and Discussion

Syntheses and Characterization. The general synthesis for the covalently linked bipyridyl ligand b-b used in the preparation of the polynuclear complexes is reported in an earlier paper.[9] The mononuclear complex $[(dmb)_2Ru(b\text{-}b)]^{2+}$ is prepared by slow addition of $[Ru(dmb)_2Cl_2]$ to an excess of b-b and is isolated in high yield after chromatography on neutral alumina. Scheme I illustrates the use of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ in the preparation of the complexes $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, and $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$. The symmetrically bridged dimer $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ is readily prepared in high yield (80–90%) by the stoichiometric addition of 2 equiv of $[Ru(dmb)_2Cl_2]$ to 1 equiv of b-b or by the method outlined in Scheme I. The complex $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is prepared by refluxing 3 equiv of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ with $RuCl_3$ in ethanol; yields are typically 60% after chromatography. Separation of the large, highly charged tetranuclear cluster from unreacted $[(dmb)_2Ru(b\text{-}b)]^{2+}$ was achieved by using size exclusion chromatography since $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is immobile on alumina. When Sephadex G-10-120 is used, the unreacted monomer, $[(dmb)_2Ru(b\text{-}b)]^{2+}$, is retained by the column while $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ elutes with the solvent front. Since the ruthenium centers of each complex are chiral, the dinuclear complex exists as a mixture of the meso and racemic forms and there are four *d,l* pairs possible for the tetranuclear cluster. No attempt was made to separate the diastereomers for either complex. The complexes $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ were prepared by methods analogous to those used for $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, respectively. Relatively poor yields were obtained for complexes having decb ligands since partial ester hydrolysis occurs during workup, giving zwitterions that irreversibly bind to both

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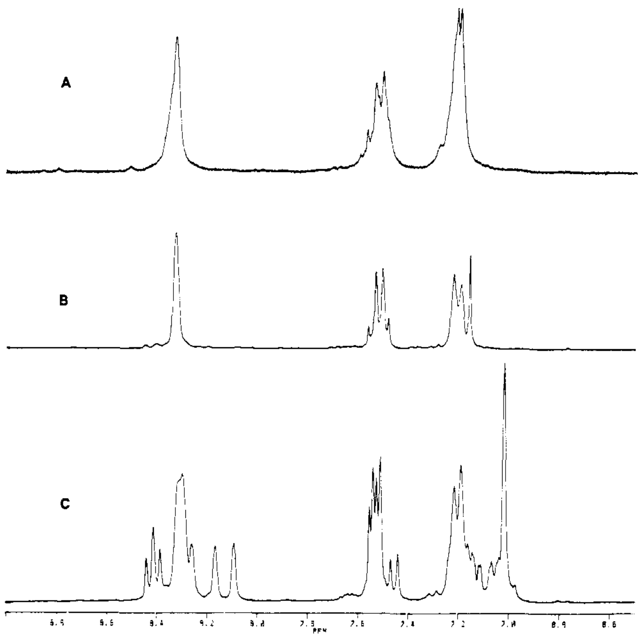

Figure 1. ^{1}H NMR spectra of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ (A), $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ (B), and $[(dmb)_2Ru(b\text{-}b)]^{2+}$ (C) in the aromatic region between $\delta = 6.5$ and $\delta = 9.0$ ppm (CD_3CN solvent; TMS reference).

alumina and Sephadex gels. Reaction of $[Ru(decb)_2Cl_2]$ with $[(dmb)_2Ru(b\text{-}b)]^{2+}$ is relatively slow, and long reflux times are required, which increases the degree of ester hydrolysis during the reaction. Reflux times required for the preparation of $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ can be significantly decreased by initial removal of coordinated Cl^- from $[Ru(decb)_2Cl_2]$ with $AgBF_4$ followed by addition of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ (eq 1 for the complex $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$).

$$[Ru(decb)_2Cl_2] \xrightarrow{AgBF_4,\ EtOH} [Ru(decb)_2(EtOH)_2]^{2+} \xrightarrow{[(dmb)_2Ru(b\text{-}b)]^{2+},\ EtOH} [(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+} \quad (1)$$

