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- (47) See, for instance, ref 8–10.
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Synthesis and Electrochemical and Photoemission Properties of Mononuclear and Binuclear Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,9-Dimethyl-1,10-phenanthroline, 2,2'-Bipyrimidine, 2,2'-Biimidazole, and 2-Pyridinecarboxaldimine Ligands

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Four new *mononuclear* ruthenium(II) complexes, [Ru(PTPI)₃]²⁺ (PTPI = 2-*p*-tolylpyridinecarboxaldimine) and [Ru(bpy)₂B]²⁺ [B = 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂phen), 4,4'-dimethyl-2,2'-bipyrimidine (4,4'-Me₂bpyrm), and 2,2'-biimidazole (biimH₂)], have been prepared as PF₆⁻ salts and their electrochemical and photoemission properties investigated in solution. In addition, the ligand-bridged *binuclear* species [Ru(bpy)₂(B)Ru(bpy)₂](PF₆)₄ (B = bpyrm and 4,4'-Me₂bpyrm) have also been obtained as by-products in the synthesis of the mononuclear complexes and separated from their mononuclear analogues by Sephadex chromatography. The *mononuclear* compounds all exhibit polarograms in acetonitrile consistent with quasi-reversible, one-electron [Ru(II) → Ru(III)] oxidation processes with $E_{1/2}$ potentials (SCE) ranging from 0.93 to 1.29 V. The $E_{1/2}$ potentials suggest an ordering in the B ligand π -acceptor ability of biimH₂ << 2,9-Me₂phen ~ bpy < 4,4'-Me₂bpyrm < bpyrm. The *binuclear* [Ru(II),Ru(II)] complexes possess polarograms displaying two, one-electron oxidation processes ($\Delta E_{1/2} = 0.18$ V) corresponding to production of the mixed-valence [(Ru(II),Ru(III))] and fully oxidized [Ru(III),Ru(III)] species. At room temperature and in acetonitrile, the mononuclear B = 2,9-Me₂phen, bpyrm, 4,4'-Me₂bpyrm, and biimH₂ complexes have $d\pi^*$ absorption and luminescence spectra similar to that of [Ru(bpy)₃]²⁺, with emission bands occurring between 588 and 600 nm in all cases. Under similar conditions, the bipyrimidine-bridged *binuclear* complexes do not exhibit emission spectra in the 350–800-nm region. The emission spectrum observed for the [Ru(PTPI)₃]²⁺ complex is probably not of $d\pi^*$ origin, with the emission bands being blue shifted (at ~345 and 400 nm) relative to the 496- and 552-nm $d\pi^*$ absorption bands.

Introduction

The synthesis of [Ru(bpy)₃]₂X₂·nH₂O by Burstall² (bpy = 2,2'-bipyridine) in 1936 led to little interest in the complex until 1959 when Paris and Brandt³ discovered its visible-region luminescence at 77 K. After further inquiries mainly by Crosby and co-workers,^{4–6} a large amount of evidence accumulated from luminescence lifetime studies of [Ru(bpy)₃]²⁺ and related complexes that strongly supported a $d\pi^*$ ^{5,7,8} heavy-atom perturbed,⁹ spin-forbidden process as the basis for the observed phenomenon. This suggests an analogy to the more familiar spin-forbidden organic phosphorescence phe-

nomena where the electronic decay is from a triplet excited state to the singlet ground state. For the [Ru(bpy)₃]²⁺ case, however, there exist four emitting states, and spin labels on these states have recently been abandoned because of the large spin-orbit coupling expected for the formally d⁵ metal center of the $d\pi^*$ excited states.¹⁰ Further, it has been proposed that (1) metal–ligand $d\pi^*$ charge transfer must be at lower energy than dd^* ligand field or $\pi\pi^*$ ligand antibonding states,¹¹ (2) the ground-state complex must be diamagnetic,¹¹ and (3) the metal ion d electrons in the $d\pi^*$ excited state must also be as "paired" as possible.^{12,13} These conditions apparently constitute

a necessary but insufficient set to guarantee $d\pi^*$ luminescence.¹² Thus, the search for new complexes exhibiting such behavior is important for the eventual definition of the set of criteria necessary and sufficient to induce $d\pi^*$ luminescence.

Recently, Whitten et al.¹⁴ have demonstrated that visible wavelength irradiation of some samples of the complexes $[\text{Ru}(\text{bpy})_2(4,4'-(\text{ROOC})_2\text{bpy})]^{2+}$ ($\text{R} =$ dihydrocholesteryl and octadecyl), under special experimental conditions, causes photoinduced cleavage of H_2O into H_2 and O_2 . Although there are still problems to be resolved concerning the identification of the exact species responsible for this effect¹⁵ (repurified samples of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{ROOC})_2\text{bpy})]^{2+}$ itself have been shown to be inactive¹⁶), it is likely that they are still bis-(bipyridine)ruthenium(II) complexes, probably transformed from the intended diester complex by some process such as transesterification. Thus, bis(bipyridine)ruthenium(II) complexes possessing a third, strong-field bidentate ligand are important candidates for continuing studies in this area. To date, relatively few such $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$ complexes (where B is a neutral, strong-field bidentate ligand) have been reported. Dwyer and co-workers reported the $\text{B} =$ ethylenediamine complex¹⁷ which does not luminesce at room temperature.⁵ Meyer et al.¹⁸ later reported the above complex and its electrochemical oxidation product, $[\text{Ru}(\text{bpy})_2(\text{NH}=\text{CH}-\text{CH}=\text{NH})]^{2+}$, as well as others generated from $\text{B} =$ diamine complexes, and recently the complexes with $\text{B} =$ 1,8-naphthyridine and similar aromatic ligands have been isolated and characterized by Staniewicz and co-workers.¹⁹ Finally, only the $[\text{Ru}(\text{bpy})_2(\text{phen})]^{2+}$ species^{20,21} and the recently reported $[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$ compound (bpyrm = bipyrimidine) are known.²²

