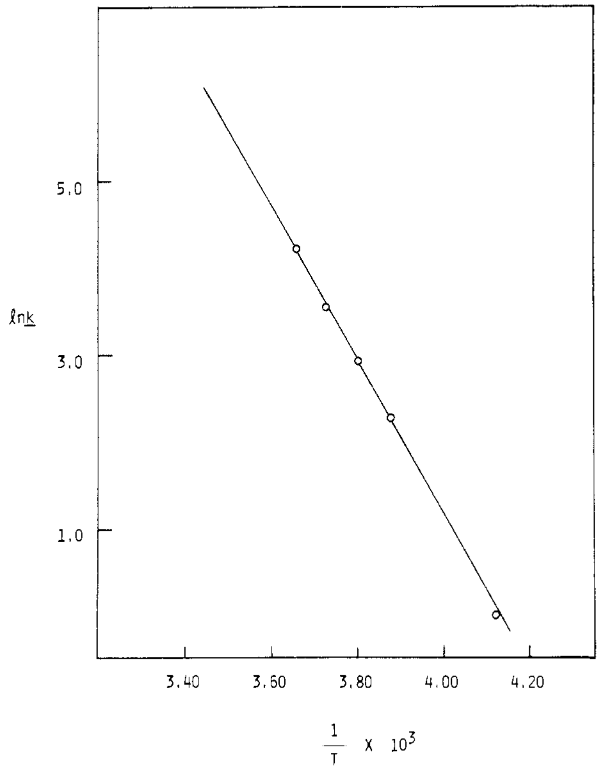

Figure 2. Arrhenius plot for the intramolecular CO ligand exchange process in [PPN][$HCr(CO)_5$] in tetrahydrofuran.

and equatorial CO groups is shown in Figure 1. The values used for the relative site populations were varied slightly from the ideal to offset the observed differential nuclear Overhauser effects.[14]

An Arrhenius plot (Figure 2) yielded an activation energy of 18.5 ± 0.5 kcal/mol with $\Delta H^{\ddagger} = 18.0 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 14.0 \pm 2$ eu, and $\Delta G^{\ddagger}_{298} = 13.8 \pm 0.5$ kcal/mol. Error limits represent 90% confidence limit. Two specific mechanisms to explain the solution dynamic behavior of the $HCr(CO)_5^-$ anion can be proposed: Scheme Ia, a trigonal-twist mechanism, with or without substantial metal–ligand bond breaking in the transition state;[3,15] Scheme Ib, a hydride migration mechanism.[16]

A twist mechanism that provides a pathway for intramolecular axial–equatorial CO exchange is favored. This mechanism would be consistent with that proposed for the related $M(CO)_5PR_3$ (M = Cr, W) derivatives.[3] The more facile exchange process observed in $HCr(CO)_5^-$ as compared with $Cr(CO)_5PR_3$ species most likely reflects the large angle between axial and equatorial MCO vectors observed both in the solid state (95.4°) and in solution (94.9°) for the hydride complex.[17] The alternative, the hydride migration mechanism, is less favored from the viewpoint of chemical precedence (supported by thermodynamic considerations).[18] Furthermore, the rate of methyl migration in $CH_3Cr(CO)_5^-$ is a relatively slow process.[19] Since hydride migration would be anticipated to be even slower,[20] this latter process (Scheme Ib) can be ruled out as a pathway for rapid axial–equatorial CO exchange. It should as well be reiterated here that intermolecular CO exchange does not readily occur under the conditions of this rearrangement process.

Axial–equatorial carbon monoxide exchange in the $HW(CO)_5^-$ anion is a much less rapid process than that reported upon herein for the $HCr(CO)_5^-$ species. That is, only a slight broadening of the two CO resonances (211.0 (CO_{axial}), 207.2 ppm ($CO_{equatorial}$)) was noted at +50 °C in tetrahydrofuran. Intramolecular CO scrambling in the $W(CO)_5PR_3$ derivatives are similarly less facile than in the chromium analogues.[3]

Acknowledgment. Support for this work from the National Science Foundation, Grant Nos. CHE83-08281 (to D.J.D.) and CHE83-04162 (to M.Y.D.), is greatly appreciated.

Registry No. [PPN][$HCr(CO)_4(^{13}CO)$], 100243-50-3; $W(^{13}CO)_6$, 25941-11-1; $W(^{13}CO)_5NMe_3$, 100228-87-3; $Cr(CO)_4(^{13}CO)$pip, 100348-10-5; [PPN][$HW(^{13}CO)_5$], 100243-52-5.