TLC on neutral alumina provides a measure of purity for all the complexes since retention times differ significantly depending on the cluster size. Both tetranuclear complexes, $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ bind irreversibly to common adsorption chromatographic media and have R_f values of 0 on neutral alumina when eluted with 1:1 CH_3CN:toluene mixtures. On acidic alumina, the mononuclear complexes $[(dmb)_2Ru(b\text{-}b)]^{2+}$ and $[(decb)_2Ru(b\text{-}b)]^{2+}$ have R_f values of 0, possibly due to protonation of the pendant noncoordinated bipyridine.

The physical properties of the complexes $[(dmb)_2Ru(b\text{-}b)]^{2+}$, $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ are very similar, and adequate characterization requires a combination of ^{1}H and ^{13}C NMR, electroanaalytical methods, and elemental analyses. The ^{1}H NMR spectrum of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ exhibits distinct sets of aromatic resonances for both coordinated and uncoordinated bipyridines present (Figure 1).[23] In the free ligand, b-b, resonances for the 3,3′, 5,5′, and 6,6′ protons appear at 8.2, 7.1, and 8.5 ppm, respectively. Upon coordination of both bipyridines of b-b to form $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, the 3,3′ protons shift downfield to 8.3 ppm, the 5,5′ protons do not change, and the 6,6′ protons shift upfield to 7.5 ppm. The ^{1}H and ^{13}C NMR spectra for the symmetrical complexes $[(dmb)_2Ru(b\text{-}b)]^{2+}$, $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ are shown in Figures 1 and 2. In the dinuclear and tetranuclear complexes $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, only the coordinated bipyridine resonances are observed, whereas in $[(dmb)_2Ru(b\text{-}b)]^{2+}$ resonances for both free and coordinated b-b are observed. In ^{13}C spectra, aliphatic carbons of the bridge of b-b exhibit four distinct resonances for $[(dmb)_2Ru(b\text{-}b)]^{2+}$ while the complexes $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ have only two resonances in the same region of the spectrum. The resonance at 21.3 ppm is that of the 4-methyl group of both b-b and dmb ligands. For the complexes $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ ^{1}H NMR spectra yield integrations for the aliphatic and aromatic regions that are consistent with the presence of two and six ethyl ester moieties for the dimer, $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$, and the tetramer, $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, respectively. The ^{13}C NMR spectrum of the dinuclear complex, $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$, shows only two carbon resonances in the region of the linking ethyl moieties, similar to the complex $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$. Integration of the ^{1}H spectra of all complexes gave good agreement between observed and expected values (Table II).

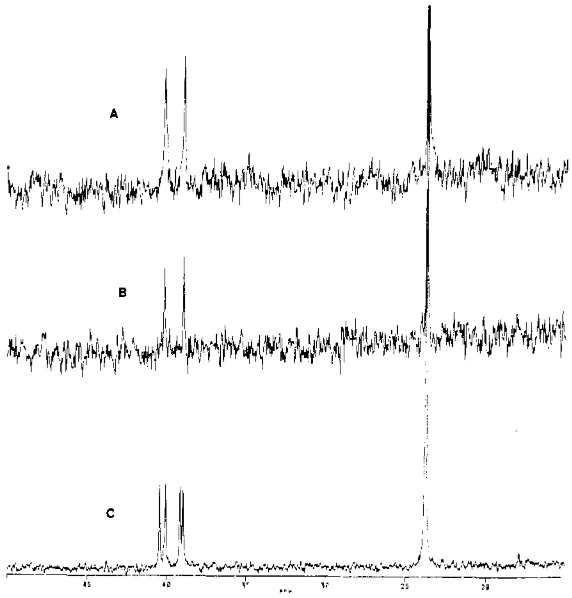

Figure 2. ^{13}C NMR spectra of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ (A), $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ (B), and $[(dmb)_2Ru(b\text{-}b)]^{2+}$ (C) in the aliphatic region between $\delta = 15$ and $\delta = 50$ ppm (CD_3CN solvent; TMS reference).