In the present work we report the synthesis, characterization, and study of three new $[\text{Ru}(\text{bpy})_2\text{B}](\text{PF}_6)_2$ compounds, where $\text{B} =$ 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂phen, see b in Figure 1), 4,4'-dimethyl-2,2'-bipyrimidine (4,4'-Me₂bpyrm, d with $\text{R} =$ methyl), 2,2'-biimidazole (biimH₂, e), as well as the tris complex $[\text{Ru}(\text{PTPI})_3](\text{PF}_6)_2$ (where PTPI = 2-*p*-tolylpyridinecarboxaldimine, c). In addition, the $[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$ complex of Hunziker and Ludi ($\text{B} =$ bpyrm, d with $\text{R} =$ H) has also been prepared and further investigated.²² As interesting by-products of the above syntheses where $\text{B} =$ bpyrm or 4,4'-Me₂bpyrm, the binuclear complexes $[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ ²² and $[\text{Ru}(\text{bpy})_2(4,4'-\text{Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2](\text{PF}_6)_4$ have also been obtained and separated from their mononuclear products by Sephadex chromatography. These species resemble the $[\text{Ru}(\text{II}),\text{Ru}(\text{II})]$ binuclear $[\text{Ru}(\text{NH}_3)_5(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{4+}$ ($\text{pyr} =$ pyrazine) complex of Creutz and Taube²³ for which the single-electron (pentavalent) oxidation product is a $[\text{Ru}(\text{II}),\text{Ru}(\text{III})]$ mixed-valence ion. In addition to the Creutz-Taube ion, several other $[\text{Ru}(\text{II}),\text{Ru}(\text{II})]$ complexes have also been reported and their electrochemical behavior studied²⁴⁻³⁰ in order to investigate the extent of electronic interaction between the two metal centers, and, while it is true that the previously known complexes of this type display a broad range of molecular and electronic structures, they all include bridging ligands which are only monodentate toward each ruthenium ion. Thus, the present $[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}(\text{bpy})_2(4,4'-\text{Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ complexes are the first binuclear species to utilize a bridging ligand which is bidentate with respect to both ruthenium centers, thereby providing a dual pathway for metal-metal interaction.

Experimental Section

Physical Measurements. Elemental analyses were obtained commercially. Solution conductivities were obtained at $30 \pm 1^\circ\text{C}$ with a Model 31 YSI conductivity bridge. Polarograms were obtained using a PAR Model 174 polarographic analyzer and a rotating Pt electrode (RPE). The solutions were 10^{-4} M in ruthenium complex and 0.1 M in NaClO_4 as the supporting electrolyte. All measurements

were performed at $23 \pm 2^\circ\text{C}$ in degassed (N_2) acetonitrile and are reported vs. the saturated potassium calomel electrode (SCE). The reported potentials are uncorrected for junction potentials. A standard three-electrode circuit was employed with the reference electrode isolated from the sample solution by a fritted disk. The $E_{1/2}$, Δ (slope), and i_d values were obtained from the polarograms by nonlinear least-squares minimization of $S = \sum (i - i_{\text{calcd}})^2$ where $i_{\text{calcd}} = [(A_0 + B_0E) + (A_d + B_dE)Z]/(Z + 1)$, $i_d = [(A_d - A_0) + (B_d - B_0)E_{1/2}]$, and $Z = \exp[-(E - E_{1/2})/\Delta]$.³¹ Visible spectra were obtained on a Cary 17 spectrophotometer. Luminescence spectra at $25 \pm 2^\circ\text{C}$ were obtained with a Perkin-Elmer Model MPF-4A fluorescence spectrometer using a Hamamatsu Type R106 phototube. The spectra are corrected for self-absorption for the samples of optical density 0-0.5 in the region of interest and are uncorrected for instrument response. A 4-16-nm band-pass was used for excitation and a 4-8 nm emission band-pass was employed.

Materials and Syntheses. Acetonitrile was dried over 4-Å molecular sieves for 48 h and distilled, the first and last 10% being discarded. Reagent grade 2,2'-bipyridine was sublimed twice before use. All ethanol used was absolute. Sephadex LH-20 was obtained from Pharmacia or Sigma Chemical; the column used measured 1 m \times 2.5 cm (i.d.) with a flow rate of ca. 100 mL h⁻¹. The 2-pyridinecarboxaldehyde was distilled, and methanol was dried and distilled from magnesium before use. All other reagents and commercially obtained organics (Aldrich) were reagent grade and were used as received. C, H, N, and Ru analyses for all the Ru(II) compounds were judged satisfactory by two referees.

Preparations. 2-*p*-Tolylpyridinecarboxaldimine (PTPI). 2-Pyridinecarboxaldehyde, 2.7 g (25 mmol), was dissolved in 10 mL of absolute ethanol and then stirred. *p*-Toluidine, 2.7 g (25 mmol), was dissolved in 25 mL absolute ethanol, filtered, and added dropwise. **Caution!** Use gloves in the hood. After 2 h of stirring, the solution was added dropwise to about 20 mL of vigorously agitated H_2O . After crystallization and collection, the solid was washed with large volumes of H_2O and dried in vacuo over CaCl_2 for 12 h, yielding 3.34 g (68%) of yellow crystals.

$[\text{Ru}(\text{PTPI})_3](\text{PF}_6)_2$. $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$, 75 mg (200 μmol), was dissolved in 5 mL of H_2O , and 120 mg (600 μmol) of PTPI in 8 mL of methanol was added dropwise with stirring. After refluxing of the mixture for 1.5 h, 74 mg (400 μmol) of KPF_6 in 20 mL of methanol was added with filtration, and the mixture was stirred 10 min further. The solvent was removed under vacuum and the remaining solid was dried in vacuo at 35°C for 10 min. The solid was extracted into dry (Na_2SO_4) dichloromethane and filtered, and then the solvent was removed under vacuum. After drying the solid in vacuo at 35°C for 10 min, the material was extracted with ethyl ether and recrystallized from dry dichloromethane-ethyl ether, yielding 57 mg (29%) of red-brown plates which were dried in vacuo over P_2O_5 at 100°C for 72 h.

$[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$. The complex was prepared by the method of Whitten et al.¹⁶ on a 20% scale.

2,2'-Biimidazole (biimH₂). The ligand was prepared by the method of Debus³² except that N_2 was bubbled through the cold solution to remove some of the NH_3 before collection of the product.

