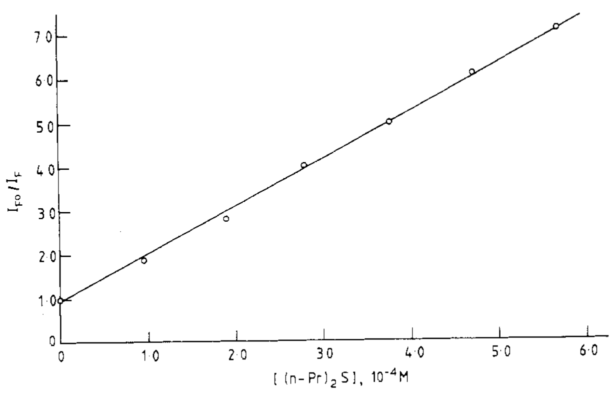

Figure 5. Stern–Volmer plot for the quenching of the luminescence intensity of uranyl ion by di-*n*-propyl sulfide: $[UO_2(NO_3)_2] = 0.05$ M, $[HClO_4] = 0.1$ M, $\lambda_{exc} = 410 \pm 10$ nm, $\lambda_{em} = 510 \pm 10$ nm, solvent 75%:25% MeCN–H_2O.

acetate in 0.1 M sulfuric acid as 3.46 μs, which implies a second-order quenching rate constant of 0.225×10^9 M^{-1} s^{-1}, i.e. rather lower than our values given in Table V. Accordingly we have measured K^{SV} for the quenching of excited [U(VI)] acetate (0.02 M) in dilute H_2SO_4 (0.1 M) in a water–acetone medium (3:4 v/v) by di-*n*-butyl sulfide as 1402 ± 20 M^{-1}, in fair agreement with the figures for other R_2S compounds given in ref 1; i.e., the use of acetate salt gives a ca. factor of 5 reduction in K^{SV} compared with the value for the nitrate salt. Finally we determined the absolute second-order quenching rate constant for quenching of $[U(VI)]^*$ in this same system as $(3.10 \pm 0.53) \times 10^8$ M^{-1} s^{-1}; i.e., the excited U(VI) acetate is only one-third as reactive as the excited nitrate salt (cf. Table IV).

Clearly there are some unusual features associated with the quenching by R_2S of $[UO_2^{2+}]^*$; thus a large kinetic quenching rate constant, nearing the diffusion-control limit of ca 1.8×10^{10} dm^3 mol^{-1} s^{-1} is *not* matched by a large photoredox quantum yield, implying that the vast majority of exciplexes $[R_2S{\cdot}UO_2^{2+}]^*$ decay by nonchemical pathways, particularly those described by k_5 and k_{-4} in the reaction scheme.

In summary, we support the values given in ref 1 for K^{SV}, we note a marked difference in kinetic reactivity toward R_2S between excited uranium(VI) nitrate and acetate, and we believe the quantum yields for U(IV) production in ref 1 are erroneously high.

Registry No. $(n\text{-}C_4H_9)_2S$, 544-40-1; $(n\text{-}C_3H_7)_2S$, 111-47-7; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; uranyl acetate, 541-09-3; uranyl nitrate, 10102-06-4.

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Strongly Luminescing Ruthenium(II)/Ruthenium(II) and Ruthenium(II)/Platinum(II) Binuclear Complexes

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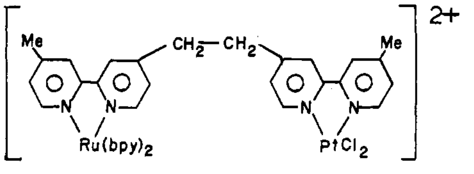
One goal in our laboratories is to prepare and characterize binuclear and oligonuclear multielectron-transfer agents designed for both light sensitivity and catalytic activity. The importance of multielectron-transfer agents can be illustrated by considering the photochemical "splitting" of water. Both $Ru(bpy)_3^{2+,1-3}$ where bpy is 2,2′-bipyridine, and metalloporphyrins[4-6] have been suggested or used as photocatalysts for this process. Unfortunately, these compounds transfer only one electron from the excited-state upon visible-light absorpton, which causes problems mechanistically in their use for the reduction or oxidation of substrates. As a step toward overcoming this dilemma, two strongly luminescing complexes have been prepared and characterized. The one is a ruthenium(II)/ruthenium(II) homobinuclear complex; the other is a ruthenium(II)/platinum(II) heterobinuclear complex. The heterobinuclear complex is shown in I for illustrative purposes.