Table II. Integrated Intensities of ^{1}H NMR Spectra[a]

	7.0–8.6 ppm		3.2–2.9 ppm		2.5–1.3 ppm	
complex	calcd	found	calcd	found	calcd	found
$[Ru(dmb)_3]^{2+}$	18	18.1			18	17.9
$[Ru(decb)_2(dmb)]^{2+}$	18	18.1	8	8.0	18	17.8
$[(dmb)_2Ru(b\text{-}b)]^{2+}$	28	28.0	8	8.0	18	18.2
$[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$	40	39.8	8	8.0	30	30.4
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	84	84.2	24	24.0	54	54.1
$[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$	40	40.9	16	16.0	30	31.6
$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	84	84.9	48	48.0	54	51.3

[a] All spectra in CD_3CN, referenced to TMS.

The redox behavior of the complexes studied in acetonitrile was examined by cyclic voltammetry, differential-pulse polarography, and coulometry (Table III). Cyclic voltammograms of the complexes $[(dmb)_2Ru(b\text{-}b)]^{2+}$, $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ have identical potentials for the Ru(3+/2+) couple. The Ru(3+/2+) couple was shown to involve one, two, and four electrons, respectively, by coulometry. Since the molecular weights of $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ differ only slightly from simple multiples of the molecular weight of $[(dmb)_2Ru(b\text{-}b)]^{2+}$, the coulometric data are presented in terms of the number of coulombs per gram expected for each complex, with each metal center assumed to

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[23] Nord, G. *Comments Inorg. Chem.* **1985**, *4*, 193.

Table III. Electrochemical Properties[a]

	complex oxidn		ligand redn			coulometry, C/g		DPP[d]		
complex	E_1, V	E_2, V	E_3, V	E_4, V	E_5, V	calcd	found	E_1, V	E_2, V	$W_{1/2}$,[e] mV
$[Ru(dmb)_3]^{2+}$	1.10		−1.46	−1.63	−1.86	102.3	101.2	1.09		95
$[Ru(decb)_2(dmb)]^{2+}$	1.44		−0.96	−1.16	−1.64	82.1	80.9	1.41		92
$[(dmb)_2Ru(b\text{-}b)]^{2+}$	1.11		−1.46	−1.65		78.5	82.4	1.10		95
$[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$	1.11		−1.46	−1.65		97.0	96.0	1.11		98
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	1.11		−1.46	−1.63	*b*	94.6	90.9	1.11		105
$[(decb)_2Ru(b\text{-}b)Ru(dmb)]^{4+}$	1.11	1.42	−0.96	−1.15	−1.46	89.5	90.6	1.10	1.41	105, 100
$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	1.11	1.42			*c*	80.8	84.2	1.11	1.41	140, 110

[a] Potentials from cyclic voltammograms ($E = (E_{p,a} - E_{p,c})/2$) vs. SSCE reference in CH_3CN with tetraethylammonium perchlorate as supporting electrolyte. v = 200 mV/s. [b] A desorption spike is observed at −1.57 V. [c] No distinct waves appear in CV due to extensive overlap of neighboring reductions. [d] DPP data were obtained in CH_3CN with a Pt disk WE, Pt-wire counter electrode, sweep rate of 17 mV/s, and an excitation pulse of 15 mV; SSCE reference. [e] Width of DPP at half-height.

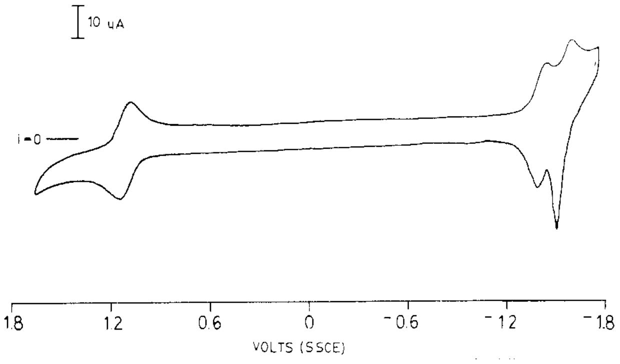

Figure 3. Cyclic voltammogram of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ in CH_3CN at a Pt disk (SSCE reference; v = 200 mV/s).