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(20) For example, the second-orderrate constant for ^{13}CO incorporation in $CH_3Mn(CO)_5$ (a process where methyl migration is indicated) is 9×10^{-3} M^{-1} s^{-1}, whereas the analogous process involving $HMn(CO)_5$, where H migration is proposed, has a rate constant of 1.2×10^{-3} M^{-1} s^{-1} at ambient temperature.[16]

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The Next Generation of (Polyazine)ruthenium(II) Complexes

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In the past, a vast body of work has focused on the excited-state electron-[1-6] and energy-transfer[7-11] reactions of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bypyridine) and its derivatives for the capture, storage, and utilization of solar energy. This interest in $Ru(bpy)_3^{2+}$ stems from the fact that the complex absorbs visible light, is sufficiently long-lived in fluid solution at room temperature to undergo spontaneous emission (τ = 600 ns),[6] has favorable potentials for both excited-state oxidation and reduction reactions of water,[3] and is thermally stable in the +3, +2, and +1 oxidation states. While considerable progress has been made in the understanding of such processes, practical utilization of the considerable energy available in the excited state of $Ru(bpy)_3^{2+}$ has been hampered by such problems as a back-reactions, diffusion-control limitations, parasitic side-electron-transfer reactions, and long-term instability of the photocatalyst.[2,6,12-14]

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Table I. Absorption, Emission, and Electrochemical Data for $Ru(ddp)_3^{2+}$, $Ru(bpy)_3^{2+}$, and $Ru(bpy)_2(dpp)^{2+}$

compd	λ_{max}^{abs},[a] nm	λ_{max}^{em},[b] nm[b]	τ_m,[c] ns[c]	$E_{1/2}^{ox}$,[d] V	$E_{1/2}^{red}(1)$,[e] V	$E_{1/2}^{red}(2)$,[e] V	$E_{1/2}^{red}(3)$,[e] V
$Ru(dpp)_3^{2+}$	455	636	270	1.68	-0.95	-1.12	-1.39
$Ru(bpy)_3^{2+}$	452[f]	630[f]	600[g]	1.26	-1.35	-1.54	-1.77
$Ru(bpy)_2(dpp)^{2+}$	430,[h] 470 (sh)	675[h]	135[h]	1.31	-1.06	-1.50	

[a] Absorption maximum of lowest energy, spin-allowed, $d_\pi \rightarrow p_\pi^*$ transition in H_2O at 25 °C. [b] Emission maximum of lowest energy $p_\pi^* \rightarrow d_\pi$ transition in H_2O at 25 °C. [c] Lifetime of emission in H_2O at 25 °C. [d] Reduction potential for first oxidation of RuL_3^{2+} in acetonitrile (0.1 M TBAH) vs. SCE. [e] Reduction potential for first, second, and third ligand reductions of RuL_3^{2+} in acetonitrile vs. SCE. [f] Reference 12. [g] Reference 6. [h] Reference 20.

We have approached the problem through the design of polymetallic photocatalysts,[15] which combine a highly absorbing yet photostable antenna fragment with a reactive fragment. The reactive fragment is a species that undergoes a useful photochemical reaction except that it generally requires ultraviolet rather than visible light. These fragments are bridged by a highly communicative, bidentate bridging ligand, such as 2,2′-bipyrimidine (bpym). The major advantage of using multifunctional polymetallic complexes is that the inherent inefficiencies of bimolecular quenching phenomena can be circumvented. Ligands such as bpym[16-19] and 2,3-bis(2-pyridyl)pyrazine (dpp)[20] have properties similar to those of bpy but allow the added advantage of multimetal systems. The intramolecular processes do not necessarily require a long excited-state lifetime; however, the longer-lived the donor excited state, the easier it is to construct a system that will undergo energy transfer in competition with relaxation. The dpp bridging ligand has some synthetic advantages over bpym in attaching the second metal center, but more importantly, the bimetallic system, $[Ru(bpy)_2]_2(dpp)^{4+}$, prepared by Gafney and co-workers is the first bimetallic system of this type with a long enough lifetime to emit in fluid solution at room temperature.

Herein, we report the synthesis and characterization of a new, highly luminescent complex of ruthenium, $Ru(dpp)_3^{2+}$, which we feel will form the basis for a new class of polymetallic complexes for energy storage and utilization.

Experimental Section

Materials. Materials used in complex preparation were reagent grade and were used without further purification. The 2,3-bis(2-pyridyl)pyrazine (dpp) used in these studies was prepared by the procedure of Goodwin and Lions.[21] Water used in absorption and emission studies was redistilled from alkaline permanganate in an all-glass apparatus. The acetonitrile (Burdick and Jackson) used in electrochemical measurements was spectroquality, and the tetrabutylammonium hexafluorophosphate (TBAH) used as supporting electrolyte was prepared from tetrabutylammonium bromide (Eastman) and HPF_6 (Alfa) and recrystallized three times from ethanol prior to use.