I

The important structural feature of the complex is the novel 4,4′-dimethyl-2,2′-bipyridine dimer, Mebpy–Mebpy,[7] which provides two bidentate sites for coordination. The mononuclear ruthenium(II), the binuclear ruthenium(II)/ruthenium(II), and heterobinuclear ruthenium(II)/platinum(II) complexes were isolated as described below. The yellow mononuclear dichloroplatinum(II) and binuclear bis(dichlorplatinum(II)) analogues were also prepared but were too insoluble for characterization studies.

The ligand, Mebpy–Mebpy, was prepared by an adaptation of the procedure of Elliott and co-workers.[7] Purification of the crude product was achieved through several recrystallizations from toluene, which resulted in a final yield of ~60%. The purity of the product was checked by melting point (186–188 °C), mass spectrometry, and NMR spectroscopy.

The preparative procedure for $[Ru(bpy)_2(Mebpy\text{–}Mebpy)](CF_3SO_3)_2$[8] involved substitution of acetone for chloride ion in the coordination sphere of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.2 mmol) by reaction with $Ag(CF_3SO_3)$ (0.40 mmol) in 80 mL of acetone.[9] The AgCl that formed was removed by filtration, and the brownish red filtrate was added drop by drop (1 drop/10 s) to a refluxing solution of 0.80 g (2.2 mmol) of Mebpy–Mebpy dissolved in 1500 mL of acetone contained in a 3-L round-bottom flask. The resulting bright orange solution, which luminesced very strongly under UV light, was allowed to reflux for 30 min after the last addition (total addition time was about 8 h). The crude product was isolated by reducing the solvent volume to ~20 mL with a rotary evaporator and precipitating the product by the addition of the concentrated solution to ether. The complex was purified by column chromatography (neutral alumina developed with acetone). The middle fraction was precipitated in 60% yield, filtered out under nitrogen in Schlenkware, and dried under vacuum.

$[(bpy)_2Ru(Mebpy\text{–}Mebpy)Ru(bpy)_2](CF_3SO_3)_4$[8] was prepared by the same procedure as the mononuclear species except the reactants were mixed in stoichiometric amounts and the reaction was allowed to reflux for 5 days. The pure binuclear complex was obtained in 81% yield.

The preparation of $[(bpy)_2Ru(Mebpy\text{–}Mebpy)PtCl_2](PF_6)_2{\cdot}2H_2O$[8] was effected in the dark. A 0.065-g (0.15-mmol) sample of *cis*-$[Pt(Me_2SO)_2Cl_2]$[10] was suspended in 75 mL of methanol

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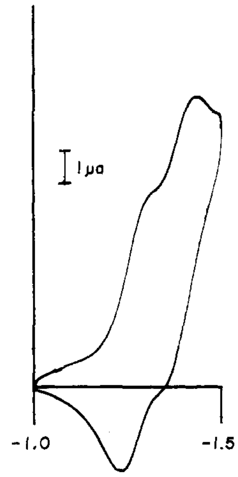

Figure 1. Cyclic voltammogram of the first reductions of $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$ in propylene carbonate. The electrolyte was 0.1 M TEAP, and the sweep rate was 200 mV/s. The measurement was recorded at a Pt-disk working electrode vs. the SSCE. The electrochemical data were obtained with a PAR 174A polarographic analyzer.

containing 0.108 g (0.1 mmol) of $[Ru(bpy)_2(Mebpy–Mebpy)](CF_3SO_3)_2$, and the mixture was refluxed under nitrogen for 8 h. The resulting orange-red solution was cooled and filtered. The volume of the filtrate was reduced to ~20 mL by rotary evaporation, and a saturated solution of NH_4PF_6(~5 mL in H_2O) was added to precipitate the PF_6^- salt. The pure heterobinuclear complex was obtained in 75% yield after filtering, washing with H_2O, and vacuum drying.

The trifluoro sulfonate salts were soluble in a wide range of solvents; the PF_6^- salt was soluble in polar organic solvents. Propylene carbonate proved useful for electrochemical and spectral investigations.