be oxidized (i.e., $n = 2$ for $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $n = 4$ for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$). Differential-pulse polarograms of $[(dmb)_2Ru(b\text{-}b)]^{2+}$, $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ between +0.7 and +1.5 V vs. SSCE also exhibit single waves. The widths at half-height, $W_{1/2}$, range from 92 mV for $[Ru(decb)_2(dmb)]^{2+}$ to 105 mV for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ (Table III). By use of the Richardson and Taube approach,[14] the conproportionation constant, K_c (eq 2), can be

$$[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+} + [(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{6+} \rightleftharpoons 2[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{5+} \quad (2)$$

estimated for the complex $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$. The value of K_c, based upon $W_{1/2}$, is less than 7, only slightly larger than the statistical value expected for two identical noninteracting redox centers. No intervalence-transfer absorption in the near-infrared region was observed for acetonitrile solutions of $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ after one-electron oxidation with Ce(IV) ($\epsilon < 10$ for the IT transition). The absence of an intervalence transition is common for mixed-valence dinuclear complexes having noninteracting redox centers.[16] For $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, the broadening of the DPP may result from the facts that there are two slightly different redox-active metal centers (central and peripheral) and that several diastereomers exist.

Two reversible reduction waves are observed in cyclic voltammetry of $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ between 0 and −1.8 V vs. SSCE (Table III). The doubly reduced form of the complex $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ adsorbs onto the Pt working electrode, and a desorption spike is observed at −1.57 V upon potential reversal (Figure 3). Similar behavior is observed in reduction of trinuclear complexes prepared from the covalently linked phenanthroline trimer 2,2′,2″-tris((1,10-phenanthroline-2-yloxy)ethyl)amine.[13] Preparation of chemically modified electrodes by electroinitiated polymerization of ruthenium bipyridyl complexes having pendant vinyl groups is believed to occur by successive hydrodimerization reactions upon reduction to yield oligomers that adsorb onto the electrode surface.[15] It is interesting to note here that adsorption and subsequent desorption are observed upon reduction of trinuclear and tetranuclear complexes but not with $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$. No coulometric analysis for the reduction of the symmetrical complexes was attempted.

Table IV. Absorption and Emission Maxima

	abs max,[a] μm^{-1}		emission max,[b] μm^{-1}	
complex	$MLCT_1$ (log ϵ)	$MLCT_2$ (log ϵ)	77 K	298 K[d]
$[Ru(dmb)_3]^{2+}$	2.18 (4.15)		1.68	1.61
$[Ru(decb)_2(dmb)]^{2+}$	2.07 (4.21)	2.26 (4.16)	1.58	1.52
$[(dmb)_2Ru(b\text{-}b)]^{2+}$	2.17 (4.15)		1.68	1.62
$[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$	2.17 (4.44)		1.66	1.62
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	2.17 (4.78)		1.67	1.61
$[(decb)_2Ru(b\text{-}b)]^{2+}$	2.07 (4.21)	2.26 (4.17)[c]		1.51
$[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$	2.16 (4.33)		1.58	1.52
$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	2.07 (4.86)	2.26 (4.81)[c]	1.56	1.51

[a] Maxima ±0.01 μm^{-1} in CH_3CN. [b] Maxima ±0.005 μm^{-1} in 4:1 EtOH:MeOH solution; λ_{ex} = 460 nm. [c] Shoulder of peak at 2.07 μm^{-1}. [d] Maxima ±0.005 μm^{-1} in CH_3CN; λ_{ex} = 460 nm.

The complexes $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ exhibit two oxidation waves in cyclic voltammetry at +1.42 and +1.11 V vs. SSCE, corresponding to oxidation of the ruthenium centers with and without decb ligands, respectively. The more positive potential is nearly identical with that of $[Ru(decb)_2(dmb)]^{2+}$ (Table III).[12] Integration of oxidative DPP's of $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ indicate a 1:1 ratio for the waves at 1.42 and 1.11 V for the complex $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and a 3:1 ratio for the complex $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, consistent with the stoichiometry of the complexes. The width at half-height, $W_{1/2}$, for the first oxidative wave of $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is the largest of all the complexes examined. Since this wave corresponds to one-electron oxidation of the $[Ru(b\text{-}b)_3)]$ moiety occupying the center of the cluster, the large width may reflect kinetic irreversibility due to restricted approach of the central Ru to the electrode.