2,2'-Bipyrimidine (bpyrm) and 4,4'-Dimethyl-2,2'-bipyrimidine (4,4'-Me₂bpyrm). 2-Bromopyrimidine was prepared from 2-aminopyrimidine by the method of Bly and Mellon³³ except that the reaction was kept between 0 and -5°C . Five grams of 2-bromopyrimidine was then coupled as described by Bly and Mellon to yield 2,2'-bipyrimidine with the copper catalyst being activated by the method of Kleiderer and Adams.³⁴ 2-Bromo-4-methylpyrimidine (from 2-amino-4-methylpyrimidine) was prepared and coupled as above to yield the 4,4'-dimethyl-2,2'-bipyrimidine analogue.

$[\text{Ru}(\text{bpy})_2(2,9\text{-Me}_2\text{phen})](\text{PF}_6)_2$. $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$, 200 mg (380 μmol), was dissolved in 20 mL of 75% ethanol-water and was refluxed and stirred vigorously for 20 min. After subsequent addition of 100 mg (460 μmol) of 2,9-dimethyl-1,10-phenanthroline (neocuproine) monohydrate and refluxing 4 h further, the solution assumed a pink-orange color. The solvent was removed under vacuum and the solid was dried in vacuo at room temperature for 2 h. The solid was then extracted twice with ethyl ether, dried, and dissolved in about 3 mL of methanol. This solution was filtered and passed down a Sephadex column (see above for column description). The light orange luminescent band (normally the first to elute) was collected and the solvent removed under vacuum without heating. After dissolution in 5 mL of H_2O , a filtered solution of 0.05 M $\text{KPF}_6 \cdot \text{H}_2\text{O}$ was added

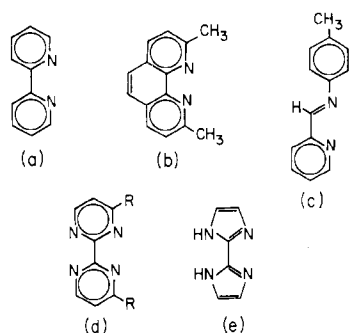


Figure 1. Structure of the ligands: (a) 2,2'-bipyridine (bpy), (b) 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂phen), (c) 2-*p*-tolylpyridinecarboxaldimine (PTPI), (d) 2,2'-bipyrimidine with R = H (bpyrm) and 4,4'-dimethyl-2,2'-bipyrimidine with R = methyl (4,4'-Me₂bpyrm), and (e) 2,2'-biimidazole (biimH₂).

dropwise until no further precipitation occurred. The solid was collected and recrystallized from dry (Na₂SO₄) acetone-ethyl ether and dried in vacuo at 80 °C for 24 h to yield 25 mg (7%) of red-orange crystals.

[Ru(bpy)₂(biimH₂)](PF₆)₂. The preparation was the same as that for [Ru(bpy)₂(2,9-Me₂phen)](PF₆)₂, but using instead 62 mg (460 μmol) of biimH₂, except that (1) the reflux time was 2 h and (2) 0.5 mL of 1 M HCl was added just before addition of the filtered KPF₆-H₂O solution. Recrystallization from dry acetone-ethyl ether and drying in vacuo at 80 °C for 24 h yielded 103 mg (33%) of red crystals.

[Ru(bpy)₂(bpyrm)](PF₆)₂ and [Ru(bpy)₂(bpyrm)Ru(bpy)₂](PF₆)₄·3H₂O. The preparation was the same as that for [Ru(bpy)₂(2,9-Me₂phen)](PF₆)₂, but using instead 63 mg (380 μmol) of bpyrm, except that (1) the reflux time was 2 h and (2) the green and red bands, which eluted on the Sephadex column after 190 and 215 mL, respectively, were collected separately, and each fraction was passed separately down the column a second time. Each product was then metathesized to a PF₆⁻ salt and recrystallized, yielding 35 mg (11%) of red crystals of the mononuclear [Ru(bpy)₂(bpyrm)](PF₆)₂ compound and 12 mg (2%) of brown crystals (from the green band) of the binuclear [Ru(bpy)₂(bpyrm)Ru(bpy)₂](PF₆)₂·3H₂O compound. Refluxing a mixture of 100 mg (190 μmol) of [Ru(bpy)₂Cl₂]·2H₂O with 16 mg (100 μmol) of bpyrm, instead of the above amounts, yielded 37 mg (12%) of [Ru(bpy)₂(bpyrm)Ru(bpy)₂](PF₆)₄·3H₂O.

[Ru(bpy)₂(4,4'-Me₂bpyrm)](PF₆)₂·H₂O and [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂](PF₆)₄. These complexes were prepared as above for [Ru(bpy)₂(bpyrm)](PF₆)₂ and [Ru(bpy)₂(bpyrm)Ru(bpy)₂](PF₆)₄, using 72 mg (380 μmol) of 4,4'-Me₂bpyrm to yield 50 mg (15%) of red crystals of [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂](PF₆)₂·H₂O and 24 mg (4%) of brown crystals of [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂](PF₆)₄.

Results and Discussion

Synthetic and Structural Considerations. The five ruthenium(II) complexes, [Ru(bpy)₂B]²⁺ (B = biimH₂, 4,4'-Me₂bpyrm, and 2,9-Me₂phen), [Ru(PTPI)₃]²⁺, and [Ru(bpy)₂(B)Ru(bpy)₂]⁴⁺ (B = 4,4'-Me₂bpyrm), reported here are synthetically new. The mononuclear B = bipyrm complex, [Ru(bpy)₂(bpyrm)]²⁺, and its binuclear analogue, [Ru(bpy)₂(bpyrm)Ru(bpy)₂]⁴⁺, have already been reported;²² however, their synthesis and separation have been effected here, for the first time, by Sephadex chromatography. The structures of bipyridine, the B ligands, and PTPI are shown in Figure 1. The two binuclear complexes, shown in Figure 2, have been isolated as by-products of the reactions leading to the mononuclear [Ru(bpy)₂B]²⁺ (B = bipyrm and 4,4'-Me₂bpyrm) complexes and are, to our knowledge, the first doubly bridged [Ru(II),Ru(II)] complexes reported. Analytical results and conductivity measurements characterize [Ru(PTPI)₃](PF₆)₂ and the [Ru(bpy)₂B](PF₆)₂ compounds as 1:2 electrolytes in acetonitrile. The range of conductivities, 37.3–50.6 μmho cm⁻¹ at 10⁻⁴ M, compares with the value of 40.8 μmho cm⁻¹ obtained for 10⁻⁴ M [Ru(bpy)₃](PF₆)₂ in acetonitrile. Likewise, the binuclear complexes have analyses