The redox properties of Ru(II), Ru(II)/Ru(II), and Ru(II)/Pt(II) complexes resemble each other. All exhibit a reversible $Ru^{3+/2+}$ redox process at 1.19 V and a reversible one-electron reduction of −1.38 V vs. SSCE, which is associated with reduction of one of the bipyridine ligands coordinated to ruthenium(II) (eq 1). The assignment is reasonable given the fact that the Me_2bpy

$$[Ru(Mebpy–Mebpy)(bpy)(bpy)] + e^- \rightleftarrows [Ru(Mebpy–Mebpy)(bpy)(bpy^-)]^+ \quad (1)$$

ligand reduction in $Ru(Me_2bpy)_3^{2+}$, where Me_2bpy is 4,4′-dimethyl-2,2′-bipyridine, occurs at −1.46 V[11] compared to −1.31 V for the reduction of bpy in $Ru(bpy)_3^{2+}$.[12]

The heterobinuclear complex exhibits another reversible one-electron process at $E_{1/2} = -1.27$ V, as shown in Figure 1. This redox process corresponds to reduction of the "Mebpy" unit coordinated to platinum(II) (eq 2). This was verified by inde-

$$[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+} + e^- \rightleftarrows [(bpy)_2Ru(Mebpy–Mebpy^-)PtCl_2]^+ \quad (2)$$

pendently synthesizing and studying the redox properties of $[(Me_2bpy)PtCl_2]$, which underwent reduction at −1.31 V vs. SSCE.

The more positive ligand reduction potential for the platinum(II) complex compared to those of ruthenium(II) complexes is related to π-back-bonding properties, since both have similar charges and, hence, a similar electrostatic influence on the energy of the π* ligand orbitals. Apparently, the dπ levels of platinum(II) are too different in energy from the π* ligand levels to overlap appreciably. Thus, the π* ligand levels remain stabilized in the presence of platinum(II) whereas they are destabilized when coordinated to ruthenium(II) by π back-bonding of the dπ metal orbitals with the π* orbitals of the ligand.[13]

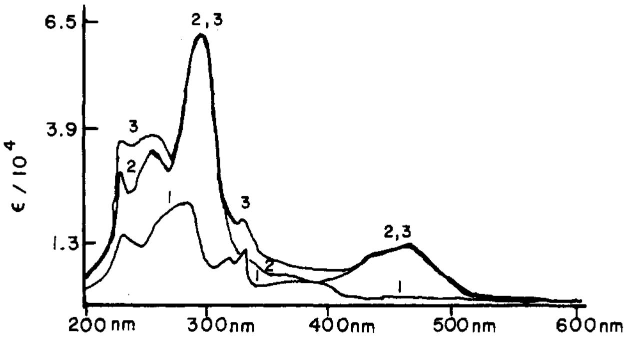

Figure 2. Visible–UV electronic spectral comparison of the complexes $[(Me_2bpy)PtCl_2]$ (1), $[(bpy)_2Ru(Mebpy–Mebpy)]^{2+}$ (2), and $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$ (3) in propylene carbonate. The λ_{max} (in nm) and $\epsilon(M^{-1}\ cm^{-1})$ (in parentheses) values for $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$ are 457 (1.3×10^4), 324 (1.8×10^4), 289 (7.7×10^4), 249 (3.6×10^4) and 223 (3.5×10^4). The data were obtained with a Perkin-Elmer Lamda Array 3840 diode-array spectrophotometer.

The visible spectra of the Ru(II), Ru(II)/Ru(II), and Ru(II)/Pt(II) complexes in propylene carbonate are quite similar. The $d\pi \rightarrow \pi_1^*$ transitions are centered at 457 nm, the $d\pi \rightarrow \pi_2^*$ transitions are observed at 360 nm, and the $\pi \rightarrow \pi^*$ transitions are located at 289, 250, and 220 nm. For equimolar solutions, the absorption coefficients for the various optical transitions of $[(bpy)_2Ru(Mebpy–Mebpy)Ru(bpy)_2]^{4+}$ are approximately twice as large as those for $[(bpy)_2Ru(Mebpy–Mebpy)]^{2+}$ or $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$, and this is in accord with the presence of two ruthenium(II) centers. In Figure 2, the spectral overlay of $[(Me_2bpy)PtCl_2]$, $[(bpy)_2Ru(Mebpy–Mebpy)]^{2+}$, and $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$ clearly shows that the absorptions of the "$Ru(bpy)_2$(Mebpy–)" component predominate in the spectrum of the heterobinuclear complex, although one additional intense band at 324 nm ($\epsilon = 1.8 \times 10^4\ M^{-1}\ cm^{-1}$) is present for $[(bpy)_2Ru(Mebpy–Mebpy)PtCl_2]^{2+}$. This is probably an MLCT band associated with the transition of an electron from one of the filled d orbitals of platinum(II) to the empty π* orbital of the heterocyclic ligand.