Spectroscopic Properties of Symmetrical Oligomers. Maxima from electronic absorption spectra and luminescence spectra are given in Table IV. The absorption maxima (460 ± 2 nm) are identical for $[Ru(dmb)_2(dmb)]^{2+}$, $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$, and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$; molar extinction coefficients are proportional to the number of ruthenium bipyridyl centers present. Both room-temperature and 77 K emission maxima are identical for the three symmetrical complexes. Emission quantum yields and lifetimes measured at room temperature and luminescence lifetimes at 77 K are reported in Table V. Room-temperature luminescence quantum yields measured in acetonitrile indicate that $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ has a quantum yield only 60% of that of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ while the measured lifetimes of the two complexes are very similar. Emission lifetimes were measured with low-intensity excitation from a pulsed nitrogen laser (~200 μJ/pulse) where the probability of simultaneously exciting two centers on cluster $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is low. There are four

Table V. Emission Quantum Yields and Luminescence Lifetime Parameters

complex	ϕ_{em}(298 K)[a]	τ(298 K),[b] ns	τ(77 K),[c] ns	k, 10^{-4} s^{-1}
$[Ru(dmb)_3]^{2+}$	0.107 ± 0.005	1060	3990	10.0
$[Ru(decb)_2(dmb)]^{2+}$	0.085 ± 0.004	870	5305	9.8
$[(dmb)_2Ru(b\text{-}b)]^{2+}$	0.068 ± 0.003	820	4380	8.3
$[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$	0.066 ± 0.004	820	4190	8.0
$\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	0.041 ± 0.003	770	4100	5.3
$[(decb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$	0.076 ± 0.005	1140	5310	6.7
$\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$	0.044 ± 0.004	970	4740	4.5

[a] Emission quantum yields were calculated from integrated emission spectra relative to $[Ru(bpy)_3]^{2+}$ in water ($\phi = 0.042$ at 298 K) and corrected for refractive index differences between H_2O and CH_3CN.[12] [b] In N_2-purged CH_3CN solutions; all lifetimes ±20 ns. [c] Lifetimes measured in 4:1 EtOH:MeOH solution; all lifetimes ±50 ns.

reasonable explanations for the observed decrease in the emission quantum yield of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$: (a) the radiative decay rate of the complex has decreased relative to the nonradiative decay rate, (b) quenching by a neighboring ground-state chromophore, (c) quenching by self-annihilation of two neighboring excited centers, and (d) an inner-filtering effect brought about by the high local chromophore concentrations in $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$. Intramolecular-energy-transfer quenching in $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ and $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, known to occur for $[Ru(bpy)_3]^{2+}$ in homogeneous solution,[24] will not affect either the luminescence lifetime or the emission quantum yield. If self-quenching involves annihilation of two excited centers and the rate of annihilation on $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ is very fast, the observed emission decay would be the combination of a fast and a slow component where the slow component would result from complexes in which only one center is excited, as in $[(dmb)_2Ru(b\text{-}b)]^{2+}$. The complex $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ should also exhibit an excitation-intensity-dependent emission quantum yield if self-annihilation is the quenching mechanism; at low excitation intensities the emission yield should nearly equal that of $[(dmb)_2Ru(b\text{-}b)]^{2+}$. However, no intensity dependence is observed in emission quantum yields of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ upon decreasing the excitation intensity by a factor of 10. If quenching is by a neighboring center in its ground state, an emission quantum yield change would be expected for $[(dmb)_2Ru(b\text{-}b)Ru(dmb)_2]^{4+}$ as well as $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$, unless quenching is by the unique central ruthenium in the tetranuclear complex. This mode of decay requires that the luminesence lifetime and quantum yield decrease for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ by the same relative amount. A local inner-filter effect could also result in a decreased observed emission quantum yield for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$. In this case the emission quantum yield should exhibit a wavelength dependence, reaching a minimum at the wavelength of maximum absorbance of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$. Since this is not the case, the combination of the unchanged lifetime relative to that of $[(dmb)_2Ru(b\text{-}b)]^{2+}$ and the decreased emission quantum yield suggests that $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ has a decreased radiative decay rate (*a*). It is interesting to note that the molar absorptivity of $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ per metal center is 6% greater than that of the parent monomer, $[(dmb)_2Ru(b\text{-}b)]^{2+}$, suggesting a *faster* radiative decay rate from the ^{1}MLCT state for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$.