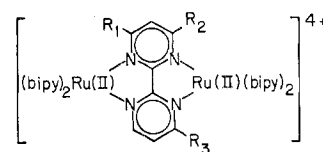


Figure 2. Structure of the binuclear [Ru(bpy)₂(B)Ru(bpy)₂]⁴⁺ cations. B = bpyrm where R₁ = R₂ = R₃ = H and B = 4,4'-Me₂bpyrm where R₁ = H, and R₂ = R₃ = CH₃ (cis isomer) or R₂ = H and R₁ = R₃ = CH₃ (trans isomer).

and conductivities consistent with their proposed formulations as 1:4 electrolytes with $\Lambda_c \approx 80 \mu\text{mho cm}^{-1}$ at 10⁻⁴ M.

The tris complex [Ru(PTPI)₃]²⁺ was prepared by the reaction of K₂[RuCl₅(H₂O)] with 3 equiv of ligand in methanol. Strong acid, as is sometimes used in the synthesis of [Ru(bpy)₃]²⁺,³⁵ must be excluded to prevent hydrolysis of the acid-sensitive imine linkages. Also, the use of sodium hypophosphite as a reducing agent was found to be unnecessary because of the apparent autoreduction of Ru(III) in the presence of the PTPI ligand and refluxing hydroxylic solvents. Attempts to isolate similar tris chelates of the methyl, propyl, and benzyl imines of pyridinaldehyde³⁶ invariably failed to yield pure compounds. Although the [Ru(bpy)₂(PTPI)]²⁺ complex was not obtained in our hands by reacting [Ru(bpy)₂Cl₂] with the PTPI ligand in methanol (as was successful for the other [Ru(bpy)₂B]²⁺ chelates), the B = 2-(imino-methyl)pyridine complex has been previously prepared by Meyer and co-workers³⁷ by electrochemical oxidation of the B = 2-(aminomethyl)pyridine complex. The [Ru(PTPI)₃](PF₆)₂ compound, as prepared here, should be dried over P₂O₅ and under vacuum at elevated temperatures for extended periods of time to eliminate excess ligand which was frequently found to contaminate the recrystallized product. Being a tris-chelate compound with unsymmetrical bidentate ligands, there exist cis (*fac*) and trans (*mer*) geometrical isomer possibilities for the [Ru(PTPI)₃]²⁺ ion.³⁸ The cis form would place the three *p*-tolyl moieties as close together as possible and would most likely be thermodynamically disfavored relative to the trans (*mer*) isomer where the groups would experience the minimum possible nonbonding interactions. We have not yet identified which form(s) is (are) present; however, ¹H NMR³⁹ and column chromatographic studies are underway to attempt detection and possibly the isolation of the two isomers. Interest in this venture stems from the fact that absorption and photoemission spectral properties of the [Ru(PTPI)₃]²⁺ ion (see below) are suggestive of the presence of more than one emitting species.

Preparation of the [Ru(bpy)₂B]²⁺ (B = bipyrm, 4,4'-Me₂bpyrm, biimH₂, 2,9-Me₂phen) complexes are synthetically straightforward, yielding products whose six-coordinate structures closely resemble those of [Ru(bpy)₃]²⁺ and the previously reported [Ru(bpy)₂(phen)]²⁺ cations.²⁰ Replacement of the chloride ligands in [Ru(bpy)₂Cl₂] by refluxing the compound in ethanol-water in the presence of the appropriate B ligand occurs in 1–2 h¹⁹ or more rapidly than previously reported for other [Ru(bpy)₂B]²⁺ complexes.^{16,20–22}

Although no tris complexes of the B ligands in the present work are known for Ru(II), in the mononuclear [Ru(bpy)₂B]²⁺ complexes the ligands all apparently function in the predicted bidentate fashion. In addition, both methyl groups of the [Ru(bpy)₂(4,4'-Me₂bpyrm)]²⁺ complex are most likely directed away from the Ru(II) ion due to the expected higher degree of steric hindrance (methyl group-bpy ring) that any alternative configuration would introduce. The existence of similar steric interactions in the [Ru(bpy)₂(2,9-Me₂phen)]²⁺ cation also argues against stability for this species and, indeed, the synthetic yield appears unusually low (7%). Furthermore, during the emission studies on this compound we noticed some

indication of decomposition under UV irradiation at $\lambda < 360$ nm; such behavior was undetected for any of the other present complexes.

In spite of the similarity in structures, it should be stressed that there exists considerable variation in the syntheses for the present $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$ complexes. Although the simplest of the syntheses is that for $\text{B} = 2,9\text{-Me}_2\text{phen}$, a longer reflux time is necessary to obtain a reasonable yield. The $\text{B} = \text{biimH}_2$ complex must be isolated under acidic conditions to ensure that the biimH_2 ligand is fully protonated.⁴⁰ Finally, the preparations of the $\text{B} = \text{bpyrm}$ and $4,4'\text{-Me}_2\text{bpyrm}$ complexes are much like that for $\text{B} = 2,9\text{-Me}_2\text{phen}$ except for the shorter reaction times and the chromatography step to remove small amounts of the binuclear complex which was always found to contaminate the monomer product.

The binuclear complexes, $[\text{Ru}(\text{bpy})_2(\text{B})\text{Ru}(\text{bpy})_2]^{4+}$ ($\text{B} = \text{bpyrm}$ and $4,4'\text{-Me}_2\text{bpyrm}$), were isolated and purified by repeated elution of the green band which elutes first down the Sephadex column during the separation of the monomer (red band) from the binuclear (green band) compound. The ratio of the yields for the monomer and binuclear complexes is highly dependent on the relative amounts of $[\text{Ru}(\text{bpy})\text{Cl}_2]$ and B ligand used (see Experimental Section); also, longer reflux times were found to slightly favor the binuclear form. Solutions of the binuclear complexes are stable over a period of hours at room temperature and will keep for days at 0°C . No analogous binuclear complex was observed when $[\text{Ru}(\text{bpy})_2(\text{biimH}_2)]^{2+}$ was prepared. This is perhaps somewhat surprising in view of recently reported biimidazolate-bridged species⁴¹ and because a $(\text{biim})^{2-}$ bridging dianion would provide for an overall charge reduction on the binuclear cation relative to the present $[\text{Ru}(\text{bpy})_2(\text{B})\text{Ru}(\text{bpy})_2]^{4+}$ complexes (also see ref 40).