Synthesis. The complex $[Ru(dpp)_3](PF_6)_2 \cdot H_2O$ was prepared by reacting a sixfold excess of dpp (0.75 g, 3.2 mmol) with $RuCl_3 \cdot 3H_2O$ (0.133 g, 0.5 mmol) in a refluxing 2:1 ethanol/water mixture (30 mL) for ca. 4 h. After the mixture was cooled and filtered, a saturated aqueous solution of KPF_6 (5 mL) was added and the ethanol was removed by rotary evaporation to induce precipitation. The greenish brown precipitate was dissolved in a 2:1 toluene/acetonitrile mixture, filtered to remove a highly charged blue material, and chromatographed on a 20-cm alumina column. The first band eluted was orange and luminescent. Concentration of the solution on a rotary evaporator yielded an orange precipitate that analyzed well for $[Ru(dpp)_3](PF_6)_2 \cdot H_2O$ (Atlanta Microlabs).

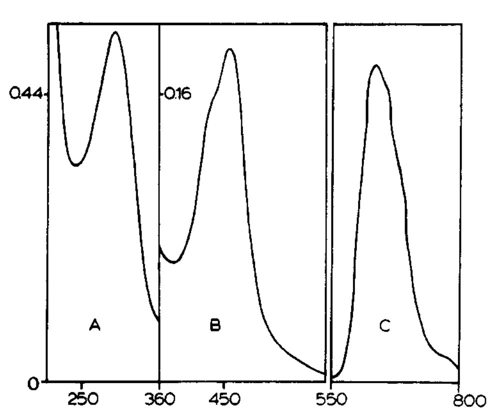

Figure 1. Electronic absorption and emission spectra of $Ru(dpp)_3^{2+}$ in aqueous solution at 25 °C: (A) absorption spectrum at wavelengths less than 360 nm; (B) absorption spectrum at wavelengths longer than 360 nm; (C) emission spectrum. For parts A and B, the *y* axis is absorbance and $[Ru(dpp)_3^{2+}] = 1.13 \times 10^{-3}$ M, *L* = 1 cm.

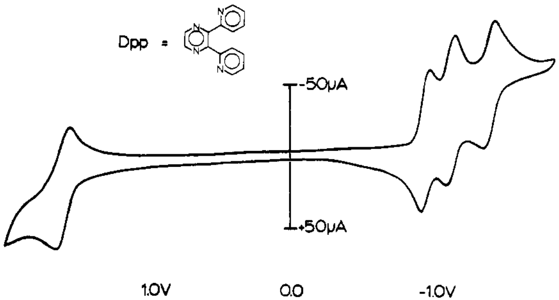

Figure 2. Cyclic voltammogram of $Ru(dpp)_3^{2+}$ vs. SCE in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Spectroscopy. Absorption spectra were recorded on a Bausch-Lomb Spectronic 2000 at room temperature in neutral, aqueous solution. Emission spectra were recorded on the same solution used for absorption spectra by using a Perkin-Elmer Model 650-40 spectrofluorimeter.

Lifetime measurements were recorded on a system consisting of a Photochemical Research Associates LN 1000 pulsed-nitrogen laser, a Stanford Research Systems boxcar averager, a Jobin-Yvon Model H-10 monochromator held at 636 nm following the sample (at a right angle to the incident laser light) and using a thermoelectrically cooled Products for Research Model TE104RF housing, and a Hamamatsu R 943-02 red-sensitive photomultiplier tube to detect the emission. The entire system was controlled by an IBM PC using software supplied by Stanford Research Systems. Calibration of the emission and lifetime apparatus was confirmed by using $Ru(bpy)_3^{2+}$ as a standard.

Electrochemistry. Cyclic voltammograms were recorded in acetonitrile, with 0.1 M TBAH as a supporting electrolyte, on an IBM EC/225 system. The exact configuration and procedures for these measurements have been previously reported.[18]

Results and Discussion

The electronic absorption and emission spectra of $Ru(dpp)_3^{2+}$ in water (Figure 1) yielded a λ_{max} at 455 nm ($\epsilon_{max} = 1.65 \times 10^4$ M^{-1} cm^{-1}) and at 297 nm ($\epsilon_{max} = 5.13 \times 10^4$ M^{-1} cm^{-1}). The emission spectrum shows a maximum at 636 nm in H_2O with vibrational shoulders on the low-energy side of the band. The lifetime of the luminescing excited state was measured by pulsed-laser techniques and found to be 270 ns in nitrogen-de-