When $[Ru(bpy)_3]^{2+}$ is incorporated into colloidal smectites and montmorillonite clays, the luminescence decay observed upon high-intensity laser excitation is multiexponential and exhibits a rapid component having a lifetime of approximately 60 ns.[4b,5] In smectites, low-intensity excitation in luminescence lifetime experiments results in a single exponential decay with a lifetime of 800 ns. The intensity dependence of the luminescence decay provides evidence that the observed self-quenching involves triplet–triplet annihilation. In montmorillonite clays, a decrease in both luminescence lifetime and relative emission quantum is observed even with low-intensity excitation. Further, the relative degree of quenching is greater in intensity measurements than in lifetime measurements. The greater intensity quenching was attributed to static quenching by impurities in the colloid. The fact that similar changes in emission properties are observed for $\{[(dmb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ in these studies, where static impurity quenching is highly unlikely, suggests that the emission yield decrease observed for $[Ru(bpy)_3]^{2+}$ in montmorillonite may occur as described above.

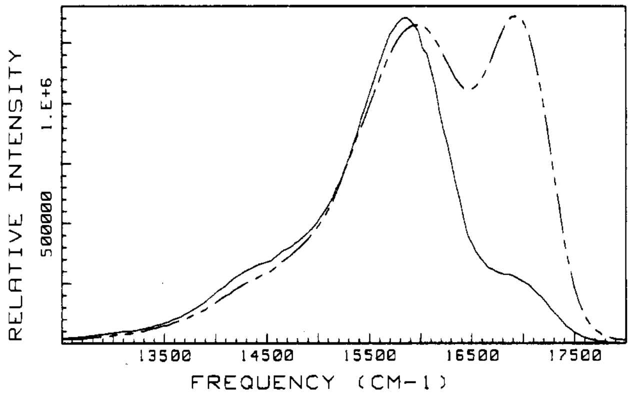

Figure 4. Emission spectra of a 1:1 mixture of $[Ru(dmb)_3]^{2+}$ and $[Ru(decb)_2(dmb)]^{2+}$ (---) and of the complex $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ (—) in 4:1 ethanol:methanol solution at 77 K with excitation at 450 nm.