The binuclear complexes are presumably products of the reaction of $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$ with $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$. For the $\text{B} = 4,4'\text{-Me}_2\text{bpyrm}$ case, the question of geometrical isomers again arises. If reaction occurs between the above two species, and if the isomer selection is kinetically controlled, then the methyl groups might be expected to be cis to one another in positions R_2 and R_3 in the structure shown in Figure 2. However, if the product formed in the reaction rearranges to a presumably more thermodynamically favored form, then the $\text{R}_1 = \text{R}_3 = \text{CH}_3$ trans isomer would be the product. Although information as to the isomer or mixture of isomers present may eventually be obtained by ¹H NMR studies, X-ray studies will probably be required to settle the question definitely.

Electrochemical Studies. A summary of the polarography data for the present complexes in acetonitrile is presented in Table I. All of the $[\text{Ru}(\text{II}) \rightarrow \text{Ru}(\text{III})]$ oxidation waves, except that for $[\text{Ru}(\text{PTPI})_3]^{2+}$, appear to be reversible or quasi-reversible one-electron processes with Δ (the slope of E vs. $\log [i/(i - i_d)]$) approximating 60 mV and the measured half-wave potentials and slopes being essentially independent of both scan rate and compound concentration. Similar behavior has also usually been found for other $[\text{Ru}(\text{bpy})_2(\alpha\text{-diimine})]^{2+}$ complexes which have been studied electrochemically.⁴³ However, the polarogram for $[\text{Ru}(\text{PTPI})_3]^{2+}$ indicates a lower degree of reversibility. The $E_{1/2}$ and Δ values obtained for the $[\text{Ru}(\text{II}) \rightarrow \text{Ru}(\text{III})]$ oxidation waves are very dependent on scan rate, and the compound tends to decompose (red \rightarrow brown color change) after current is passed through the solution for about 60 s. Nevertheless, scans made at faster rates than used for the other complexes yielded a half-wave potential of 1.17 V and a diffusion current of 10 μA , compared with that for $[\text{Ru}(\text{bpy})_3]^{2+}$ of 10.2 μA . This result, along with an observed slope Δ of about 100 mV, implies that the electrochemical oxidation of $[\text{Ru}(\text{PTPI})_3]^{2+}$ is a one-electron process, albeit a highly irreversible one. The $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$

Table I. Polarography Data for the Ruthenium(II) Complexes in Acetonitrile^a

complex	$E_{1/2}$, V	Δ , mV	i_d , μA
$[\text{Ru}(\text{bpy})_2(\text{biimH}_2)]^{2+,3+}$	0.93 ^b	63	10.6
$[\text{Ru}(\text{PTPI})_3]^{2+,3+}$	1.17 ^c	100	10.0
$[\text{Ru}(\text{bpy})_2(2,9\text{-Me}_2\text{phen})]^{2+,3+}$	1.18	67	11.3
$[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+,3+}$	1.25	73	10.7
$[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+,3+}$	1.29	79	12.4
$[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+,5+}$	1.43 ^d	62 ^e	19.1
$[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{5+,6+}$	1.60 ^d	64 ^e	
$[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+,5+}$	1.44 ^d	64 ^e	
$[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{5+,6+}$	1.62 ^d	68 ^e	20.4

^a Half-wave potentials measured at $23 \pm 2^\circ\text{C}$ at a rotating Pt electrode (RPE) in deaerated 1.0×10^{-4} M solutions of the complexes, 0.1 M in NaClO_4 as the supporting electrolyte. The estimated maximum errors in the half-wave potentials ($E_{1/2}$), slopes of $E_{1/2}$ vs. $\log [i/(i - i_d)]$ plots (Δ), and i_d are 0.01 V, 2 mV, and 0.3 μA , respectively. Values for $[\text{Ru}(\text{bpy})_3]^{2+,3+}$ under the same conditions are 1.19 V, 63 mV, and 10.2 μA , respectively. Unless otherwise noted, the scan rate was 5 mV s^{-1} . The half-wave potentials are formally reduction potentials and are reported vs. the saturated KCl calomel electrode (SCE). ^b Measured in 5×10^{-4} M $\text{HClO}_4\text{-CH}_3\text{CN}$ (see text). ^c Estimated from polarogram with a scan rate of 100 mV s^{-1} . ^d Estimated from peak maxima of the $(\delta i/\delta E)$ plot (see Figure 3). ^e Estimated from $\Delta = -1/4(i_d)(\delta i/\delta E)$ at $E = E_{1/2}^{-1}$.

species behave in a more conventional manner with properties reminiscent of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. All the compounds possess slopes in the range of $\Delta = 63\text{--}79$ mV which are characteristic of quasi-reversible one-electron oxidations. However, the wide range of half-wave potentials ($E_{1/2} = 0.93\text{--}1.29$ V) for the series is rather surprising in light of other known $[\text{Ru}(\text{bpy})_2\text{B}]^{2+}$ complexes. For instance, the $\text{B} = 1,8\text{-naphthyridine}$, $2\text{-methyl-}1,8\text{-naphthyridine}$, $2,7\text{-dimethyl-}1,8\text{-naphthyridine}$, and $\text{pyrido}[2,3\text{-}b]\text{pyrazine}$ complexes all have similar $E_{1/2}$ values ranging from only 1.25 to 1.32 V.¹⁹

The half-wave potentials in Table I suggest a π -acceptor ability^{19,44} for these neutral ligands of $\text{biimH}_2 \ll 2,9\text{-Me}_2\text{phen} \sim \text{bpy} < 4,4'\text{-Me}_2\text{bpyrm} < \text{bpyrm}$. This order is perhaps not surprising except for the seemingly poor π -acceptor ability of the biimH_2 ligand, which judging by its $E_{1/2}$ potential, makes it comparable to ammonia in $[\text{Ru}(\text{bpy})_2(\text{NH}_3)_2]^{2+}$ ($E_{1/2} = 0.92$ V).¹⁸ In addition, it is interesting to note that the coordinated biimH_2 ligand is so easily deprotonated in acetonitrile⁴⁰ that the electrochemical measurements had to be performed on solutions $125 \mu\text{M}$ in HClO_4 to ensure that the complex was kept fully protonated. It therefore seems reasonable to assume that deprotonated forms of the complex, such as $[\text{Ru}(\text{bpy})_2(\text{biimH})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{biim})]^0$, might eventually be isolatable.