The luminescence behavior of the homobinuclear and heterobinuclear complexes is comparable to that of $Ru(bpy)_3^{2+}$, although the luminescence maxima are red shifted from 615 to 620 nm. The room-temperature excited-state lifetimes of the mononuclear, homobinuclear, and heterobinuclear complexes in nitrogen-degassed propylene carbonate are 1009, 1037, and 1034 ns, respectively, compared to 980 ns for $Ru(bpy)_3^{2+*}$.[14] The luminescence quantum yields for the complexes in propylene carbonate are all about 0.06 compared to 0.07 for $Ru(bpy)_3^{2+*}$ under similar conditions.[15] This is in marked contrast to the low luminescence quantum yields of 0.003 reported by Gafney and co-workers[16] for the homobinuclear complex $[(bpy)_2Ru(dpp)Ru(bpy)_2]_4^+$ in ethanol, where dpp is 2,3-bis(2-pyridyl)pyrazine, and the low quantum yield reported by Scandola and co-workers[17] for the heterobinuclear complex $[Ru(bpy)_2(CN)_2Pt(diene)]^{2+}$, where CN^- acts as a monodentate bridging ligand and the diene is diethylenetriamine.

In summary, the attractive features of the binuclear complexes reported here are their stability due to the bidentate chelating capability of the bridging ligand, the $Ru(bpy)_3^{2+*}$-like luminescence behavior, and the insulating effect of the ethylene bridge of the Mebpy–Mebpy ligand. These features result in new complexes that will provide the opportunity for detailed photophysical

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studies related to donor–acceptor interactions and to the possibility of two simultaneous single-electron transfer events.

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^{1}H NMR Investigation of Iron(III) 5,10,15,20-Tetrakis(2,6-disubstituted phenyl)porphyrins. Isolation and Characterization of Hydroxy-Ligated (5,10,15,20-Tetrakis(2,6-difluorophenyl)porphinato)iron(III)

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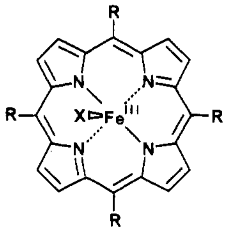
Reaction of iron(III) porphyrins with HO^- results in the formation of μ-oxo dimer species. Kinetic studies have shown that hydroxy ligation is a first step in the formation of the μ-oxo dimer. The sequence of reactions of eq 1 have been suggested (where (P)

$$\begin{aligned}(P)Fe^{III}OH &\rightleftarrows [(P)Fe^{III}]^+ + HO^- \\ (P)Fe^{III}OH + [(P)Fe^{III}]^+ &\rightarrow [(P)Fe^{III}]_2O + H^+\end{aligned} \tag{1}$$

= porphyrin dianion).[1] Several reports of the characterization of hydroxy-ligated iron(III) porphyrins have recently appeared.[2-5] Success in their preparation is dependent upon the use of porphyrins carrying bulky substituents that prevent face to face approach of the porphyrin rings. This has been accomplished with iron(III) ligated by (i) a "basket-handle" porphyrin,[5] (ii) a "picket fence" porphyrin,[3] and (iii) 5,10,15,20-tetraphenylporphyrins carrying bulky substituents in the 2,6-positions of the phenyl rings.[2]

We now wish to report the preparation and the characterization of hydroxide-ligated (5,10,15,20-tetrakis(2,6-difluorophenyl)-porphinato)iron(III) ((F_8TPP)Fe^{III}OH) as well as ^{1}H NMR studies of various HO^- and Cl^--ligated (5,10,15,20-tetrakis(2,6-disubstituted phenyl)porphinato)iron(III) salts.



R	structural abbreviation
phenyl	(TPP)Fe^{III}X
2,6-dimethylphenyl	(Me_8TPP)Fe^{III}X
2,4,6-trimethylphenyl	(Me_{12}TPP)Fe^{III}X
2,6-dichlorophenyl	(Cl_8TPP)Fe^{III}X
2,6-difluorophenyl	(F_8TPP)Fe^{III}X
pentafluorophenyl	(F_{20}TPP)Fe^{III}X

Table I. ^{1}H NMR Spectral Positions of Iron(III) Porphyrin Complexes (Solvent CD_2Cl_2; Reference Me_4Si at 25 °C)

	δ					
compd	pyrrole	meta	para	ortho	OH[a,b]	ref
(F_8TPP)Fe^{III}Cl	81.1 (358 ± 9)[d]	13.9 12.6	7.5			*c*
(F_8TPP)Fe^{III}OH	81.0 (831 ± 6)	10.6 11.5	7.6		23.8	*c*
(Cl_8TPP)Fe^{III}Cl	80.7 (380 ± 9)	12.8 14.1	8.3			*c*
(Cl_8TPP)Fe^{III}OH	80.6 (702 ± 6)	10.8 11.4	8.1		23.2	*c*
(Me_8TPP)Fe^{III}Cl	80.0 (365 ± 8)	15.8 14.2	8.2	3.8[b] 6.6[b]		*c*
(Me_8TPP)Fe^{III}OH	81.1 (809 ± 9)	12.1 11.3	8.0	2.8[b]	24.9	*c*
(Me_{12}TPP)Fe^{III}OH	79.2 (535 ± 25)	11.1 12.0	3.3			2

[a] Tentatively assigned to OH group. [b] Broad signal. [c] This work. [d] Line width at half-height in hertz.