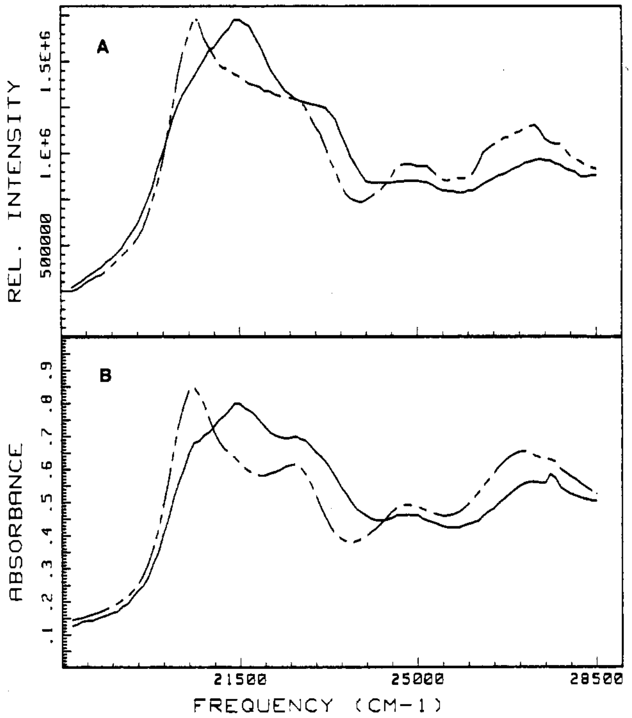

Figure 5. (A) Excitation spectra of $[Ru(decb)_2(dmb)]^{2+}$ (---) and $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ (—) monitoring emission at 650 nm. (B) Absorption spectra of $[Ru(decb)_2(dmb)]^{2+}$ (---) and $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ (—). Both sets of spectra were measured at 77 K in 4:1 ethanol:methanol solution.

Spectroscopic Properties of Unsymmetrical Oligomers. The complexes $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ have two distinct emissive centers. Absorption and emission maxima for mononuclear complexes having coordination environments identical with the two centers of $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ are given in Table IV. The MLCT transitions of the two complexes composing $[(dmb)_2Ru(b\text{-}b)Ru(decb)_2]^{4+}$ and $\{[(decb)_2Ru(b\text{-}b)]_3Ru\}^{8+}$ exhibit

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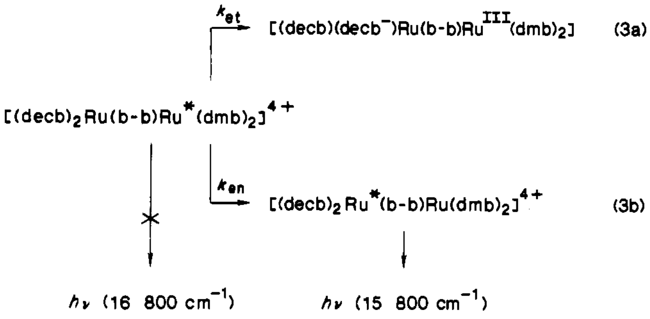
(24) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

considerable overlap; however, selective excitation of the lower energy center, [Ru(decb)$_2$(dmb)], is possible. Figure 4 shows 77 K emission spectra of [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ and a 1:1 mixture of [Ru(dmb)$_3$]$^{2+}$ and [Ru(decb)$_2$(dmb)]$^{2+}$ upon excitation at 450 nm, close to the absorption maximum of the [(dmb)$_2$Ru(b-b)] center. The solution of the two chromophores (1:1 mixture) exhibits emission from both centers with maxima at 1.68 μm^{-1} for the [Ru(dmb)$_2$(b-b)] chromophore and 1.58 μm^{-1} for the [Ru(decb)$_2$(b-b)] center, whereas [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ shows extremely weak emission from the higher energy center. Luminescence lifetimes measured by using 460-nm coumarin I dye laser excitation and monitoring the emission decay at 1.68 μm^{-1} exhibit only a single exponential decay with a lifetime equal to the lifetime measured from the emission at 1.58 μm^{-1}. Decays with lifetimes shorter than 10 ns cannot be measured with the system used. Emission spectra of [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ at ~5 K also show only weak emission from the higher energy ruthenium center, suggesting that the quenching of the higher energy emission of [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ is extremely efficient.