The effect of methyl-group substitution for the $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+}$ compound is to shift the half-wave potential -0.02 V per group as compared to the parent $[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$ complex, and qualitatively, this same substituent effect has also been observed for $[\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3]^{2+}$ and $[\text{Ru}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ were $\Delta E_{1/2} = -0.027$ and -0.028 V per methyl group relative to the unsubstituted parent compounds.³⁵ However, an analogous substituent effect is not observed in the case of the $[\text{Ru}(\text{bpy})_2(2,9\text{-Me}_2\text{phen})]^{2+}$ complex, since the $E_{1/2} = 1.18$ V value is essentially that expected for $[\text{Ru}(\text{bpy})_2(\text{phen})]^{2+}$; i.e., $E_{1/2}([\text{Ru}(\text{bpy})_3]^{2+}) = 1.19$ V and $E_{1/2}([\text{Ru}(\text{phen})_3]^{2+}) = 1.18$ V. Thus, the normally observed methyl group electronic effect is apparently absent or offset by some additional effect(s), possibly steric in origin.

The polarograms of the binuclear complexes each consist of two, one-electron oxidation steps. Actual data for the $\text{B} = 4,4'\text{-Me}_2\text{bpyrm}$ binuclear and mononuclear species are displayed in Figure 3. Simple charge accumulation in the

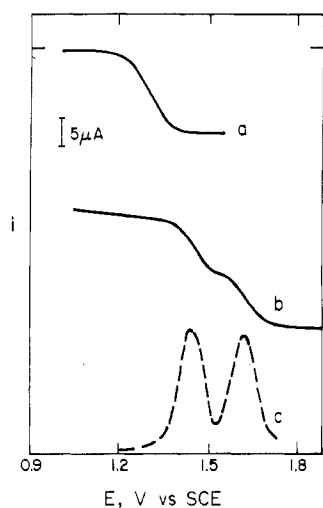


Figure 3. Polarograms in acetonitrile: (a) $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+}$, (b) $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$, (c) derivative ($\delta i/\delta E$) of (b).

Table II. Absorption and Emission Spectral Data for the Ruthenium(II) Complexes in Acetonitrile at Room Temperature^a

compd	absorption ($d\pi^*$)		emission λ_{max} , nm
	λ_{max} , nm	$10^{-4}\epsilon_{\text{max}}$, $\text{M}^{-1}\text{cm}^{-1}$	
$[\text{Ru}(\text{PTPI})_3]^{2+}$	552	0.72	~ 345 sh,
	496	0.63	400
$[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$	420	1.05	600
$[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+}$	442	1.09	598
$[\text{Ru}(\text{bpy})_2(2,9\text{-Me}_2\text{phen})]^{2+}$	452	1.36	588
	378	0.60	
$[\text{Ru}(\text{bpy})_2(\text{biimH}_2)]^{2+}$	448 ^b	0.95	595
$[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$	592	0.79	none
	408	2.98	
$[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{-Ru}(\text{bpy})_2]^{4+}$	578	0.72	none
	412	2.41	

^a Measured at 2×10^{-5} M. ^b Measured in 5×10^{-4} M in HClO_4 .

binuclear complex probably accounts for the more positive potentials relative to the mononuclear form. In addition, the observed slopes of $\Delta = 62\text{--}68$ for the binuclear compound oxidation waves indicate an increased degree of reversibility over the corresponding mononuclear complexes ($\Delta = 73$ and 79). This trend seems reasonable since the degree of $[\text{Pt}(\text{electrode})\text{-N}(\text{complex})]$ adsorption, leading to irreversible electrode processes, would likely increase according to the order binuclear compounds $< [\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+} < [\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$. The total diffusion currents (i_d) of 19.1 and 20.4 for the binuclear species are approximately twice those of the mononuclear complexes as expected.

The two, one-electron wave nature of the binuclear compound oxidations is reminiscent of the two-step oxidation pattern exhibited by the Creutz-Taube ion, $[\text{Ru}(\text{NH}_3)_5(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{4+}$ (pyr = pyrazine), which can be oxidized stepwise ($\Delta E_{1/2} = 0.36$ V) to yield the mixed-valence $[\text{Ru}(\text{II}),\text{Ru}(\text{III})]$ and fully oxidized $[\text{Ru}(\text{III}),\text{Ru}(\text{III})]$ species.⁴⁵ In the $[\text{Ru}(\text{III}),\text{Ru}(\text{III})]$ complex, the two $S = 1/2$ centers undergo a weak magnetic exchange interaction across the pyrazine bridge with an antiferromagnetic coupling constant of $-J \approx 5 \text{ cm}^{-1}$.⁴⁶ For the present $[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ and $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ complexes where $\Delta E_{1/2} \approx 0.18$ V in each case, it is also likely that the mixed-valence (5+) and fully oxidized (6+) complexes can be isolated either by Ce(IV) oxidative titration or by controlled-potential electrochemical synthesis. These efforts are currently underway since the fully oxidized species, with two δ and π -conjugated pathways between $S =$