The (F_8TPP)Fe^{III}OH salt is of particular interest because of the small steric demands of the fluoro substituent.

Experimental Section

Materials. Pyrrole, 2,4,6-collidine, 2,6-dichlorobenzaldehyde, and 2,6-difluorobenzaldehyde were purchased from Aldrich. Pyrrole and 2,4,6-collidine were purified by vacuum distillation. 2,6-Dimethylbenzaldehyde was purchased from Chemical Services, Inc., Hanover, NJ. Solvents used in all studies were AR grade. Neutral alumina, activity grade 1, type WN-3 was used in all chromatographic studies. 5,10,15,20-Tetrakis(2,6-dimethylphenyl)porphyrin (**1**), 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**2**), and 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrin (**3**) were synthesized by the Rothemund method[6] using 2,4,6-collidine instead of pyridine, followed by demetalation of the intermediate zinc(II) complexes in concentrated HCl. The substantial amount of chlorin was converted to the free-base porphyrin by refluxing with 2,3-dichloro-5,6-dicyano-4-benzoquinone in toluene.[7] The purification of the free-base porphyrins was performed by dry chromatography on neutral alumina with $CHCl_3$ as eluent and recrystallization from CH_2Cl_2/hexane. The UV/visible spectrum of **2** is virtually identical with the literature value.[8] Compounds **1** and **3** were characterized as follows. **1**: ^{1}H NMR ($CDCl_3$) δ 8.63 s (8 H, pyrrole H), 7.58–7.63 t (4 H, Ph *p*-H), 7.45–7.48 d (8 H, Ph *m*-H), 1.91 s (24 H, Ph *o*-CH_3), −2.44 s (2 H, NH); UV/visible (CH_2Cl_2) λ_{max} ($\epsilon \times 10^{-3}$) 647 (3.27), 592 (6.54), 547 (5.88), 517 (20.3), 418 (385) nm; mass spectrometry *m/z* 727 (M^+ + 1). **3**: ^{1}H NMR ($CDCl_3$) δ 8.86 s (8 H, pyrrole H), 7.77–7.82 t (4 H, Ph *p*-H), 7.35–7.40 m (8 H, Ph *m*-H), −2.5 s (2 H, NH); UV/visible (CH_2Cl_2) λ_{max} ($\epsilon \times 10^{-3}$) 654 (2.17), 584 (6.3), 508 (19.0), 417 (230) nm; mass spectrometry *m/z* 758 (M^+).

All porphyrins were converted to the hemin chlorides by the method of Kobayashi.[9] The iron(III) hydroxo complexes (Me_8TPP)Fe^{III}OH and (Cl_8TPP)Fe^{III}OH were obtained either by stirring a $CHCl_3$ solution of hemin chloride with aqueous sodium hydroxide or by chromatography on neutral alumina with $CHCl_3$ as eluent. The latter procedure was employed to prepare (F_8TPP)Fe^{III}OH. (F_{20}TPP)Fe^{III}Cl (Porphyrin Products) was converted to a mixture of μ-oxo and hydroxy species by stirring with aqueous sodium hydroxide as described previously[2] and the composition of the mixture established by ^{1}H NMR spectroscopy (pyrrole resonances: δ 81.9, 14.1).

Instruments. Proton NMR spectra were recorded on a Nicolet NT-300 spectrometer (300 MHz); chemical shifts are reported with respect to internal Me_4Si, and downfield shifts are given a positive sign. Spectra were run in methylene-d_2 chloride. Mass spectra for (F_8TPP)-Fe^{III}OH were performed under the auspices of the Mass Spectral Facility at UCR. UV/visible spectra were recorded on a Perkin-Elmer Model 553 spectrophotometer. Mass spectra for the free-base porphyrins were measured on a VG 70-250 HF mass spectrometer. Infrared spectra were recorded on a Bio-Rad Digilab Division FTS-60. EPR spectra were

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