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gassed water at room temperature. The intensity of the emission, when compared to that of $Ru(bpy)_3^{2+}$ under identical conditions, suggests that the complexes have similar luminescence quantum yields. A cyclic voltammogram in acetonitrile shows reversible waves at $E_{1/2}$ values of +1.68, -0.95, -1.12, and -1.39 V vs. the saturated calomel electrode (Figure 2). The positive wave is assigned to a Ru^{II}/Ru^{III} oxidation, and the three negative waves are assigned to ligand-localized reductions, by analogy with $Ru(bpy)_3^{2+}$ and related complexes.[16]

Qualitatively, the electronic absorption and emission spectra of $Ru(dpp)_3^{2+}$ look similar to those of $Ru(bpy)_3^{2+}$ but are shifted to longer wavelengths owing to the lower energy π^* LUMO on dpp compared to that on bpy.[22] From these data, the excitation energy of the thermally equilibrated $^*Ru(dpp)_3^{2+}$ complex can be calculated[4] as 2.08 eV. With the $E_{1/2}$ values for $Ru(dpp)_3^{3+/2+/+}$ from Table I, the excited-state potentials can be estimated by (1) and (2). In comparison with $Ru(bpy)_3^{2+}$, the

$$Ru(dpp)_3^{3+} + e^- \rightleftharpoons {}^*Ru(dpp)_3^{2+} \qquad E_{1/2} = -0.40\ V \qquad (1)$$

$$^*Ru(dpp)_3^{2+} + e^- \rightleftharpoons Ru(dpp)_3^{+} \qquad E_{1/2} = +1.13\ V \qquad (2)$$

excited state for the dpp complex is the more powerful oxidizing agent by 0.4 V but is ~0.4 V less reducing.

Table I contains the absorption, emission, and electrochemical data on $Ru(dpp)_3^{2+}$ and the mixed-ligand complex $Ru(bpy)_2(dpp)^{2+}$ originally prepared by Gafney and co-workers.[20] The energy gaps between the first oxidation and the first reduction are 2.63, 2.61, and 2.37 V for $Ru(dpp)_3^{2+}$, $Ru(bpy)_3^{2+}$, and $Ru(bpy)_2(dpp)^{2+}$, respectively. In viewing the reduction potentials of $Ru(bpy)_2(dpp)^{2+}$, one sees that the first reduction is similar in potential to the first reduction of $Ru(dpp)_3^{2+}$, while the second reduction is similar to the second reduction in $Ru(bpy)_3^{2+}$, suggesting the following:

$$Ru^{II}(bpy)_2(dpp)^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ru^{II}(bpy)_2(dpp^{-}\cdot)^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ru^{II}(bpy)(bpy^{-}\cdot)(dpp^{-}\cdot)$$

While the excited-state lifetime of $Ru(dpp)_3^{2+}$ is shorter than that of the bpy analogue, the former complex has an advantage in energy storage and transfer reactions. The ability of dpp to bind as a chelate to a second metal center enables the $Ru(dpp)_3^{2+}$ complex to serve as a hub for the formation of polymetallic complexes capable of intramolecular energy- or electron-transfer reactions. There is a great potential for the use of polymetallic complexes with dpp as the bridging ligand. In fact, the presence of three bidentate remote binding sites in $Ru(dpp)_3^{2+}$ raises the possibility of preparing polymetallic clusters[23] with appreciable excited-state lifetimes, thus generating systems capable of photocatalyzing multielectron reactions like the oxidation of water to dioxygen.

Acknowledgment. J.D.P. acknowledges the Office of Basic Energy Sciences, Department of Energy, for support of this research. J.D.P. and S.R.S. acknowledge the South Carolina Energy Research and Development Center for partially supporting the purchase of the equipment used for lifetime measurements. The ruthenium used in these studies was supplied on loan from Johnson-Matthey, Inc.

Registry No. $[Ru(dpp)_3](PF_6)_2$, 100334-03-0; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_2(dpp)^{2+}$, 88635-47-6.

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[22] Behlow, H. W., Jr.; Lee, L.; Petersen, J. D., unpublished observations.

[23] Brewer, K. J.; Gettliffe, G.; Murphy, W. R., Jr.; Petersen, J. D., manuscript in preparation.

Additions and Corrections

1985, Volume 24

Shunji Utsuno,* Hiroshi Miyamae, Soichiro Horikoshi, and Izumi Endo: Chiroptical Properties of Trigonal-Bipyramidal Complexes of Copper(II), Nickel(II), and Cobalt(II) Containing an Optically Active Tetraamine.

Page 1349. Figure 1 was incorrectly replaced with the figure of the enantiomer. The structure shown in Figure 2 and the parameters in Table III are correct.—Shunji Utsuno and Hiroshi Miyamae