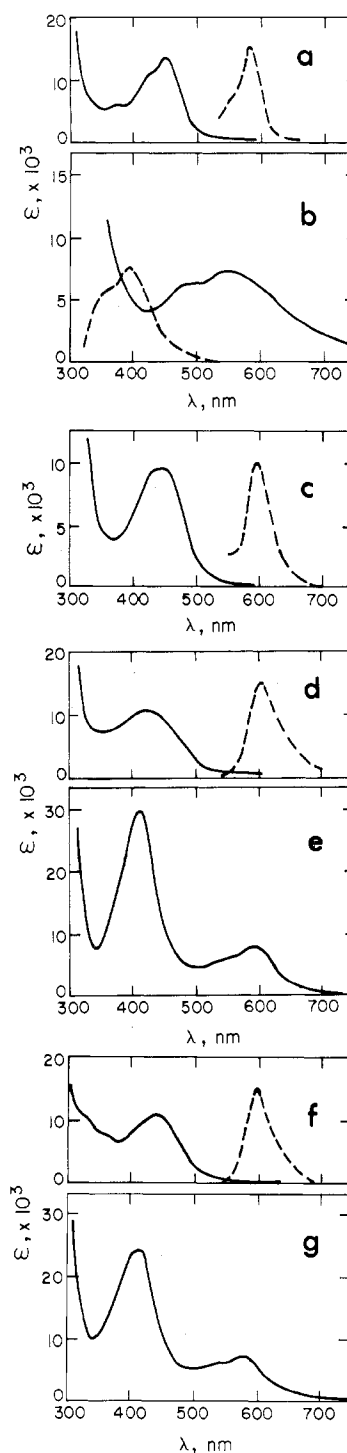


Figure 4. Absorption and emission spectra (in broken line) for the ruthenium(II) complexes at 10^{-4} M in acetonitrile at room temperature: (a) $[\text{Ru}(\text{bpy})_2(2,9\text{-Me}_2\text{phen})]^{2+}$, (b) $[\text{Ru}(\text{PTPI})_2]^{2+}$, (c) $[\text{Ru}(\text{bpy})_2(\text{biimH}_2)]^{2+}$ (5×10^{-4} M in HClO_4), (d) $[\text{Ru}(\text{bpy})_2(\text{bpyrm})]^{2+}$, (e) $[\text{Ru}(\text{bpy})_2(\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ (no emission observed), (f) $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})]^{2+}$, (g) $[\text{Ru}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpyrm})\text{Ru}(\text{bpy})_2]^{4+}$ (no emission observed).

$1/2$ ruthenium centers, would be of interest for comparative magnetic exchange studies with the Creutz-Taube ion where only one pathway exists.

Visible Absorption and Luminescence Spectral Studies. Absorption and emission spectral data for the compounds in acetonitrile are given in Table II. The actual absorption and emission spectra (at arbitrary intensity) are displayed in Figure 4.

The absorption spectrum of [Ru(PTPI)]²⁺ in Figure 4b appears to display two very broad peaks, one at 552 nm and a less intense one at 496 nm, which are probably *dπ** in origin. This behavior is very unlike the sharper band spectra of the other [Ru(bpy)₂B]²⁺ complexes but is similar to the spectrum of the B = 2-(iminomethyl)pyridine complex,³⁷ although the spectrum for the [Ru(PTPI)₃]²⁺ complex is at lower energy. The spectrum is otherwise unremarkable except that a strong emission also occurs in the 330–450-nm region which is very similar in shape and pattern to the absorption spectrum. This result is consistent with the possibility of cis–trans isomerism for this complex (*vide supra*) if one absorption and emission peak is due to each of the isomers. Because of the short wavelength of the emission, it is unlikely that it is *dπ** charge transfer in origin. The free PTPI ligand itself has no emission spectrum in the region.

The absorption spectra of the [Ru(bpy)₂B]²⁺ complexes are very similar to that of [Ru(bpy)₃]²⁺ in intensity, energy, and shape; however, the presumably *dπ** absorption bands are, in general, weaker in intensity than for [Ru(bpy)₃]²⁺ (ϵ 1.46×10^4 M⁻¹ cm⁻¹).⁴⁷ The emission spectra of the [Ru(bpy)₂B]²⁺ complexes are equally reminiscent to that of [Ru(bpy)₃]²⁺. The relatively narrow bands are centered around 600 nm⁴⁸ and are observed upon sample irradiation at all wavelengths shorter than 500 nm. The emission intensity varies with excitation wavelength much like that for [Ru(bpy)₃]²⁺, indicating that the near-unity efficiency of $\pi\pi^*$ –*dπ** conversion found for [Ru(bpy)₃]²⁺⁴⁹ may also be operative in the present series as well. The emission maxima for the complexes span a range of only 588–600 nm, a far narrower range than previously found for a [Ru(bpy)₂X₂] series⁴⁹ or [Ru(4,4'-R₂bpy)₃]²⁺ series⁵⁰ of complexes.

The visible absorption spectra of the [Ru(bpy)₂(B)Ru(bpy)₂]⁴⁺ binuclear complexes are dominated by a strong band at about 410 nm and a much weaker band at about 580–590 nm. The 410-nm bands, due to their sharpness and intensity (about twice that of the [Ru(bpy)₂B]²⁺ *dπ** bands), are probably the same type *dπ** charge-transfer bands as found in the related mononuclear species. The shift to slightly higher energies can be rationalized by assuming a small additional electrostatic energy required to remove the optical electron from one Ru(II) ion to an adjacent bipyridine ligand and, thus, further from the other electropositive Ru(II) ion. Emission in the visible region from irradiated samples of the [Ru(bpy)₂(B)Ru(bpy)₂]⁴⁺ complexes is not observed at room temperature in solution (Figure 4), although Hunziker and Ludi have observed 769- and 850-nm emission bands for the B = bpyrm complex in the solid at ~15 K.²² It therefore appears that further temperature-dependent emission (and lifetime) studies of these [Ru(bpy)₂(B)Ru(bpy)₂]⁴⁺⁵¹ pure and possibly mixed-valence binuclear species will be of considerable interest.

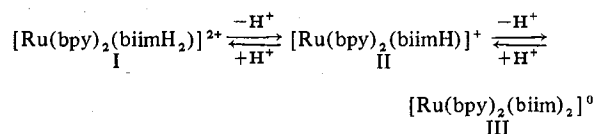
Acknowledgment. We wish to thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation (under Grant C-627) for support of this work. We also thank Mr. Randall Petty and Mr. Ken Goldsby for preparing the bipyrimidine ligands.