The emission quenching of the [Ru(dmb)$_2$(b-b)] center of the dimer may result from either energy or electron transfer to the [Ru(decb)$_2$(b-b)] center (eq 3). The energy of the emitting state of the [Ru(dmb)$_2$(b-b)] center is approximately 2.00 eV on the basis of the room-temperature emission maximum, and the Ru(3+/2+) potential is 1.11 V vs. SSCE in acetonitrile. The first reduction of [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ results in formation of a coordinated decb$^-$ (eq 4).[17] Thus, the electron-transfer-quenching step is slightly endergonic ($\Delta G \approx 0.07$ eV) when the electrostatic work term is ignored.[18] Energy transfer quenching is exergonic by approximately 0.12 eV (0.93 μm^{-1}). In previous studies involving tetranuclear clusters of the type {[(bpy)$_2$Ru(b-b)]$_3$Fe}$^{8+}$, energy transfer of the excited ruthenium centers by the central iron bipyridyl was shown to occur by a mixture of Förster[19] (dipole–dipole) and Dexter[20] (exchange) processes.[9] Recently, Schanze, Neyhart, and Meyer described intramolecular quenching in 1,2-bis(4-pyridyl)ethane-bridged complexes of osmium having two emitting Os(II) centers.[21] Both energy and electron transfer are exergonic, and excitation spectra of the lower energy emitting chromophore reveal that energy transfer is not an important process for the quenching of the higher energy Os chromophore emission. By contrast, excitation spectra of [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$ at 77 K, monitoring emission from the [Ru(decb)$_2$(b-b)] center, clearly indicate sensitization by the [Ru(dmb)$_2$(b-b)] chromophore (Figure 5) since the excitation spectrum of the complex exhibits features characteristic of *both* chromophores.[25] This evidence strongly suggests that energy transfer is the predominant mode of quenching of the [Ru(dmb)$_2$(b-b)] center in this system; however, selective excitation of the donor is not possible for these systems and emission from both centers in the excitation spectra cannot be excluded since there is significant overlap in the emissions from both chromophores (Figure 4). Very recently, we have prepared the complex having the same donor but [Ru(biq)$_2$(b-b)] as acceptor, [(dmb)$_2$Ru(b-b)Ru(biq)$_2$]$^{4+}$ (biq = 2,2′-biquinoline). The emission of the [Ru(biq)$_2$(b-b)] center is at 1.33 μm^{-1}, 0.35 μm^{-1} lower in energy than the donor emission. The low-temperature (~5 K) time-resolved luminescence of the [Ru(biq)$_2$(b-b)] center shows a rise and fall, clearly illustrating energy transfer from [Ru(dmb)$_2$(b-b)], even though electron-transfer quenching is also exergonic.[22] We are currently examining luminescence in mixed osmium–ruthenium and rhenium–ruthenium dinuclear complexes in an effort to better understand factors influencing energy/electron transfer in these systems.



$$[(\mathrm{dmb})_2\mathrm{Ru^{III}}(\mathrm{b\text{-}b})\mathrm{Ru}(\mathrm{decb})_2]^{5+} \underset{}{\overset{-e^-}{\rightleftharpoons}} [(\mathrm{dmb})_2\mathrm{Ru}(\mathrm{b\text{-}b})\mathrm{Ru}(\mathrm{decb})_2]^{4+} \overset{+e^-}{\rightleftharpoons} [(\mathrm{dmb})_2\mathrm{Ru}(\mathrm{b\text{-}b})\mathrm{Ru}(\mathrm{decb})(\mathrm{decb}^-)]^{3+} \quad (4)$$

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Registry No. *cis*-[Ru(dmb)$_2$Cl$_2$], 68510-55-4; *cis*-[Ru(decb)$_2$Cl$_2$], 109835-97-4; [Ru(dmb)$_3$]$^{2+}$, 32881-03-1; [Ru(decb)$_2$(dmb)]$^{2+}$, 96897-28-8; [Ru(dmb)$_2$(b-b)](PF$_6$)$_2$, 109745-35-9; [Ru(dmb)$_2$(b-b)]Cl$_2$, 109745-42-8; [Ru(decb)$_2$(b-b)](PF$_6$)$_2$, 109745-37-1; [Ru(decb)$_2$(b-b)]Cl$_2$, 109745-33-7; [Ru(dmb)$_2$(b-b)Ru(dmb)$_2$](PF$_6$)$_4$, 109745-39-3; [(dmb)$_2$Ru(b-b)Ru(decb)$_2$]$^{4+}$, 109745-43-9; {[(dmb)$_2$Ru(b-b)]$_3$Ru}(PF$_6$)$_8$, 109745-41-7; {[(decb)$_2$Ru(b-b)]Ru}(PF$_6$)$_8$, 109764-52-5.

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(25) To ensure that the excitation spectrum observed monitoring emission at a particular wavelength does not represent emission from two luminescent centers, excitation spectra were measured at several wavelengths on the low-energy side of the acceptor emission. All excitation spectra exhibited the same relative intensity throughout.