Registry No. [Ru(PTPI)₃](PF₆)₂, 66810-62-6; [Ru(bpy)₂(2,9-Me₂phen)](PF₆)₂, 66810-60-4; [Ru(bpy)₂(biimH₂)](PF₆)₂, 66826-58-2; [Ru(bpy)₂(bpyrm)](PF₆)₂, 65013-23-2; [Ru(bpy)₂(bpyrm)Ru(bpy)₂](PF₆)₄, 65013-25-4; [Ru(bpy)₂(4,4'-Me₂bpyrm)](PF₆)₂, 66826-65-1; [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂](PF₆)₄, 67114-13-0; [Ru(bpy)₂(biimH₂)]³⁺, 66826-63-9; [Ru(PTPI)₃]³⁺, 66826-62-8; [Ru(bpy)₂(2,9-Me₂phen)]³⁺, 66826-61-7; [Ru(bpy)₂(4,4'-Me₂bpyrm)]³⁺, 66826-60-6; [Ru(bpy)₂(bpyrm)]³⁺, 66826-59-3; [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂]³⁺, 67113-70-6; [Ru(bpy)₂(4,4'-Me₂bpyrm)Ru(bpy)₂]⁶⁺, 67114-14-1; [Ru(bpy)₂(bpyrm)Ru(bpy)₂]⁶⁺, 67113-73-9; [Ru(bpy)₂(bpyrm)Ru(bpy)₂]⁶⁺, 66859-37-8;

PTPI, 7471-13-8; 2-pyridinecarboxaldehyde, 1121-60-4; *p*-toluidine, 25640-74-8; K₂[RuCl₅(H₂O)], 14404-33-2; Ru(bpy)₂Cl₂, 15746-57-3.

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Manganese(II) and Chromium(II) Porphyrin Complexes: Synthesis and Characterization

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The chromous acetylacetonone reduction method has been applied to the synthesis of the highly reactive, coordinatively unsaturated, metalloporphyrins M(TPP) (TPP = tetraphenylporphyrin) and M(OEP) (OEP = octaethylporphyrin) for M = Mn(II) and Cr(II); all are high-spin complexes. Five-coordinate high-spin derivatives Mn(TPP)L and Mn(OEP)L are formed with axial ligands L = pyridines or imidazoles. No six-coordinate low-spin derivatives are formed with Mn(II). However, six-coordinate Cr(TPP)L₂ derivatives are readily formed and are low spin having two unpaired electrons. Synthesis and characterization difficulties are discussed in detail.

Our long term interest in the study of new dioxygen adducts of transition-metal complexes has necessitated the development of convenient synthetic routes to their low-valent precursors. In many cases the existence of low-valent metalloporphyrins has been indicated by electrochemical investigations and solution spectral observations² but the isolation and definitive structural characterization of such complexes have often proved difficult. In particular, the exact nature and number of axial ligands in many transition-metal porphyrin complexes has been ill-defined especially when the oxidation states involved are ones other than those of common occurrence with aerobic stability. The more recent application of alternate synthetic methods, aided well by the user-convenient inert atmosphere glovebox, has allowed the isolation of pure crystalline materials many of which have been the subject of single-crystal x-ray investigations to ultimately establish their structural identity. For example, all possible axial ligation states of iron(II) tetraphenylporphyrin complexes have been characterized,³⁻⁵ as have those for cobalt(II).⁶⁻⁸ The structural interest in these complexes has largely centered around the interplay of magnetic states and metal-ligand bond lengths (particularly out-of-plane displacements of the metal from the porphyrin) as a function of dⁿ configuration and axial ligation states.⁹ A consistent pattern of structural features, satisfyingly rationalized by simple ligand field considerations, is now emerging and its importance to the understanding of hemo-protein stereochemistry has been widely discussed.^{10,11}

One particularly attractive synthetic route to low-valent metalloporphyrins is the reduction of halogeno higher oxidation state derivatives with the acetylacetonone complex of chromium(II) since not only is Cr(acac)₂ a powerful one-electron reductant but it usually sequesters the halogeno ligand thereby creating a vacant coordination site (eq 1). A number of

$$M^{III}Cl(\text{por}) + \text{Cr}(\text{acac})_2 \rightarrow M^{II}(\text{por}) + \text{CrCl}(\text{acac})_2 \quad (1)$$

por = porphyrin

hitherto unknown "bare" metalloporphyrins (without axial ligands) have been generated in this way providing convenient substrates for the addition of axial ligands of choice. In one case the assumed bridging ligand atom-transfer nature of the redox process implied by eq 1 has been established by tracer

methods.¹³ The other notable feature of Cr(acac)₂ is its solubility in organic solvents such as toluene allowing one to avoid the use of donor solvents which might otherwise end up as ligands. One interesting feature emanating from the structures of the toluene solvates Cr(TPP)·2(toluene)¹⁴ and Mn(TPP)·2(toluene)¹⁵ is the weak but significant π-complex interaction of toluene with the metalloporphyrin ring.

We have published preliminary notes on the formation of dioxygen adducts derived from manganese(II)¹⁶ and chromium(II)¹⁷ porphyrins and these studies will be the subject of future publications when their definitive structural characterization is complete. Herein we report the detailed syntheses and properties of a variety of manganese(II) and chromium(II) porphyrin complexes emphasizing how characterization difficulties have been overcome. In particular, the propensity of tetraphenylporphyrin complexes to form solvates, thereby complicating elemental analyses, led us to develop ligand and solvate analyses based on gas chromatographic techniques. In most cases good quantitative analyses were obtained. Certainly qualitative GLC solvate analyses are trivial suggesting that, at least, such solvate analysis should be obligatory for researchers who include solvates for proper fit of elemental analyses when other verification techniques such as mass or NMR spectroscopy are inaccessible. Full papers on the x-ray crystal structures of three of the compounds whose syntheses are reported herein have already been published: Mn(TPP)·2(toluene),¹⁵ Mn(TPP)(1-MeIm)·0.8THF,³⁰ and Cr(TPP)·2(toluene).¹⁴

That manganese(II) can be usefully employed as a substitute for iron in studying hemoglobin allosteric effects¹⁸ has furthered our interest in establishing the fundamental coordination chemistry of manganese(II) porphyrins. Several other hemoproteins have been investigated with manganese replacing iron.³⁷ We note in passing that manganese porphyrins have been investigated¹⁹ as possible models for the manganese-dependent evolution of oxygen in photosynthesis and also, the existence of manganese porphyrins in human²⁰ and rat²¹ erythrocytes has been reported. Their function is unknown although the similarities of their structural chemistry to iron uncovered by our studies suggest that organisms may not be able to rigorously discriminate between iron and manganese.